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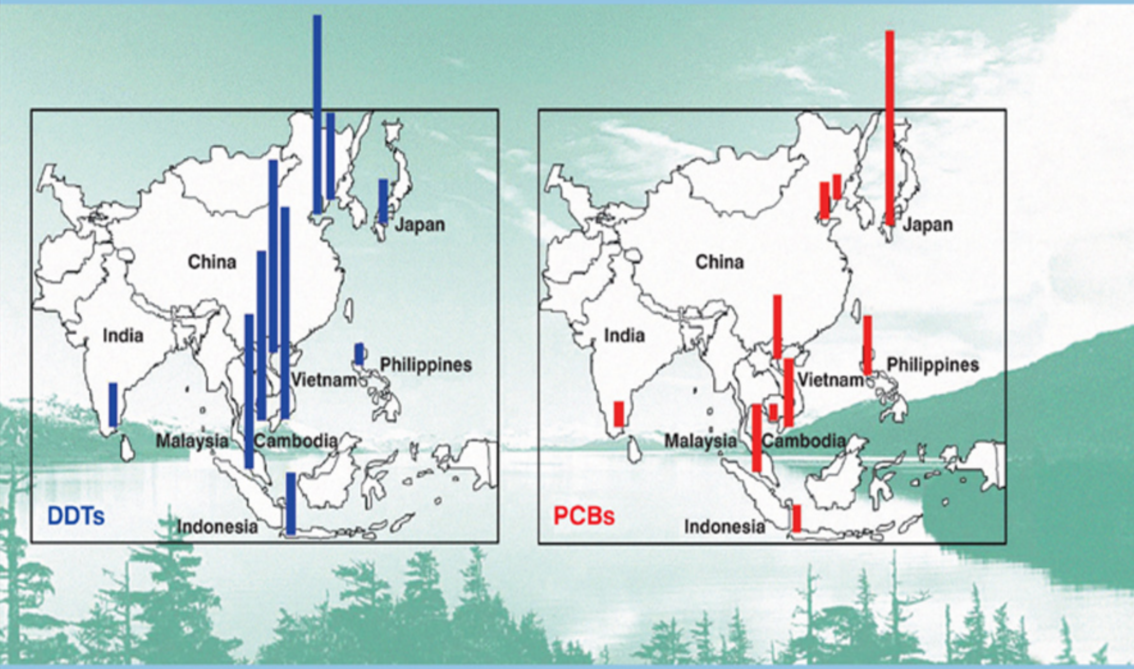
PERSISTENT ORGANIC POLLUTANTS IN ASIA

SOURCES, DISTRIBUTIONS, TRANSPORT AND FATE



Edited by
AN LI, SHINSUKE TANABE, GUIBIN JIANG,
JOHN P. GIESY AND PAUL K.S. LAM

Persistent Organic Pollutants in Asia: Sources, Distributions, Transport and Fate

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Introduction to the Book Series

Environmental pollution has played a critical role in human lives since the early history of the nomadic tribes. During the last millennium industrial revolution, increased population growth, and urbanization have been the major determinants in shaping our environmental quality.

Initially primary air pollutants such as sulfur dioxide and particulate matter were of concern. For example, the killer fog of London in 1952 resulted in significant numbers of human fatality leading to major air pollution control measures. During the 1950s, scientists also began to understand the cause and atmospheric mechanisms for the formation of the Los Angeles photochemical smog. We now know that surface level ozone and photochemical smog are a worldwide problem at regional and continental scales, with specific geographic areas of agriculture, forestry and natural resources, including their biological diversity at risk. As studies continue on the atmospheric photochemical processes, air pollutant transport, their atmospheric transformation and removal mechanisms, so is the effort to control the emissions of primary pollutants (sulfur dioxide, oxides of nitrogen, hydrocarbons, and carbon monoxide), mainly produced by fossil fuel combustion.

During mid 1970s environmental concerns regarding the occurrence of "acidic precipitation" began to emerge to the forefront. Since then, our knowledge of the adverse effects of air pollutants on human health and welfare (terrestrial and aquatic ecosystems and materials) has begun to rise substantially. Similarly, studies have been directed to improve our understanding of the accumulation of persistent inorganic (heavy metals) and organic (polyaromatic hydrocarbons, polychlorinated biphenyls) chemicals in the environment and their impacts on sensitive receptors, including human beings. Use of fertilizers (excess nutrient loading) and herbicides and pesticides in both agriculture and forestry and the related aspects of their atmospheric transport, fate and deposition; their direct runoff through the soil and impacts on ground and surface water quality and environmental toxicology have become issues of much concern.

In the recent times environmental literacy has become an increasingly important factor in our lives, particularly in the so-called developed nations. Currently the scientific, public, and political communities are much concerned with the increasing global scale air pollution and the consequent global climate change. There are efforts being made to totally ban the use of chlorofluorocarbon and organo-bromine compounds at the global scale. However, during this millennium many developing nations will become major forces governing environmental health as their populations and industrialization grow at a rapid pace. There is an ongoing international debate regarding policies and the mitigation strategies to be adopted to address the critical issue of climate change. Human health and environmental impacts and risk assessment and the associated cost-benefit analyses, including global economy are germane to this controversy.

An approach to understanding environmental issues in general and in most cases, mitigation of the related problems requires a systems analysis and a multi- and interdisciplinary philosophy. There is an increasing scientific awareness to integrate environmental processes and their products in evaluating the overall impacts on various receptors. As momentum is gained, this approach constitutes a challenging future direction for our scientific and technical efforts.

The objective of the book series *"Developments in Environmental Science"* is to facilitate the publication of scholarly works that address any of the described topics, as well as those that are related. In addition to edited or single and multi-authored books, the series also considers conference proceedings and paperback computer-software packages for publication. The emphasis of the series is on the importance of the subject topic, the scientific and technical quality of the content and timeliness of the work.

Sagar V. Krupa
Editor-in-Chief, Book Series

Preface

The idea of composing this book stems from the need to understand the environmental behavior of persistent organic pollutants (POPs) on a global scale. In recent decades, with the rapid economic development in Asia, the effects of various persistent pollutants on human health and the ecosystem have caused increasing concerns among scientists and administrators in the region and beyond. However, for decades research on POPs in Asia has lagged behind those in Europe and North America. Data are limited and vary greatly in quality. In addition, information is scattered among numerous journals and documents, many of which are in native languages. It is our intention to compile the most current knowledge on the sources, distributions, transport and fates of selected POPs from the rapidly developing regions of Asia.

POPs covered by this book are those of greatest concern due to their adverse health effects, and those capable of long-range transport. These include polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs), polybrominated diphenyl ethers (PBDEs) and other brominated organic pollutants, pesticides, polycyclic aromatic hydrocarbons (PAHs) and their derivatives, perfluorinated organic compounds, alkylphenols, as well as other persistent organic chemicals of high concern. Some organometallic compounds of concern are also included.

Many countries included in this book have experienced a rapid economic development during the past decades. Such development has resulted in measurable changes to their natural environments. Other Asian countries, including those in the Middle East and Central Asia, are omitted due mainly to the scarcity of reliable information. For the countries included, each is discussed in either a single chapter or multiple chapters that cover specific POPs or combinations of POPs. Most individual chapters provide regional or country-wide coverage on the targeted POPs. Three chapters describe areas of high environmental and economical importance (Hong Kong and the Pearl River Delta of China). Although not an Asian country, a chapter on Australia is included because of its location in the Eastern Hemisphere and relative proximity to Asia. This inclusion is meaningful and relevant with regard to the long-range Transport and Fate of some POPs. The last chapter of the book provides a regional perspective for POPs in the Asian countries covered by this book.

A great deal of effort has been made by our authors to collect information from numerous sources and explore the data using the principles of environmental chemistry, toxicology, and risk assessment. Additionally, this book integrates the following information to provide important context and insight:

- Government policies, available national monitoring and surveillance programs, and treaties if any;
- history of manufacturing, industrial applications, and emission sources within the region or country;
- measured concentration levels in various matrices of the physical environment;
- measured or modeled transport and transformation of POPs, and the potential influencing factors on such processes;
- the impacts of POPs on the health of people living in the region or country; and
- magnitude and pathways of cross-boundary exchange with other countries, regions, and continents.

Together, these are invaluable pieces in understanding the situation in Asia and fitting it into the global "puzzle" of environmental behavior of POPs. With the Stockholm Convention on POPs entered into force in 2004, we believe that the publication of this book is both timely and useful. We expect this book to serve as a reference for environmental researchers, various organizations, and government decision makers seeking information on POPs in Asia or on a global scale.

This book is the result of decades of hard work conducted by tens of thousands of environmental researchers all over the world. As the number of publications on the Asian environment has grown exponentially in recent years, it is highly possible and unfortunate that some excellent studies are not included in this book. We sincerely acknowledge and highly appreciate the hard work of our authors in writing the chapters.

An Li, Shinsuke Tanabe,Guibin Jiang,
John P. Giesy and Paul K.S. Lam
Editors

Part I:
East Asia–Japan, China, and Koria

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Chapter 1

Persistent Organic Pollutants Monitoring Activities in Japan

Yasuyuki Shibata and Takumi Takasuga[*]

1.1. Introduction

Japanese environmental policy and administration system has been constructed under strong influence from severe pollutions experienced under rapid economical growth and industrialization during the 1950s–1960s, including organomercury poisoning from acetaldehyde production factory (Minamata disease), cadmium poisoning from mining activity (Itai-itai disease) and air pollution at highly industrialized and/or densely populated areas. Pollution by polychlorinated biphenyls (PCBs) has also been a major issue in Japan, not only because of their extensive use in transformer oil, non-carbon paper, etc., but also because of a severe intoxication case, the Yusho incident (the Kanemi cooking oil health incident in 1968), where a number of people suffered from PCB poisoning by ingesting rice oil accidentally contaminated with PCBs used as heating medium. The toxicity mainly came from polychlorinated dibenzofurans (PCDFs) produced by oxidation of PCB during heating process.

Environment Agency was established in 1971 after these severe pollution incidents, and the first environmental monitoring by the Agency was conducted in 1974. The second monitoring was conducted in 1978 followed by the consecutive surveys monitoring conducted every year until present (Ministry of the Environment Japan, 1996, "Chemicals in the environment"). The compounds and the environmental media analyzed in the monitoring until 2003 are summarized in Table 1.1. The analytes had included not only organic compounds but also heavy metals in the first phase but have been shifted to POPs, including PCB, DDT, chlordanes (including heptachlors), hexachlorobenzene (HCB) and drins (aldrin, dieldrin, endrin).

Meanwhile the law concerning the evaluation of chemical substances and regulation of their manufacture, etc. (Law No. 117 of 1973, hereafter

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Table 1.1. Status of POPs monitoring in Japan

	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	00	01	02	03
Air																													B2	B2
Aldrin/endrin																														
Dieldrin																													B2	B2
Chlordanes													B1																B2	B2
DDTs																													B2	B2
Heptachlor													B1																B2	B2
Toxaphene/mirex																														B2
HCB																					B1				E	B1			B2	B2
PCBs																								B1		B1	B1	B1	B2	B2
PCDO/DFs													O	O	O	O	O	O	O	O	O	O	O	A	A	A	DA	DA	DA	DA
Water																														
Aldrin/endrin																									E				B2	B2
Dieldrin													B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1,E				B2	B2
Chlordanes									B1				B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1,E				B2	B2
DDTs	B1												B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1,E				B2	B2
Heptachlor									B1																				B2	B2
Toxaphene/mirex										B1																				B2
HCB	B1	B1			B1								B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1,E				B2	B2
PCBs		W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	B1.E,W	B1W	B2W	B2W
PCDO/DFs																									O	O	D	D	D	D
Soil																														
PCDO/DFs																									O	O	D	D	D	D
Bottom sediment																														
Aldrin/endrin																									E				B2	B2
Dieldrin													B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1.E				B2	B2
Chlordanes									B1				B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1.E	B1	B1	B1	B2	B2

DDTs	B1											B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1.E	B1	B1	B1	B2	B2
Heptachlor									B1																				B2	B2
Toxaphene/mirex										B1																				B2
HCB	B1	B1			B1								B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1,E	B1	B1	B1	B2	B2
PCBs																							B1	B1			B1,E	B1	B2	B2
PCDO/DFs												O	O	O	O	B	B	B	B	B	B	B	B	B	O	O	D	D	D	D
Wildlife																														
Aldrin/endrin					B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1		B1		B1					E				B2	B2
Dieldrin					B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1		B1,E				B2	B2
Chlordanes									B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1,E	B1	B1	B1	B2	B2
DDTs	B1				B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1,E	B1	B1	B1	B2	B2
Heptachlor									B1																				B2	B2
Toxaphene/mirex																														B2
HCB	B1	B1			B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1		B1,E		B1,E	B1	B2	B2
PCBs					B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1,E	B1	B2	B2
PCDO/DFs												O	O	O	O	B1	B1	B1	B1	B1	B1	B1	B1	B1	O	O	O.E	O	O	O

Notes: B1 = survey on the actual condition of chemical substances in the environment (until 2001); B2 = survey on the actual condition of chemical substances in the environment (after 2002); D = survey under the Law concerning Special Measures against Dioxins; E = survey on the environmental endocrine disrupters; W = survey under the Water Pollution Control Law; A = the air pollutants monitoring; O = other survey.

*Details of the survey on the actual condition of chemical substances in the environment: refer to Ministry of the Environment web site http://www.env.go.jp/chemi/kurchen/index.html (also refer to annual reports before FY1996).

*Details of survey under the Law concerning Special Measures against Dioxins: refer to Minister of the Environment of the web site http://www.env.go.jp/chemi/dioxin/report.html

*Details of the survey on the environmental endocrine disrupters: refer to working group materials on the Ministry of the Environment web site http://www.env.go.jp/chemi/end/index2.html

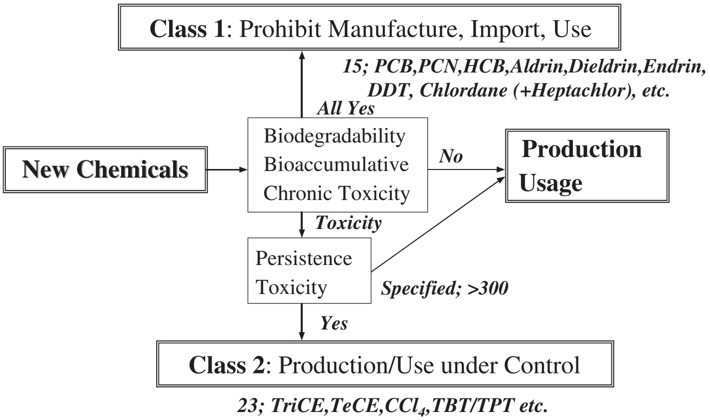

Figure 1.1. Japanese Chemical Management Law.

referred to as the Chemicals Substances Control Law) was promulgated in 1973 (Fig. 1.1). In this law, a priority of regulation was put on stable (not decomposed substantially during sewage sludge treatment), bioaccumulative and toxic chemicals, i.e., POPs-like compounds. Chemicals having these three properties together were classified as the Class 1 Designated Chemicals, and their production, import and usage were banned. PCB was designated as Class 1 in 1974, followed by HCB in 1979, aldrin, dieldrin, endrin and DDT in 1981, and chlordanes (including heptachlors) in 1986. Mirex and toxaphene have never been registered in Japan as agrochemicals, but they were also designated in 2002 as Class 1 Chemicals (Table 1.2).

The Chemical Substances Control Law was amended in 2003, to bring all the chemical substances, which are likely to cause damages to top predators in the ecosystem, within its regulation. Moreover, there were several moves to establish PCBs disposal facilities under the initiative of the private sector in order to dispose of the PCBs already produced. However, such moves failed to ensure understanding and consent from local communities, with the result that much of the PCBs had remained in stockpiling without being disposed of over nearly 30 years. It was also found that during the long-term stockpiling some transformers were lost or became untraceable and there were concerns that such stockpiled PCB might contaminate the environment. Thus, in June 2001, the law concerning special measures against PCB waste (Law No. 65 of 2001, hereafter referred to as the PCB Special Measures Law) was enacted to obligate entities possessing PCB wastes to report the status of their

Table 1.2. List of industrial and agrochemicals banned in Japan

Name	Banned as industrial chemicals	Banned as pesticides
DDT	1981	1971
Aldrin	1981	1975
Dieldrin	1981	1975
Endrin	1981	1975
Chlordane[a]	1986	1968
Heptachlor[b]	1986	1975
Mirex	2002	[c]
Toxaphene	2002	[c]
PCB	1974	
HCB	1979	[c]

[a] Used mainly for termiticides (other than agricultural purposes); between 1979 and 1986.
[b] Heptachlor was also included in technical chlordane as impurity (~10%).
[c] Never registered as agrochemicals in Japan.

stockpiling and to dispose of such wastes within a given time frame in an environmentally sound manner, with a view to facilitate the sure and perfect disposal of PCB waste.

Ministry of the Environment of Japan also conducts environmental monitoring of some POPs chemicals, including waste dumping in the seas and oceans, monitoring of water based on regulation of water environment, and monitoring of chemicals suspected to have endocrine disruptive properties (EDCs).

At the same time the issues related to the unintentionally produced dioxins and furans, i.e., polychlorinated dibenzo-*p*-dioxins (PCDDs) and PCDFs, attracted public attention in 1983 when investigations revealed that dioxins were detected in the fly ashes from municipal waste incinerators. Therefore, measures to monitor dioxins in the bottom sediment and aquatic animals and plants in the rivers, lakes, marshes and seawaters as well as the atmosphere were initiated in 1986. Investigations were implemented on the actual status of waste incinerators in 1984 and pulp and paper factories in 1990. On the basis of these findings, guidelines and administrative guidance on controlling emissions of dioxin-related chemicals were derived and established.

Furthermore, from around 1996 onward Japanese public became increasingly concerned about environmental contamination caused by releases from waste incinerator facilities. In 1997 dioxins were designated as hazardous air pollutants and measures were introduced to control their emission into the atmosphere in terms of the preventive actions taken to reduce risks of health hazards under the Air Pollution Control Law (Law No. 97 of 1968). Furthermore, in July 1999, the law concerning special measures against dioxins (Law No. 105 of 1999, hereafter referred to as the Dioxins Law) was established and the regulatory framework was put in place to implement comprehensive measures such as establishing tolerable daily intake (TDI) and environmental quality standards, regulating the release of emission gases and effluent water from a wide range of facilities, introducing enhanced regulation on waste disposal and conducting investigations on the actual status of contamination and taking measures against contaminated soil and other matters. Now these measures are strictly implemented under the law.

In Japan, under the Dioxins Law, PCDDs, PCDFs and coplanar PCBs are defined as the dioxins. According to the current scientific knowledge, the source categories and the formation processes of PCB and HCB are considered to be similar to those of unintentionally produced dioxins. Therefore, it is assumed that the release of PCBs and HCB has also been reduced through the dioxins reduction measures.

Under the Law concerning Reporting of Releases to the Environment of Specific Chemical Substances and Promoting Improvements in Their Management (Law No. 86 of 1999, hereafter referred to as the Chemical Substances Release Reporting and Management Promotion Law), dioxins and PCBs are subject to the requirements of the Pollutants Release and Transfer Register (PRTR) system.

Extensive efforts have been made in the environmental monitoring of dioxins from 1989 in biota and sediments and from 1998 in other media until present (Fig. 1.2) (Ministry of the Environment, 2002, "Dioxins monitoring in the environment"). It could be seen from these efforts, that emission of dioxins in Japan has been decreasing from 7680–8135 g-TEQ in 1997 to 323–348 g-TEQ in 2005, a 95% reduction from the 1997 level, meeting the reduction target (Ministry of the Environment, 2004, "Dioxin emission inventory"). In 2005, 3206 atmospheric samples, 2550 water samples, 1730 sediment samples, 924 ground water samples and 1782 soil samples were analyzed for their dioxin levels.

1.2. PCB and POPs pesticides monitoring

1.2.1. Results of biological monitoring by GC-ECD (from 1978 until 2001)

Gas chromatography-electron capture detector (GC-ECD) was originally selected as the analytical instrument for environmental monitoring using organisms until 2001 when MOE decided to reorganize their environmental monitoring by introducing HRGC/HRMS in order to elucidate the present levels of POPs in Japan as the baseline value for the

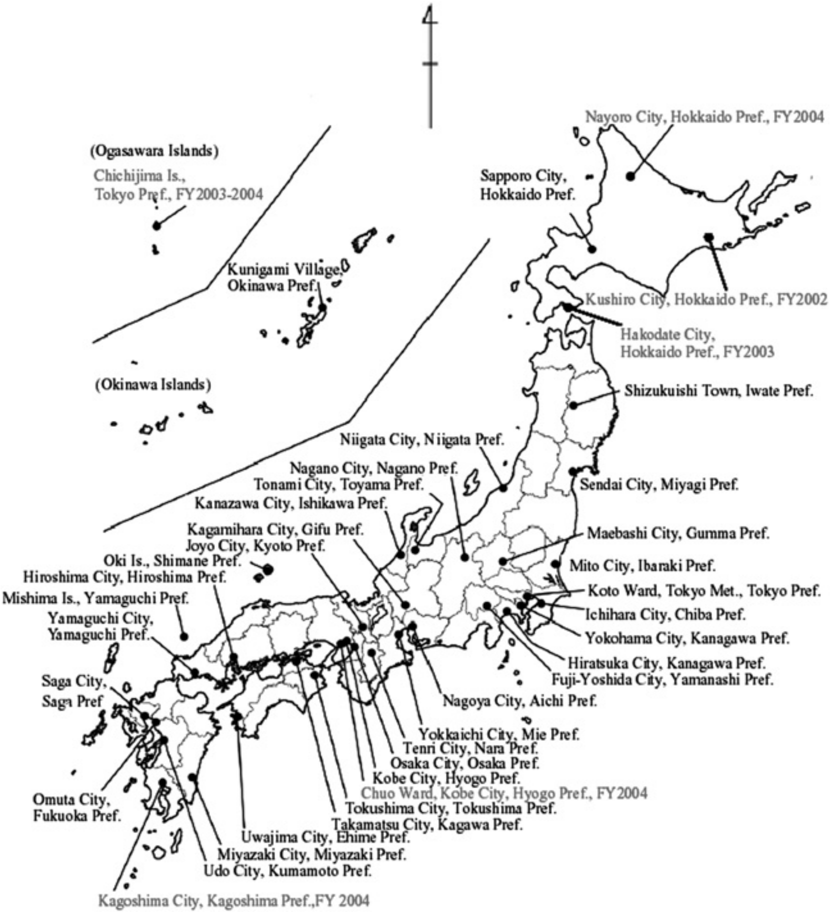

Figure 1.2. Sites for 12 POPs monitoring for atmospheric air and precipitation (FY2002–2004).

effectiveness evaluation of the Stockholm Convention. In fact, the ratios of ND (not detected) in the monitoring data had been increasing while using the GC-ECD method during the last decade of the 20th century, although data without ND have been obtained for some pollutants, such as PCBs and DDTs, in the samples like fishes collected from the coastal waters along densely populated areas, such as Tokyo Bay and Osaka Bay.

Generally speaking pollutant levels in fishes and other wildlife species have been decreasing in recent decades either in their average concentrations or in the detection frequencies (ratios of detectable sites among

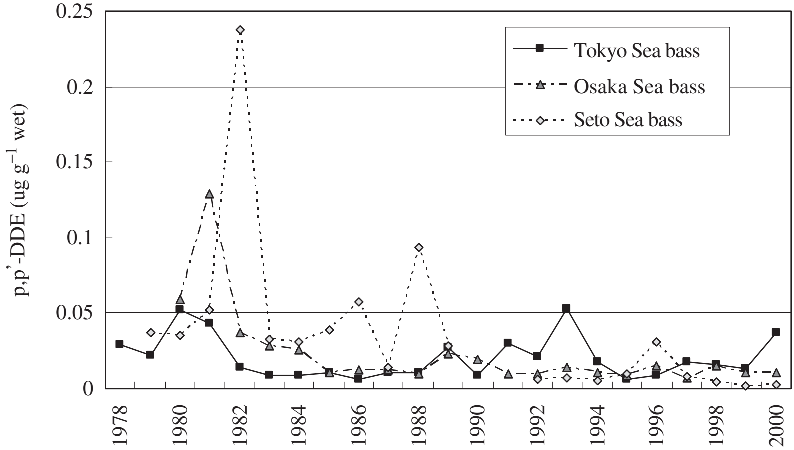

Figure 1.3. *p,p′*-DDE levels (average of five specimens' data in each location) in fishes (Sea bass) in Tokyo Bay, Osaka Bay and Seto Inland sea between 1978 and 2000.

all sampling sites). There seems to be, however, some differences among locations in the time trends of pollutant levels. As an example of such data, Fig. 1.3 shows *p,p′*-DDE levels in fishes from Tokyo Bay, Osaka Bay and Seto Inland sea. *p,p′*-DDE levels have been decreasing continuously during the last three decades in Osaka Bay and Seto Inland sea, while the levels apparently do not show clear decreasing trend in Tokyo Bay although their levels were higher in the early 1980s. All of these areas are semi-enclosed environment and thus are expected to remain polluted for a longer time. DDT concentrations in water of Sumida River and Arakawa River, both flowing into the central Tokyo Bay indicates continuous loading of DDTs, which may contribute to maintain their higher levels in Tokyo Bay. This might be the reason for the differences in the temporal patterns of DDE in these three areas.

Similar trends are also observed in PCB levels in Sea bass in the three coastal water environments as shown in Fig. 1.4. Again a clear decreasing trend was seen in Seto Inland sea, while the levels in Tokyo Bay are rather flat with a couple of fluctuations. The time trend in Osaka Bay is more or less similar to Tokyo Bay but with no clear decrease in recent decades. The difference between *p,p′*-DDE and PCB time trends in Osaka Bay might reflect either the difference in recent loading of the compounds to the Bay or the difference in their pollution histories.

Several other characteristic levels/patterns of pollutants, apparently reflecting local environmental situations were noticeable and these will be described in the next section based on the recent HRGC/HRMS data.

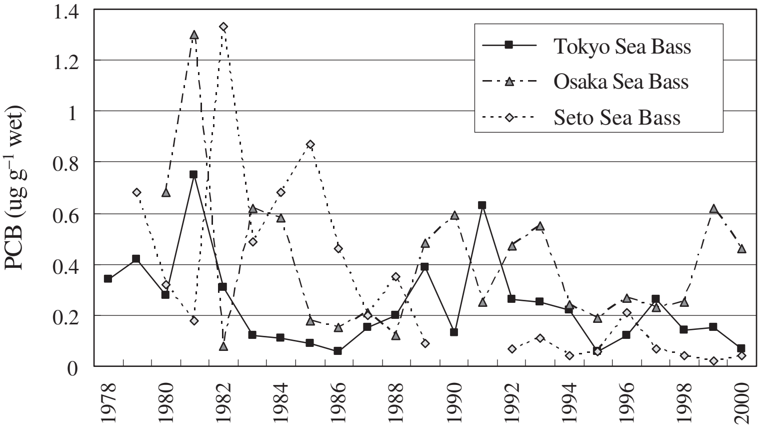

Figure 1.4. PCB levels (average of five specimens' data in each location) in fishes (Sea bass) in Tokyo Bay, Osaka Bay and Seto Inland sea between 1978 and 2000.

1.2.2. Monitoring by HRGC/HRMS (after 2002)

As stated above, MOE decided to introduce HRGC/HRMS-based monitoring method for all POPs (except toxaphene) in all the environmental media in order to clarify the present pollution status of POPs in Japan as a basis for future effective evaluation of the Stockholm Convention, and started new monitoring from FY2002. Basically the same type of samples obtained with the same sampling protocol as the previous environmental monitoring are analyzed by the new methods with ultratrace detection limits and higher fidelity (all available isotope-labeled surrogates are used for recovery correction during sampling or pretreatment before analysis).

The basic idea of sampling site selection is different among the environmental media. For air sampling, the sites are selected to cover all over Japan with similar distance between the sites (roughly 100 km in average). Water and sediments are sampled at the mouth of the major rivers, and the major ports. Biological samples, i.e., fishes, bivalves and birds, are continuously sampled according to the original design, i.e., by categorizing Japanese environment into several typical areas, such as densely populated, highly industrialized, rural area with agricultural activity, remote area, etc. and selecting a few locations in each category to collect typical biological samples in each region representing the environment. In addition to this, human breast milk, and maternal and cord blood samples were collected in two cities to evaluate the status of POPs pollution in human.

As the new monitoring system has been operating only 5 years (2002–2006) until now, it is too early to conduct trend analysis. Here a brief description of the monitoring data by the new POPs monitoring method will be presented.

1.2.2.1. Data reflecting local specificities within Japan

1.2.2.1.1. Air

In general, chlordanes and PCBs were found to be highest in the air among POPs chemicals followed by HCB, heptachlor, dieldrin, DDT, etc. (Fig. 1.5). Their levels are generally lower in winter compared with summer data summarized in Fig. 1.5. It should be noted that the median values representing majority of the sampling sites are several times lower than the average values shown in Fig. 1.5, for there are apparently a few "hotspots" data in each of the chemicals by which average levels were pushed to be higher.

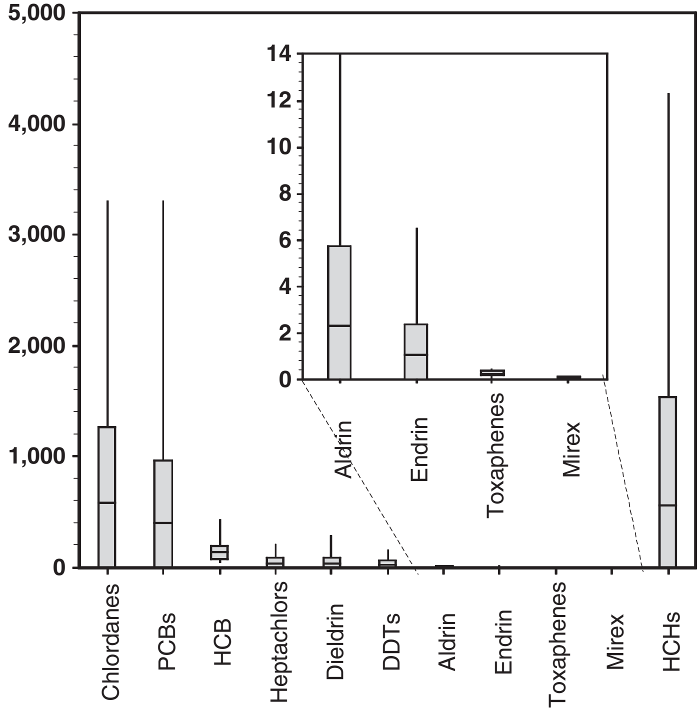

Figure 1.5. Concentrations of POPs in air (pg m^{-3}; summer in FY2004). Box represents average (middle line) ± SD; bar represents range (max. and min.) of data.

There are several "hotspots" data, i.e., characteristic POPs levels/compositions attributable to some local sources of pollution. For example, PCB level is among the highest in Takamatsu, Kagawa Prefecture with specific congener profile biased to highly chlorinated biphenyls. Their congener profile is rather similar to a PCB product used for anti-rusting paint of steel products, KC600, and above data might be attributable to some steel products or buildings located nearby the sampling site, in which KC600 had been used. Dieldrin level in the air has been among the highest in Fukuoka and Saga Prefecture, both in northern part of Kyushu, again suggesting presence of some local source of dieldrin in the area.

Trace levels of toxaphene and mirex are detected in the air with no clear differences among the sampling sites, although both had never been registered as agrochemicals in Japan. HCHs, now being evaluated as candidates of the additional POPs by POPs review committee under Stockholm Convention, are also in comparable levels to PCB and chlordanes in Japan as shown in Fig. 1.5.

1.2.2.1.2. Water, sediments and marine organisms

In Japanese water environment, again PCB and chlordanes are among the highest followed by DDT, dieldrin and others (Fig. 1.6). In sediments, PCBs are by far the highest contaminants followed by DDT, chlordanes, HCB, etc. (Fig. 1.7). It should be noted that the average levels in Figs. 1.6 and 1.7 tend to be pushed higher by few "hotspots" data as in the case of air samples. Chemical concentrations in water and river/port sediments tend to be higher in semi-enclosed bays along densely populated areas, notably PCB and DDT concentrations in water and sediments in Tokyo Bay and Osaka Bay. Specifically *o,p′*-DDE, a minor constituent in technical DDT, in water, and sediments in Sumida River and fishes in Tokyo Bay have been showing unusually significant proportion compared with samples in other locations, suggesting some specific sources of *o,p′*-DDEs (or originally *o,p′*-DDT) in the river and/or Tokyo Bay region. Several local contaminations have been identified for some specific chemicals; i.e., PCB in Sumida River, Osaka Port and Dokai Bay (both water and sediments), DDT in Sumida River, Toba Port, Osaka Port and Naha Port (sediments), chlordanes in Sumida River, Osaka Port, Takamatsu Port and Naha Port (sediments), endrin in Toba Port (sediments), dieldrin in Sumida River, Osaka Port, Takamatsu Port and Naha Port (sediments), HCB in Onahama Port and Dokai Bay (sediments), and mirex in Kure Port (sediments). Mirex levels in the sediments are detectable but rather low except for Kure, but the concentrations tend to be higher near the densely populated areas, suggesting the use of mirex-containing materials

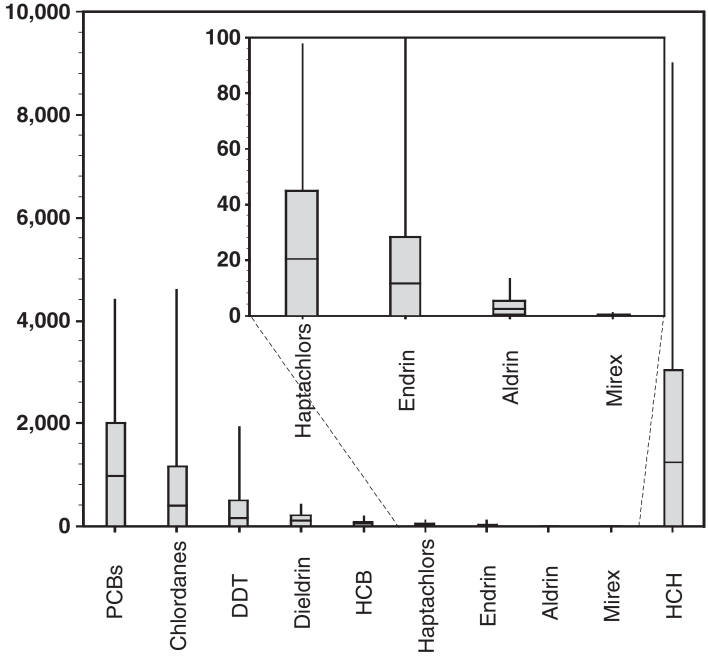

Figure 1.6. POPs levels in water (pg L^{-1}; FY2004). Box represents average (middle line) ± SD; bar represents range (max. and min.) of data.

in industries/household rather than for agricultural uses. It is reported that mirex has been used as flame retardants and also for termite control, and the above data may suggest the import/use of mirex-containing plastics or wood products. In addition, HCHs are among the highest in water while their levels are relatively moderate in sediments, apparently reflecting their water solubility.

Among fishes, Sea bass in Tokyo Bay showed the highest values for PCB, DDT and chlordanes in relation to their higher levels in waters/ sediments. Hard-shelled mussel from Tokushima has been reported to have high levels of dieldrin and also chlordanes with extremely high proportion of *cis*-chlordane, suggesting nearby source(s) of these chemicals. Interestingly, levels of both toxaphene and HCB on wet weight basis is highest in a fish living in the off-shore region of Ibaraki Prefecture compared with other fishes including those living in enclosed bays, such as Tokyo Bay and Osaka Bay, probably reflecting their long-range transportability and status of global pollution as described below.

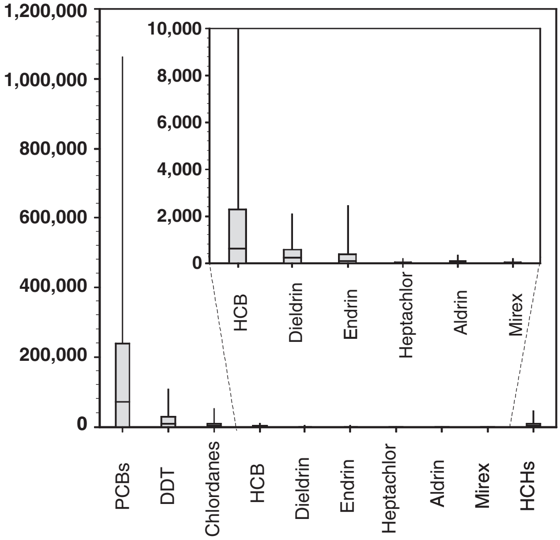

Figure 1.7. POPs levels in sediments (pg g^{-1}-wet; FY2004). Box represents average (middle line) ± SD; bar represents range (max. and min.) of data.

1.2.2.1.3. Other wildlife

DDT levels in terrestrial bird species caught in Iwate Prefecture showed higher levels of DDT while toxaphene levels are higher in juvenile sea gull compared with other species.

The government has been measuring PCB, HCB, DDT, chlordane, heptachlor epoxide and dieldrin since 1998 to identify their effects on wildlife as part of the Environmental Survey on Endocrine Disruptors. The specimens taken include land animals such as raccoons, bears, monkeys and frog, and marine mammals such as seals and whales, in addition to domestic birds and birds of prey. A relatively high concentration of POPs was seen in birds of prey and *Phalacrocorax carbo*. Eggs of mountain hawk eagles were also found to have a higher concentration of PCB, DDT, heptachlor epoxide, chlordane and dieldrin than other wildlife specimens

1.3. Regional/global transport of POPs

The data of POPs monitoring showed us general overview of the status of local pollution in Japan, although there seems to be some information from which regional/global scale information might be inferred.

1.3.1. HCB

HCB concentration in the air has always been fairly constant irrespective of the location, between 100 and 150 pg m^{-3} in late summer or 50 and 100 pg m^{-3} in early winter. HCB levels even in a background location, remote island Hateruma, are still around 50 pg m^{-3} in average (15–300), supporting the view that HCB is everywhere (Expert Working Group, 2006). Chemical property of HCB shows by far the longest transportability among 12 POPs chemicals. In fact, similar levels of HCB (50–100 pg m^{-3}) have been detected in some of the background sampling locations in East/Southeast Asian countries, such as Korea, Philippines, and Indonesia (Expert Working Group, 2006). Another data supporting the long-range transportability of HCB is its concentrations in fishes. HCB levels in wet weight basis is highest in a fish living in off-shore region of Ibaraki Prefecture followed by Sea bass in Tokyo Bay and another bottom-living fish from off-shore region off Hokkaido. It should be noted that the above mentioned first and third fish species live in off-shore water and thus reflect surface or bottom water concentration of chemicals, respectively. Although HCB levels are higher in coastal environment (e.g., Sea bass in Tokyo Bay) when presented as lipid basis, the data further supports the view that HCB contaminates not only coastal, but also open ocean environment due to its long-range transportability.

1.3.2. Toxaphene

Similar, but more impressive phenomenon was observed for toxaphene. Toxaphene has never been registered or produced in Japan; in fact, it was not detected in sediments/river waters all over Japan. However, toxaphene concentration was highest again in a fish living off-shore region of Ibaraki Prefecture followed by another bottom-dweller in Hokkaido, and Sea bass in Tokyo Bay. This time the second one is highest followed by the first and the third when the concentration is presented on a lipid basis. Although the comparison among fishes should consider various factors, including their trophic levels, the data seems to generally support the view that pollution status of toxaphene in coastal environment of Japan is similar to that of open ocean area of North Western Pacific Ocean. It should also be noted that toxaphene levels in lipid basis shows a clear trend, i.e., higher in northern part (Hokkaido) followed by central Japan compared with western Japan where its levels in any fish are much lower. This might support the view that northern Pacific water above the circumpolar front at around 40–45° north is contaminated by toxaphene more than southern warm water, possibly either reflecting their usage in northern part of northern hemisphere or reflecting evaporation in southern warm water and condensation/precipitation in cool northern environment (Wania and Mackay, 1993).

1.3.3. DDT

Another interesting phenomenon was observed on DDT in air samples. There are a couple of data showing unusually high proportion of *o,p′*-DDT in the air samples; for example, *o,p′*-DDT occupied ~65% of total DDT (sum of *p,p′*- and *o,p′*-isomers of DDT, DDE and DDD) in Okinawa in the autumn of 2002, and more than 50% in Okinawa, Saga, Shimane and Kumamoto in the summer of 2003. The *o,p′*-DDT is only a minor constituent of technical DDT and thus the above phenomenon may suggest the presence of different sources of *o,p′*-DDT other than technical DDT. In fact, it was recently reported by the Chinese scientists that dicofol, another organochlorine pesticide produced from DDT and sold in China contained fairly large proportions of un-reacted *o,p′*-DDT, up to 11% in weight on average (Qui et al., 2004, 2005). They also found unusually high proportion of *o,p′*-DDT in their air samples, and attributed their findings to the impurity of dicofol sprayed in China. The high *o,p′*-DDT found in Japanese air POPs monitoring might be attributable to long-range atmospheric transport, too.

1.3.4. Heptachlor vs. Chlordanes

Interestingly, ratios of heptachlors vs. chlordanes are higher in environmental samples, i.e., air, water and sediments, in Hokkaido compared with other locations. These data may reflect usage pattern of heptachlor as agrochemicals in Japan.

Heptachlors were spread into the environment either as an agrochemical or as impurities of technical chlordanes. In Japan, technical chlordane was used not only for agrochemicals but also for termite control, especially in south-west part where termite tends to damage houses more actively due to high temperature and humidity. Apparently the technical chlordanes used in Japan had been quite homogeneous, for chlordanes composition (proportions of *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor and oxychlordane) in air, and also in water, are quite similar to each other among the same media irrespective of the sampling locations. It is also expected that proportions of heptachlors in technical chlordanes were also stable; in fact, similar heptachlors/chlordanes ratios have been observed in many places in Japan in air, water and sediments, and majority of the data plots on chlordanes (X)

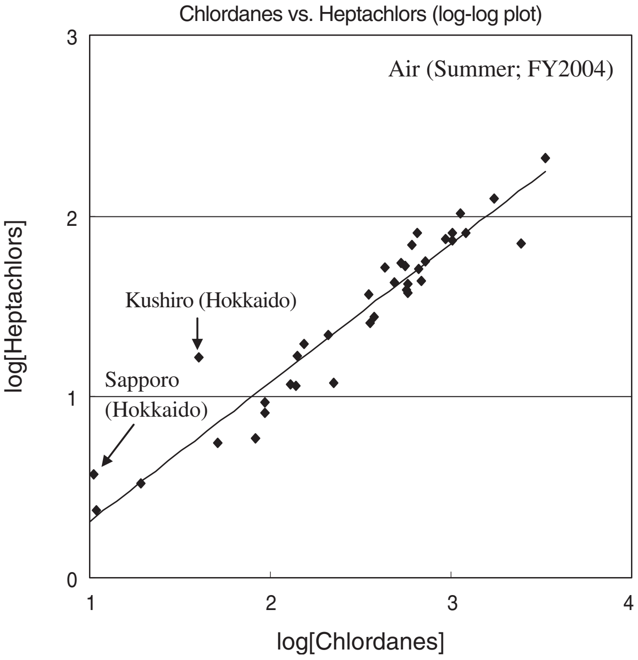

Figure 1.8. Chlordanes vs. heptachlors in air samples (summer; FY2004).

and heptachlors (*Y*) axes are on the same single line. There are, however, several data considerably biased to heptachlor side as shown in Figs. 1.8–1.10. It should be noted that these data correspond to sampling sites in Hokkaido, showing that the samples from Hokkaido are biased to higher proportion of heptachlors compared with other locations. In fact, heptachlors had been used in Hokkaido mostly for agricultural purposes while chlordanes were not used so much in Hokkaido due to its cold climate and absence of termite problem. This may be the reason why environmental media in Hokkaido showed relatively higher proportion of heptachlors.

1.3.5. Other proposed POPs

The environmental survey and/or monitoring data on the chemicals relevant to the five substances that were proposed for listing in Annex A of Stockholm Convention and considered at the first meeting of the Persistent Organic Pollutants Review Committee (POPRC) held in November 2005, are pentabromodiphenyl ether (PeBDE), chlordecone,

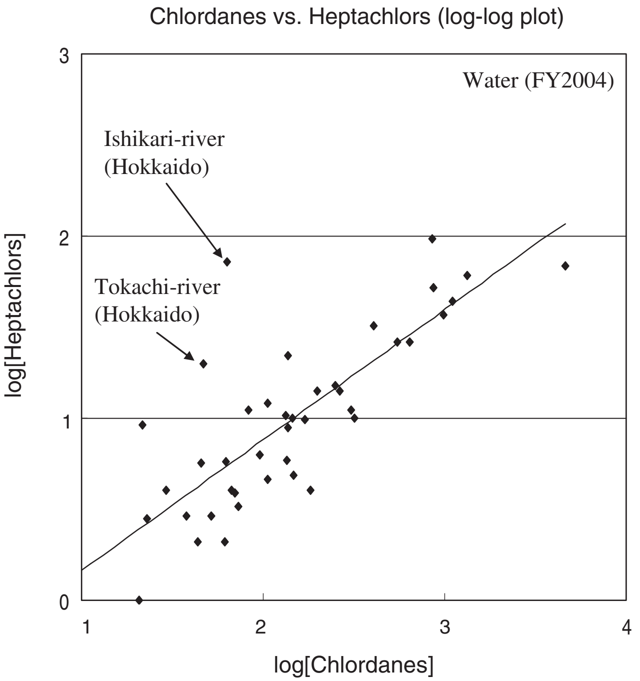

Figure 1.9. Chlordanes vs. heptachlors in water samples (FY2004).

hexabromobiphenyl, lindane and perfluorooctane sulfonate (PFOS). Although the proposal was made for lindane, this chapter includes the data on alpha, beta, gamma as well as delta isomers of HCH.

1.3.5.1. Pentabromodiphenyl ether (PeBDE)

1.3.5.1.1. Atmospheric air and precipitation

A survey was conducted in FY2001 with a detection limit of 0.09 pg m^{-3}, and the substance (PeBDE) was detected at all the 12 surveyed sites with a detection range between 0.10 and 9.3 pg m^{-3}. The survey conducted in FY2004 with a detection limit of 0.06 pg m^{-3} detected the substance at all of the three surveyed sites with a detection range between 0.35 and 5.4 pg m^{-3}. The persistence levels of the substance were comparable to the previous data.

A survey of the substance in bottom sediment was conducted for the first time in FY2004 with a detection limit of 0.035 ng g^{-1}-dry, and the substance was detected at one of the four survey sites with a detection value of 0.050 ng g^{-1}-dry. PeBDE has not been surveyed or monitored in

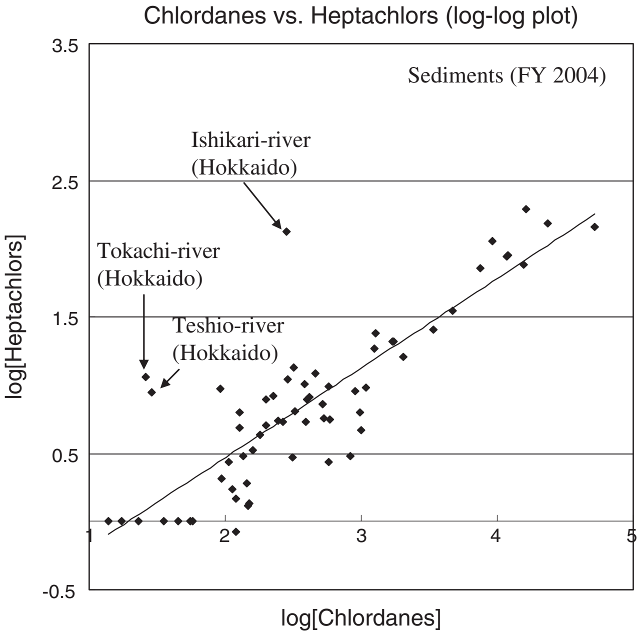

Figure 1.10. Chlordanes vs. heptachlors in sediment samples (FY2004).

other media—wildlife and bottom sediment in the Environmental Survey and Monitoring of Chemicals Program. Many laboratories in Japan have investigated PBDEs in recent years and reported varying levels of contamination by these chemicals in different environmental and biotic matrices including human samples (Ohta et al., 2002; Akutsu et al., 2003; Watanabe et al., 2004; Kajiwara et al., 2004; Ueno et al., 2004; Takasuga et al., 2004; Senthilkumar et al., 2005; Inoue et al., 2006).

1.3.5.2. Hexabromobiphenyl

A survey of this substance in the atmosphere was conducted for the first time in FY2004 with a detection limit of 0.25 pg m^{-3}. The substance was not detected at the single surveyed site.

A survey for hexabromobiphenyl in the surface water was conducted in FY2003. The detection limit was 15 pg L^{-1}. The substance was not detected at any of the four surveyed sites.

A survey of the substance in bottom sediment was conducted in FY2003 with a detection limit of 8700 pg g^{-1}-dry, and the substance was not detected at any of the two surveyed sites.

Hexabromobiphenyl has not been surveyed or monitored in biota in the Environmental Survey and Monitoring of Chemicals Program. There is the first report of PBB detection in cormorants and fish from Japan by Watanabe et al. (2004).

1.3.5.3. PFOS

This was the first survey to investigate PFOS persisting in atmospheric air. The survey was conducted with a detection limit of 0.09 pg m^{-3}, and the substance was detected in 57 of the 60 samples from all the 20 survey sites, with a maximum concentration of 44 pg m^{-3}.

A survey for PFOS in the surface water, which was the first environmental survey/monitoring for the substance in Japan, was conducted in FY2002. The detection limit was 40 ng L^{-1}. The substance was detected at all the surveyed sites (20 sites). Maximum concentration was 24,000 pg L^{-1}.

PFOS has not been surveyed or monitored in the biota and bottom sediment in the Environmental Survey and Monitoring of Chemicals Program.

1.4. Monitoring of dioxins (polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and coplanar PCBs)

As shown above, dioxins monitoring in various environmental media has been conducted actively in Japan from late 1990s until present together with extensive efforts to make reliable inventories and operate effective regulation to reduce their emission to the environment. The major emission sources were found to be incinerators for both municipal and industrial wastes, thus severe regulation was enforced on the incinerators to reduce total emissions of dioxins. In fact, dioxin levels in the air (Fig. 1.11) have been decreasing significantly during recent years in accordance with the estimated decrease of dioxin emissions inventory (Fig. 1.12).

Dioxin levels in the surface water and ground water have been decreasing steadily but rather slowly compared with levels in air, and their levels in sediments and soil do not seem to have decreased clearly. In general, these tendencies are consistent with the estimated behavior based on their chemical properties.

In addition to the incineration processes, herbicides, CNP (2,4,6-trichlorophenyl-4′-nitrophenyl ether) and PCP (pentachlorophenol) usage was reported as the major source of dioxins, especially during the late 1960s–1970s. While CNP contained particular non-toxic dioxin congeners such as 1,3,6,8-TeCDD and 1,3,7,9-TeCDD (Yamagishi et al.,

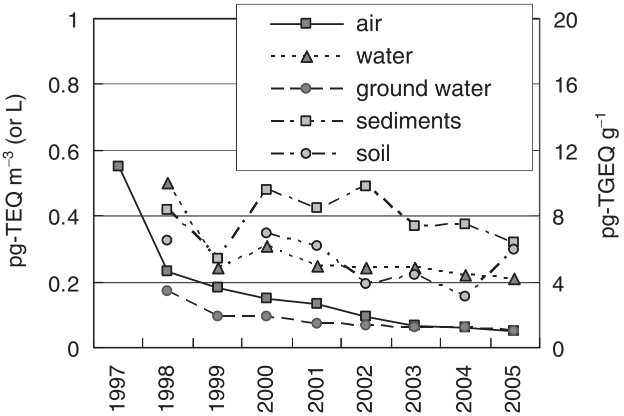

Figure 1.11. Dioxin levels in environmental media. Left axis for air, surface water, ground water; right axis for sediments, soil. Note that the data are sum of PCDDs, PCDFs and dioxin-like PCBs.

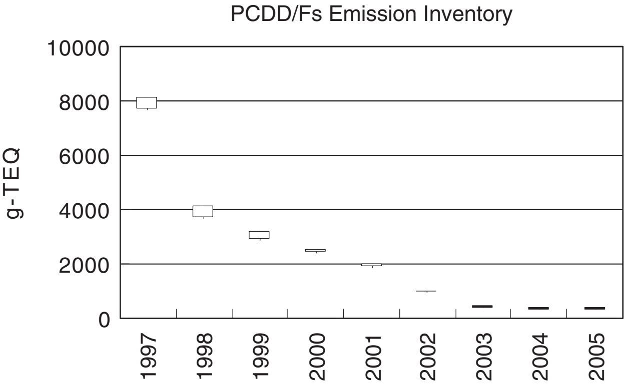

Figure 1.12. Emission inventory of PCDD/Fs in Japan. Each box represents upper and lower estimates of the total emission.

1981), PCP was found to have OCDD/F (Sakurai et al., 1998; Masunaga et al., 2003). Further, studies by Masunaga et al. (2001) indicated the existence of toxic 2,3,7,8-substituted congeners both in CNP and PCP. There are several reports on the time trend of dioxins pollution by analyzing sediment core samples (Yamashita et al., 2000; Kubota et al., 2002; Sakurai et al., 2002; Sakurai, 2003; Okumura et al., 2004). There are also reports concerning the topic by analyzing stored materials, including human samples (Konishi et al., 2001—Fig. 1.13; Choi et al., 2002, 2003).

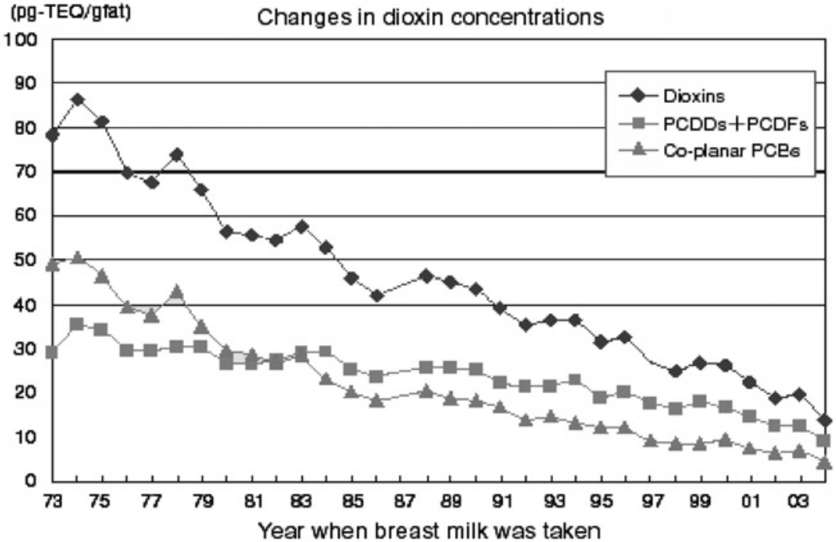

Figure 1.13. Dioxin concentrations in breast milk. Source: FY2004 Health and Labour Science Research Grants "Studies on Dioxins in Breast Milk".

1.5. Stockpiles and wastes of POPs

1.5.1. Development of detoxification methods for agricultural chemicals containing POPs

In Japan, organic chlorine agricultural chemicals including certain POPs (aldrin, dieldrin, endrin, DDT and BHC) are usually stored underground. The result of the investigation on the conditions of stored chemicals published by the Ministry of Agriculture, Forestry and Fisheries in December 2001 shows that the total amount of stored agricultural chemicals and the number of the stored places identified on this investigation was 3680 tons and 174 places, respectively. A field investigation was carried out by MOE in two districts with a view to assessing the actual conditions of the storage by farmers of agricultural chemicals containing POPs, etc., which revealed that approximately 1–2% of farmers had held 2066 kg of agricultural chemicals containing POPs, etc. 97,228 kg of the agricultural chemicals containing dioxins were collected by farmers' cooperation, etc. from 1998 to 2002.

The detoxification methods for agricultural chemicals containing POPs, etc. have been verified and these chemicals are properly disposed of by these methods.

1.5.2. State of PCB waste in storage and disposal under the PCB special measures law

MOE has released the state of PCB waste in storage that has been reported under the PCB Special Measures Law. The data on the storage and disposal status of PCB waste as of March 31, 2003, was submitted from businesses to prefectural and municipal governments.

Compared with the previous report as of March 31, 2002, the amount of PCBs stored has been increasing while the use of PCBs has been decreasing. This trend is due to the progress in gathering information on PCB waste because of the enforcement of reporting under the Law. Besides this, shift from using PCBs to storing them during this period also influenced such a trend.

The government will implement a project to develop wide-area waste disposal facilities nationwide in the pivotal cities of Kitakyushu, Toyota, Tokyo, Osaka and Muroran, as listed below, through the Japan Environmental Safety Corporation (JESCO), and in co-ordination with local public authorities.

Most PCB wastes come from high-voltage transformers and a limited number of other products, and these would require immediate attention.

The project will therefore focus initially on these products. As to smaller waste electrical devices such as stabilizers and other contaminated materials, including carbonless copying paper, which contain only a small amount of PCB, deliberation will be accelerated on the establishment of a treatment system for these materials. At the same time, it is necessary to evaluate new and existing waste disposal technologies, with top priority placed on ensuring safety. The recent advancement of disposal technology for PCB wastes from stabilizers now enables safer treatment of stabilizers. In project sites where large volumes of disused stabilizers are left untreated, an appropriate treatment system will be launched as soon as possible. For other devices and project sites, effort will be strengthened to develop a comprehensive waste disposal system in line with new technologies expected in the future.

In the construction of wide-area waste disposal facilities, JESCO is targeting small- and medium-sized enterprises and other business institutions which can commission JESCO to treat their PCB wastes and in doing so reduce their financial burden. The corporation plans to ensure the minimum treatment capacity for these facilities by having these wastes brought to the facilities in a systematic manner during the treatment period.

Enterprises which hold large volumes of waste PCBs, PCB-containing waste oils and disused pole-mounted transformers that contain PCB-containing insulation oils are building or planning to build treatment facilities on their own. It is essential for the government to assist and encourage their effort. For pole-mounted transformers and insulation oils extracted from these pole-mounted transformers, concerted actions will be taken in line with the efforts of electric power companies which store those PCB wastes.

Tables 1.3–1.5 show the estimated disuse volume, storage volume and disposal volume of wastes generated from disuse of PCB-containing high-voltage transformers and high-voltage condensers, and other large electrical devices during the period up to 2016, when treatment of PCB wastes is to be terminated under the law.

1.5.3. Study for proper disposal of POPs wastes

Stored agricultural chemicals containing the chemicals mentioned above and ashes from incineration plants, etc. containing dioxins must be disposed of appropriately as wastes containing POPs. Wastes containing dioxins are properly disposed under the Dioxins Law and the Waste Management and Public Cleansing Law (Law No. 137 of 1970, hereafter

Table 1.3. High-voltage transformer and other devices

Fiscal year	Disused volume (units)	Disposal volume (units)	Storage volume (units)
Current March–2002	–	–	High-voltage transformer 11,079; high-voltage condenser: 219,106; other devices: 40,744
2002–2008	High-voltage transformer: 1800; high-voltage condenser: 31,200; other devices: 5900	High-voltage transformer: 4400; high-voltage condenser: 83,400; other devices: 15,500	(March 2009); high-voltage transformer: 8500; high-voltage condenser: 166,900; other devices: 31,100
2009–2016	High-voltage transformer: 1600; high-voltage condenser: 26,800; other devices: 5000	High-voltage transformer: 10,100; high-voltage condenser: 193,700; other devices: 36,100	High-voltage transformer: 0; high-voltage condenser: 0; other devices: 0

Note 1: "Disused volume" refers to the amount of wastes generated from electronic devices as they are used during the corresponding period.
Note 2: "Other devices" refers to any of low-voltage transformers, low-voltage condensers, reactors, discharge coils, surge absorbers, meter transformers, switches, breakers and rectifiers that are as large as a high-voltage transformer or high-voltage condenser.
Note 3: Figures are rounded to 100 units except for the current storage volume.

Table 1.4. Waste polychlorinated biphenyl (waste PCBs) and other wastes

Fiscal year	Disused volume (t)	Disposal volume (t)	Storage volume (t)
Current–March 2002	–	–	Waste PCBs: 70; PCB-containing waste oils: 2610
2002–2008	Waste PCBs: 0; PCB-containing waste oils: 0	Waste PCBs: 0; PCB-containing waste oils: 800	(March 2009); waste PCBs: 100; PCB-containing waste oils: 1800
2009–2016	Waste PCBs: 0; PCB-containing waste oils: 0	Waste PCBs: 100; PCB-containing waste oils: 1800	(July 2016); waste PCBs: 0; PCB-containing waste oils: 0

Table 1.5. Pole-mounted transformer

Fiscal year	Disused volume (units)	Disposal volume (units)	Storage volume (units)
Current–March 2002	–	–	Case: 1,863,225; oil equivalent: 178,320 t
2002–2008	Case: 1,072,000; oil equivalent: 61,000 t	Case: 1,228,000; oil equivalent: 143,000 t	(March 2009); Case: 1,702,000; oil equivalent: 95,000 t
2009–2016	Case: 880,000; oil equivalent: 38,000 t	Case: 2,582,000; oil equivalent: 133,000 t	(July 2016); Case:0; oil equivalent: 0

Note: Figures are rounded to 1000 units or 1000 t except for the current storage volume.

referred to as the Waste Management Law). Wastes containing PCB are disposed under the PCB Special Measures Law.

The following are being addressed for other POPs based on the outcomes of the above mentioned development of detoxification methods with a view to understand the actual wastes emissions and formulating their disposal standards.

- Estimation of the existing quantity of unintentionally produced POPs.
- Compilations of technical issues to be considered in respect of methods of collection, transportation and storage of POPs wastes.
- Necessary studies for the development of POPs wastes disposal standard.
- Studying the monitoring method on the maintenance and management of POPs wastes disposal process.

1.6. Conclusion

Brief outlines of POPs monitoring activities in Japan are summarized in this chapter. In Japan, government has been carrying-out extensive environmental monitoring as the basis to plan and conduct environmental management of chemicals. After more than two decades of operation, the monitoring was reorganized recently to use HRGC/HRMS in order to know precisely and accurately the present levels of POPs contamination in Japan. Also the new monitoring method is now being implemented to East Asian countries to conduct regional monitoring of POPs in the background air sampling locations as per the requirement of Stockholm Convention (Expert Working Group, 2006). The government has also been conducting development of new analytical methods for compounds not yet monitored, including those evaluated as additional chemicals for Stockholm Convention, such as PBDEs and PFOS, and perform exposure assessment of these new chemicals to human. Furthermore, parts of the samples collected for regular environmental monitoring under the framework of "Chemicals in the Environment" were stored in frozen state for future (Environmental Specimen Banking). These activities, together with extensive researches and monitoring in national/local governmental institutes, universities and private sectors, will help the world to keep and improve quality of life by managing these chemicals properly.

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Chapter 2

Emission, Contamination and Exposure, Fate and Transport, and National Management Strategy of Persistent Organic Pollutants in South Korea

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Abstract

Public concern over persistent organic pollutants (POPs) re-emerged in the 1990s due to studies describing endocrine disrupting effects of some POPs. While monitoring data suggested that concentrations of contaminants were less in South Korea than in more industrialized countries, the public perception was that there were significant risks posed by POPs. This perception may have resulted from inaccurate and insufficient information about the status of POPs in South Korea. The South Korean government, as a signatory authority of the Stockholm Convention, is obliged to submit a national implementation plan to ban or minimize POPs emissions. To date, little has been known regarding the overall POPs status including inventories, usage patterns, sources, emission, fate, and distribution in South Korea. To assess the status of four emerging POPs as well as the 12 existing classical POPs in South Korea we have compiled and reviewed all the available literature published since the mid-1990s on POPs in South Korea. We present and discuss: (1) emission inventories of individual POPs; (2) concentrations of the various POPs in various compartments of the environment; (3) conducted ecosystem and human exposure assessments; (4) report a case study of fate and multi-media transport of POPs; and finally (5) propose an appropriate strategy to minimize the risks of POPs in South Korea. In brief, concentrations of POPs were found to be relatively small, compared to most other industrialized countries. In fact, concentrations of many of the classical POPs were less than the environmental quality criteria suggested by government agencies, except for a few 'hot spots'. However, due to a lack of sufficient information, the status and trends of PCDDs/DFs,

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DDTs, PBDEs and PFAs could not be assessed. Additional information from monitoring studies would be needed for certain locations. For instance, the emission of dioxin-like compounds, expressed on a per area basis, was estimated to be one of the greatest in the world, even though the recent governmental efforts to reduce the emission have resulted in decreased releases of several classes of POPs. Concentrations of some perfluoroalkylated compounds (PFAs), in some freshwater locations were found to be some of the greatest in the world. Identification of hot spots followed by remediation (for classical POPs) and nationwide monitoring surveys (for emerging POPs) would be strongly needed.

2.1. Introduction

The 'dirty dozen' or the 12 legacy organochlorine substances, consist of two byproducts (polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs/DFs)), one industrial product (polychlorinated biphenyls (PCBs)), and nine pesticides (DDTs, chlordanes, heptachlor, aldrin, endrin, dieldrin, toxaphene, mirex, and hexachlorobenzene (HCB)) (Stockholm Convention on Persistent Organic Pollutants, 2001). PCBs and HCB are also emitted as byproduct or impurities (UN-ECE/EMEP, 2002; Breivik et al., 2004). These dirty dozen persistent organic pollutants (POPs) were prioritized for global action by the Stockholm Convention on POPs, developed under the auspices of the United Nations Environment Program (UNEP). The criteria for prioritization included persistence, bioaccumulation potential, and toxic potency (PBT) in addition to their potential for long-range transport (LRT).

Since 1998, the United Nations/Economic Commission for Europe (UN/ECE, 1998) has included, in addition to the dirty dozen POPs, hexachlorocyclohexanes (HCHs), polycyclic aromatic hydrocarbons (PAHs), chlorodecone, and hexabromobiphenyl. The New Protocol on Persistent Organic Pollutants to the Convention on Long-Range Trans-boundary Air Pollutant (CLRT protocol) has served as the basis for these criteria. Besides the 12 existing POPs, the emerging POPs such as polybrominated diphenyl ethers (PBDEs) (Palm et al., 2002; Tanabe, 2004) and perfluoroalkyl acids (PFAs) (Giesy and Kannan, 2001; Renner, 2001a,b; Prevedouros et al., 2006) are also of increasing concern due to their extensive worldwide usage as well as possible PBT and LRT characteristics. Alkylphenols (APs) such as nonylphenol (NP) and octylphenol (OP) with endocrine disrupting properties are also stable in the environment with a half-life of approximately two months in water and in the order of years in sediments (Mackay et al., 2000; Ying et al., 2002).

National concern regarding POPs in South Korea was amplified in the mid-1990s when dioxins, carcinogenic, and endocrine disrupting compounds (EDCs), were reported to be emitted primarily from waste incinerators throughout South Korea. The total number of incinerators in South Korea reached a maximum of 16,000 in 1998. During the same period, it was reported that some of the POPs, including dioxins, could cause effects, such as breast cancer and reduced semen quality and potentially be 'environmental hormones'. The South Korean government classified them as priority pollutants for regulatory actions in South Korea. Based on a survey conducted in 2003, 91.4% of South Koreans responded that they had heard the term 'environmental hormone' at least once in their life (Kim, 2003). A survey of risk communication and perception in environmental problems (Kim et al., 2002a), found that over 82% of 574 people surveyed thought that the South Korean environment was polluted. Nevertheless, little was known in the public surveyed (i.e., <2.5 points of total 13 points) about the causes, pathways, toxic effects, and there was no personal action plan to decrease exposure to dioxins and other POPs. Most of the people responded that their knowledge regarding POPs was acquired from the mass media rather than from the scientific research papers. Recent nationwide monitoring studies have found that concentrations of POPs such as PCBs and organochlorine pesticides (OCPs) in the environment, are less than those in other industrialized countries such as the USA and Japan, and generally less than the established criteria, except for some hot spots (Kim et al., 2002b; Hong et al., 2006). Thus, in addition to having only limited information on the status and trends of contaminants and their potential toxic effects with which to conduct risk assessments and implement risk management, there was also a gap in risk communication. Thus, the public could not assess the real risks that POPs may pose to the health of the South Korean population and ecosystem.

In addition to public concern, international conventions to reduce or eliminate emissions of POPs in South Korea took effect in May 2004. The South Korean Government, as a signatory participant of the Stockholm Convention on POPs, plans to ratify the convention. Then the government is obliged to submit a National Implementation Plant (NIP) to minimize POPs emission and update the plan and provide a status report every two years from the time of ratification (Stockholm Convention on Persistent Organic Pollutants, 2001). Therefore, it is inevitable that a scientific assessment and review of the domestic status and history of the POPs pollution including emissions, contamination levels (or distribution), exposures, and risks will be needed. This information will be disseminated to the public and also used to develop efficient control strategies to minimize exposure of humans and the wildlife to the POPs. Here, we facilitate this process by bringing together in one place, for the first time, a comprehensive compendium of information available on POPs in Korea.

Studies of POPs in South Korea can be arbitrarily categorized into 3 periods: from the 1960s to mid-1990s, mid-1990s to 2000, and 2001 and later. The first study of POPs in South Korea to appear in the literature was about OCPs residues in South Korean foodstuffs performed by the 'Rural Development Administration' in 1967 before the beginning of restriction of the use of OCPs in South Korea (Lee, 1982). Until the mid-1990s, most studies of POPs in South Korea had been conducted on OCP residues in agricultural products such as vegetables (Park and Yoo, 1972; Park et al., 1974; Kim et al., 1981), foods (Kim and Lee, 1980; Lee, 1982; Ryu et al., 1986), agricultural soils (Park and Ma, 1982; Choi et al., 1987), and marine food/sediment (Lee et al., 1976, 1977; You and Park, 1984; Suh et al., 1986). The most extensive collection of data during the 1960s to mid-1990s appeared on OCPs and specifically for calculation of daily intake rates (Lee, 1982) and on the investigation of OCP residues in 236 agricultural soils (Park and Ma, 1982). Due to these initiatives and some pioneering efforts, the uses of POPs have been restricted in South Korea since late 1960s. Because early analytical techniques involving packed GC columns were less accurate and sensitive than more modern methods, the accuracy of the historical analyses of OCPs is questionable. Since the mid-1990s, several studies by academic institutions applied state-of-the-art analytical techniques to quantify POPs. During this period, in 1996, standard analytical methods were established for quantifying dioxins in air. The development of sensitive and standard analytical techniques improved the accuracy of POPs quantification, which made international comparisons of concentrations possible. These data were available for robust meta-analyses. Governmental efforts began only in the last decade for through investigation and effective management of POPs. Since 1999, the South Korean government and the Ministry of Environment (KMOE) began nationwide monitoring of POPs in the environment and in humans. Since 2001, comprehensive projects have been undertaken to establish the national emission inventory of some priority POPs (dioxins in particular).

While comprehensive research and surveys were delayed, or lacking, no significant effort had been put toward the overview of the existing data of emissions, sources, distribution, exposure, and fate of POPs. Lee and Kim (1999) collected published data on concentrations of EDCs for almost all environmental media and human tissues and performed a meta-analysis to examine the relationship between the sperm quality of South Korean males and exposure to EDCs. Environmental concentrations and rates of emission of POPs, such as PCBs and OCPs, have been reviewed by KMOE (KMOE, 2004a). These preliminary studies were limited to the collection of data on concentrations in various environmental compartments.

In an attempt to provide an overview and assessment of the POPs in South Korea, we have conducted a comprehensive literature search and compiled the existing POPs data (including the emerging POPs) from surveys conducted since the mid-1990s in South Korea. This chapter presents: (1) emission inventories of individual POPs; (2) concentrations in various environmental including humans; (3) exposure assessment in the ecosystem and humans; (4) a case study of fate and multi-media transport of POPs; and finally, (5) a proposal for a strategy to minimize releases and ultimately eliminate POPs in South Korea.

2.2. Methodology: Literature survey and target POPs

For this chapter, we searched the peer-reviewed, open, scientific literature by using the Science Citation Index (SCI) and 'ScienceDirect', 'SCIRUS', and 'SpringerLink'. Domestic articles that would not be listed in these citation services were collected using online websites of 33 South Korean science societies and 'Korean studies Information Service System (KISS)' of Korean Studies Information Corporation. Literature collected includes: (1) 91 articles published in SCI journals; (2) 57 domestic articles; (3) 40 research reports performed or funded by governmental agencies; and (4) 4 dissertations (Fig. 2.1). Reports quoted consisted of 25 regular nationwide monitoring studies (6 by National Institute of Environment Research (NIER), 16 by the South Korea Food and Drug Administration (KFDA), and 3 by the Ministry of Maritime Affairs and Fishery (MOMAF)), 12 emission inventories, and 3 exposures and meta-analyses. Most inventories of emissions were either performed or funded by the KMOE or NIER.

In the present study, 17 compounds including dirty dozen POPs (OCPs, PCDDs/DFs, PCBs), two emerging POPs (PBDEs and PFAs), and two potential POPs (APs and PAHs) in the South Korean environment were reviewed (Table 2.1 and 2.2). Among the 17 POPs, the most studied pollutant was determined to be chlorinated dioxins and dioxin-like compounds such as PCDDs/DFs and dioxin-like PCBs for which occurrence, distribution, contamination level, fate, exposure, and control techniques have been fairly thoroughly investigated. The literature on dioxin research included 42 SCI articles and 57 domestic articles. Because most of

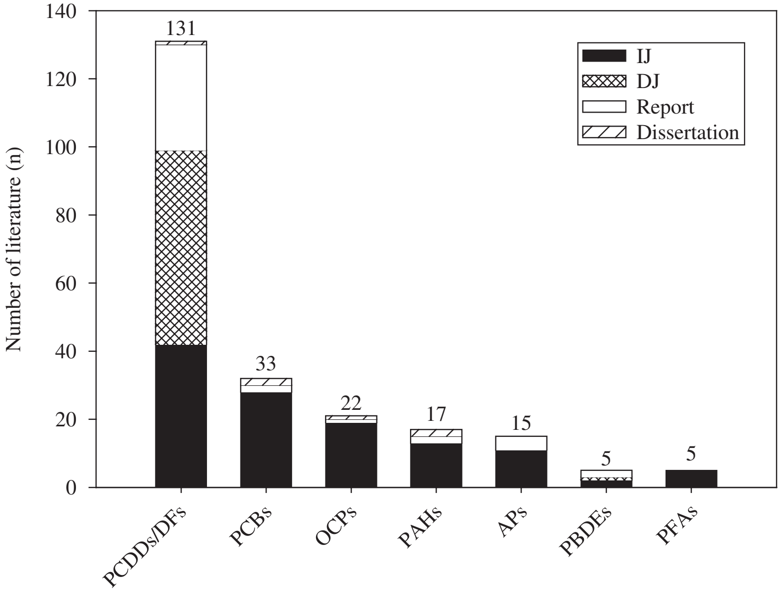


Fig. 2.1. Korean literatures collected for meta-analysis of target POPs substances: SCI article (IJ), Domestic article (DJ), Research report (Report), and PhD dissertation.

the data originated from 13 laboratories certified for dioxin analysis, the domestic articles were also included in this survey. Although 80 domestic articles were reviewed, information from only 33 SCI articles were used for the meta-analysis of PCBs, OCPs, and PAHs because they were considered to provide sufficient information to allow us to describe distribution and concentrations in the environment. Most of these articles reported concentrations in the environment as well as possible sources. In addition to legacy POPs, we also reviewed information on emerging contaminants of concern. Data on alkylphenols were extracted from 11 SCI articles and 4 reports; PBDEs from 2 SCI articles, 1 domestic article, and 2 reports; PFAs from 5 SCI articles. The number and volume of the literature indicates that the South Korean POP studies have primarily focused on legacy POPs (i.e., dioxins, PCBs, and OCPs) while little attention is given to emerging POPs (i.e., PBDEs and PFAs).

The physico-chemical properties of these POPs are illustrated in Fig. 2.2. APs and PFAs (hydrophilic substances) are relatively more water soluble than the legacy POPs, which suggests that these pollutants could easily reside in water column and then can be carried to remote areas by hydrospheric movement (Yamashita et al., 2005).

Table 2.1. Target POPs involved in this study and the regulatory action in Korea

Pollutant category	Major use in Korea	Regulatory action						
		ACMA[a]	TCCA[b]	ISHA[c]	EBA[d]	CACA[e]/ WQCA[f]/ SECA[g]	WCA[h]	Food residual level[i]
Existing POPs								
Polychlorinated biphenyls (PCBs)	Dielectic fluid etc.	–	Ban ('96) (> 50 ppm, '99)	Ban ('03)	Ban ('79)	Specific hazardous chemical	Hazardous waste (> 2 ppm)[k]	–
OCPs[j]								
DDTs	Insecticide	Ban ('69)	Ban (> 1%, '91)	Ban	–	–	–	<0.1 ppm
Chlordanes (CHLs)	Insecticide/additive agent	Ban ('69)	Ban (> 1%, '99)	Ban	–	–	–	<0.02 ppm
Hexachlorocyclohexane (HCHs)	Insecticide	Ban ('69)	Ban (> 1.5%, '91)	Ban	–	–	–	
Aldrin	Insecticide/additive agent	Ban ('69)	Ban (> 0.1%, '99)	Ban	–	–	–	<0.01 ppm
Endrin	Insecticide/additive agent	Ban ('69)	Ban (> 1%, '99)	Ban	–	–	–	<0.01 ppm
Dieldrin	Insecticide/additive agent	Ban ('70)	Ban (> 1%, '99)	Ban	–	–	–	<0.01 ppm
Heptachlor	Insecticide/additive agent	Ban ('79)	Ban (> 6%, '99)	Ban	–	–	–	<0.01 ppm
Toxaphene (Camphechlor)	Insecticide	Ban ('82)	Ban (> 1%, '91)	Ban	–	–	–	–
Endosulfan	Insecticide	–	Ban (> 1%, <'03)	Ban	–	–	–	–
Tetrachlorobenzene (TeCB)	Intermediate in pesticide	–	–	–	–	–	–	–
Pentachlorobenzene (PeCB)	Intermediate in pesticide	–	Ban (> 1%, <'03)	Ban	–	–	–	–
Hexachlorobenzene (HCB)	Domestic no use	–	–	–	–	–	–	–
Mirex	Domestic no use	–	–	–	–	–	–	–
Dioxins/furans (PCDDs/DFs)	By-products	–	–	–	–	–	Restricted release ('97)[l]	–
Coplanar PCBs (coPCBs)	By-products	–	–	–	–	–		–
Hexachlorobenzene (HCB)	By-products	–	–	–	–	–	–	–

Table 2.1. (*Continued*)

Pollutant category	Major use in Korea	Regulatory action						
		ACMA[a]	TCCA[b]	ISHA[c]	EBA[d]	CACA[e]/ WQCA[f]/ SECA[g]	WCA[h]	Food residual level[i]
Emerging POPs								
Polybrominated diphenyl ethers (PBDEs)	Flame retardant	–	–	–	–	–	–	
Perfluoroalkyl acids (PFAs)	Acids of fluoropolymer, rust/oil/ water retardant							
Others								
Alkylphenols (APs)		–	–	–	–	–	–	–
Polycyclic aromatic hydrocarbons (PAHs)		–	–	–	–	–	–	–

[a] ACMA (Agrochemical Management Act); the ban of registration of pesticides, indicating implicitly the ban of import, manufacture, and selling.

[b] TCCA (Toxic Chemical Control Act); the restricted use (until '90) and the ban (from '91) of manufacture, import, and use of non -food additive agent.

[c] ISHA (Industrial Safety and Health Act); the same legal action as TCCA was enacted in 2003.

[d] EBA (Electricity Business Act); the ban of use for electric heater of facilities used PCB -containing dielectic fluid.

[e] CACA (Clean Air Conservation Act); the specific air hazardous chemical.

[f] WQCA (Water Quality Conservation Act); the water quality criteria of PCBs as specific water hazardous chemicals.

[g] SECA (Soil Environment Conservation Act); the air quality criteria of PCBs as specific water hazardous chemicals.

[h] WCA (Waste Control Act); the restriction of waste treatment.

[i] Guideline of Korean Food and Drug Administration (KMOE, 2004).

[j] OCPs (Organochlorine Pesticides).

[k] PCBs as specific hazardous waste should be treated in separated and specific method and reported and confirmed by KMOE administrator.

[l] Release guideline of waste incinerators (see Table 3).

Table 2.2. Target compounds of persistent organic pollutants (POPs) reviewed; PCDDs/DFs, PCBs, OCPs, PAHs, APs, PDBEs, and PFAs, respectively

Abbreviation	Full name
PCDDs/DFs	Polychlorinated dibenzo-*p*-dioxins/-dibenzofurans
TCDD/DF	Tetrachlorinated dibenzo-*p*-dioxin/-dibenzofuran
PeCDD/DF	Pentachlorinated dibenzo-*p*-dioxin/-dibenzofuran
HxCDD/DF	Hexachlorinated dibenzo-*p*-dioxin/-dibenzofuran
HpCDD/DF	Heptachlorinated dibenzo-*p*-dioxin/-dibenzofuran
OCDD/DF	Octachlorinated dibenzo-*p*-dioxin/-dibenzofuran
PCBs	Polychlorinated biphenyls
di-CB	Dichlorinated biphenyl
tri-CB	Trichlorinated biphenyl
tetra-CB	Tetrachlorinated biphenyl
penta-CB	Pentachlorinated biphenyl
hexa-CB	Hexachlorinated biphenyl
hepta-CB	Heptachlorinated biphenyl
octa-CB	Octachlorinated biphenyl
nona-CB	Nonachlorinated biphenyl
deca-CB	Decachlorinated biphenyl
OCPs	Organochlorine pesticides
CBs	Chlorobenzenes
1,2,3,4-TCBZ	1,2,3,4-Tetrachlorobenzene
1,2,4,5-TCBZ	1,2,4,5-Tetrachlorobenzene
PCBZ	Pentachlorobenzene
HCB	Hexachlorobenzene
HCHs	α-, β-, γ-, δ-Hexachlorocyclohexane
α-HCH	α-Hexachlorocyclohexane
β-HCH	β-Hexachlorocyclohexane
γ-HCH	γ-Hexachlorocyclohexane (lindane)
δ-HCH	δ-Hexachlorocyclohexane
CHLs	Chlordanes
PentaCA	Pentachloroanisole
HeptaC	Heptachlor
HeptaCE	Heptachlor epoxide
OxyCHL	Oxychlordane
γ-CHL	γ-Chlordane (*trans*-Chlordane)
α-CHL	α-Chlordane (*cis*-Chlordane)
cis-nonaC	*cis*-Nonachlor
trans-nonaC	*trans*-Nonachlor
Drins	Drins (Aldrin, Dieldrin, Eldrin, Endrin sulfate)
Endosulfan	Endosulfan I, II, Endosulfan sulfate
DDTs	Dichlorodiphenyl trichloroethanes
o,p'-DDE	o,p'-Dichlorodiphenyl dichloroethane
p,p'-DDE	p,p'-Dichlorodiphenyl dichloroethane
o,p'-DDD	o,p'-Dichlorodiphenyl dichloroethylne
p,p'-DDD	p,p'-Dichlorodiphenyl dichloroethylne
o,p'-DDT	o,p'-Dichlorodiphenyl trichloroethane
p,p'-DDT	p,p'-Dichlorodiphenyl trichloroethane

Table 2.2. (*Continued*)

Abbreviation	Full name
PAHs	Polycyclic aromatic hydrocarbons
NAP	Naphthalene
2-MNAP	2-Methylnaphthalene
1-MNAP	1-Methylnaphthalene
BiP	Biphenyl
2,6-DiMNAP	2,6-Dimethylnaphthalene
ACY	Acenaphthylene
ACE	Acenaphthene
2,3,5-TriMNAP	2,3,5-Trimethylnaphthalene
FLU	Fluorene
PHE	Phenanthrene
ANT	Anthracene
1-MPHE	1-Methylphenanthrene
FLT	Fluoranthene
PYR	Pyrene
BaA	Benzo[a]anthracene
CHR	Chrysene
BbF	Benzo[b]fluoranthene
BkF	Benzo[k]fluoranthene
BeP	Benzo[e]pyrene
BaP	Benzo[a]pyrene
PER	Perylene
I123cdP	Indeno[1,2,3-cd]pyrene
DahA	Dibenzo[a,h]anthracene
BghiP	Benzo[ghi]perylene
APs	Alkylphenols
NP	Nonylphenol
OP	Octylphenol
BP	Butylphenol
BPA	Bisphenol A
PBDEs	Polybrominated diphenyl ethers
penta-BDE	pentabromodiphenyl ether
octa-BDE	octabromodiphenyl ether
deca-BDE	decabromodiphenyl ether
PFAs	Perfluorinated alkyl compounds
PFOS	Perfluorooctanesulfonate
PFHxS	Perfluorohexanesulfonate
PFBS	Perfluorobutanesulfonate
PFOSA	Perfluorooctanesulfonamide
PFDA	Perfluorodecanoate
PFNA	Perfluorononanoic acid
PFOA	Perfluorooctanoate
PFHpA	Perfluoroheptanoate
PFHxA	Perfluorohexanoate

Table 2.2. (*Continued*)

Abbreviation	Full name
Dioxin-like compounds	
PCDDs	2378-TCDD, 12378-PeCDD, 123478-HxCDD, 123678-HxCDD, 123789-HxCDD, 1234678-HpCDD, OCDD
PCDFs	2378-TCDF, 12378-PeCDF, 23478-PeCDF, 123478-HxCDF, 123678-HxCDF, 123789-HxCDF, 234678-HxCDF, 1234678-HpCDF, 1234789-HpCDF, OCDF
coPCBs	non-*ortho* PCBs (PCB 77, 81, 126, 169), mono-*ortho* PCBs (PCB 105, 114, 118, 123, 156, 157, 167, 189)

2.3. POPs issues and control strategy in South Korea

Although numerous books and research articles describing the geography, climate, weather, population, and other national statistics of South Korea have been published, we provide a brief overview of these geographical and demographic characteristics of South Korea because this information is pertinent to understand the POPs issue in South Korea. Furthermore, we have provided a historical overview of government policies and regulations regarding POPs in South Korea. This overview covers the history of POPs issue, national strategy for POPs control, and national surveillance and monitoring in South Korea.

2.3.1. Description of South Korea

2.3.1.1. Geography

The Korean Peninsula is located in the northeastern part of Asia, which lies between 33°N and 43°N parallels, 124°E and 132°E meridians bordered on the north by China and Russia. South Korea is about 1100 km long and 300 km wide with total land area of ~222,000 km^2, almost the same size as the United Kingdom. The geomorphology of South Korea is characterized by mountains and hills. Such hilly terrain, while occurring mostly in the eastern part of the Korean peninsula accounts for about 70% of its territory (Fig. 2.3). More than 3200 islands are scattered along or near the southern and southwestern coastlines. Due to the many islands that make up parts of Korea, the coastal length of the islands (~8600 km) is almost equal to that of main peninsula (~8700 km). Most of the rivers flow into the Yellow Sea and the South Sea after draining the western and southern slopes of the peninsula. POPs study as well as other regular monitoring programs have covered the far eastern island (i.e., Dok-do) in the East Sea and the southern Jeju Island.

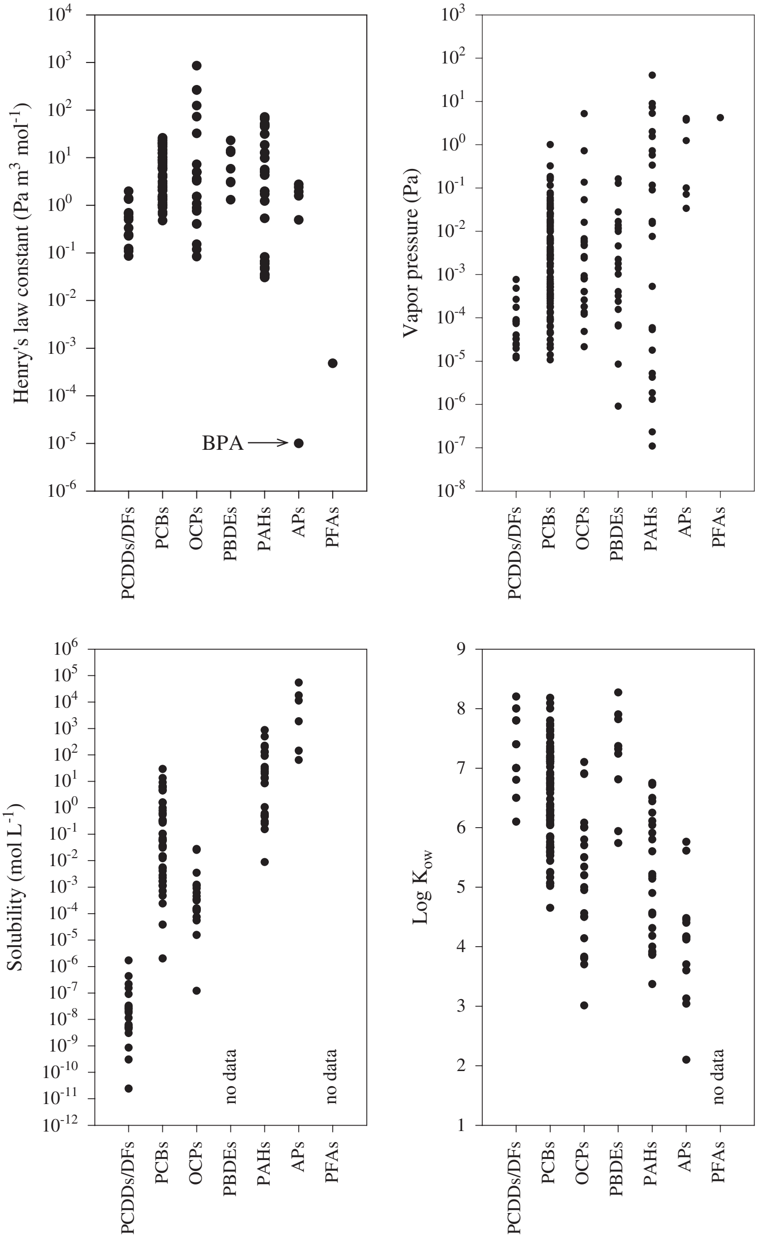


Fig. 2.2. Physicochemical properties (at 25°C) in literatures of target POPs for the present study; Mackay et al., 2000; Cetin and Odabasi, 2005; Lau et al., 2006; Bruner et al., 1990; Park et al., 2002a; Bamford et al., 1999; Paasivirta et al., 1999; Wong et al., 2001; Falconer and Bidleman, 1994; Braekevelt et al., 2003; Hawker and Connell, 1988.

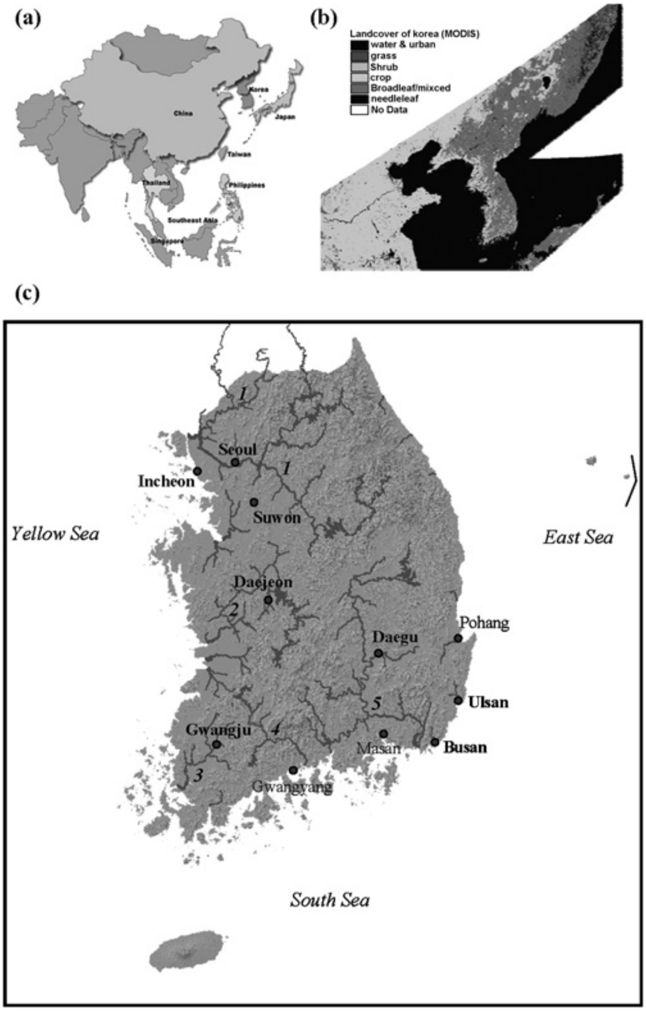


Fig. 2.3. Maps of Asia (a) and Korean peninsula: landscape (b) and digital elevation map (DEM, (c)): Major eight cities with bold character have population over one million. Iron steel mills located at Pohang, Gwangyang and Incheon, and big industrial complexes at Incheon, Ulsan, and Masan. Fiber industry complex has been developed in Daegu since 1950. Major rivers are magnified; Han River (1), Kum River (2), Youngsan River (3), Seomjin River (4), and Nakdong River (5).

2.3.1.2. Climate

The climate of South Korea is temperate monsoon, in general, but geographically and seasonally varied. The western coast open to continental Asia is vulnerable to the influence of the winter monsoon. In contrast, the eastern coast is sheltered from the winter monsoon by the Taebaeksan range, the backbone mountain of the Korean Peninsula. Winter is dry and cold (−6–7°C in January) and is influenced primarily by the Siberian air mass. Summer is hot and humid with temperatures ranging from 23 to 27°C. The climate is the result of the maritime Pacific high-pressure ridge. Temperatures in all seasons are somewhat less than those that occur at corresponding latitudes in other continents, such as North America or Western Europe. Annual precipitation is about 1500 mm in the central region. More than a half of the total rainfall is concentrated in summer, while precipitation of winter is less than 10% of the total.

2.3.1.3. Population

South Korea, the southern half of the Korean Peninsula, is composed of Seoul, seven major cities, and nine provinces with a total population of ca. 48 million (2005 Census). Seoul, the capital city of South Korea, is densly populated (11 million), accounting for about a quarter to the total population in South Korea. Other seven major cities with population of greater than 1 million are Busan, Daegu, Incheon, Gwangju, Daejeon, Ulsan, and Suwon. Since the early 1960s, South Korea has achieved a rapid economic growth, which has been termed the 'Miracle on the Han River'. Recently, the size of the economy of South Korea has grown up to be the 10th largest in the world, and the 3rd largest in Asia, next only to China and Japan.

Substantial urbanization has followed economic growth. South Korea is one of the countries where available area per capita is the least in the world (population density of South Korea is 473 km^{-2}). Futher, the concentration of population density and industries within its urban regions (viz. Seoul and seven major cities) has reached serious proportions, accounting for approximately 50% of the total population in only 5.5% of the land area and approximately 55% of the manufacturing industries in only 11.8% of the land area. In recent years, the government has sought to minimize the urbanization in the capital region, but the trend of urbanization continues to increase. Urbanization rate, the ratio of population in urban area to total population, has increased dramatically, from 28.3% in 1960 to 89.2% in 2004 (KMOE, 2005b). This implies that pollution is likely to be localized in urban and industrial areas.

Furthermore, urbanization means a significant increase in the surfaces without vegetation such as asphalt and building cover. Surface conditions could substantially influence the residence time and fate of POPs in a system. Agricultural activities, of which the dominant activity is rice cultivation, occur primarily in the western and southern areas of the South Korean peninsula. Thus, the water quality of the inland rivers is associated with OCP use history and agricultural products contamination in South Korea.

2.3.1.4. Economy and potential hot spots

Heavy industrialization together with urbanization brought by rapid economic growth has resulted in serious environmental problems in some areas. Now, more than 570 Industrial Complexes (ICs) (30 national ICs, more than 210 regional ICs, and more than 330 agricultural ICs) are in operation nationwide (http://www.kicox.or.kr). Majority of large scale ICs are located near large coastal cities such as Incheon, Busan, Ulsan, Masan, and Pohang. Since many of the ICs are situated near the larger cities, large amounts of industrial wastes together with municipal wastes from inland areas are discharged into the coastal regions. Organic contaminants could also be transported into nearby coastal areas by rivers and/or streams. Thus, greater environmental pollution with POPs and EDCs would be expected to occur along the coastal areas of highly industrialized regions.

2.3.2. POPs issues in South Korea

2.3.2.1. History of POPs issues

There have been accidental releases of pollutants that have cause effects on humans and wildlife, such as Yucheng in Taiwan, Yusho in Japan (Ikeda, 1996), PCB contamination of poultry in Belgium (Bernard et al., 1999), Seveso in Italy (Mocarelli, 2001), and dioxin contamination by redistribution and burial of contaminated soils at Love Canal in the USA (Vianna, 1983). However, despite intensive and rapid industrialization and urbanization, such massive POPs related cases have not occurred in South Korea. Since the 1990s, monitoring South Korea has rarely found POP concentrations as great as parts per million (ppm).

Public concern over POPs (or EDC) was initiated by the dioxin issue, evoked by environmental groups and mass media in the mid-1990s, on waste incinerators. The public concern was further heightened following the reports of adverse effects of tributyl tin (TBT) on mollusks in South

Korean coastal waters (Shim et al., 2000). The issue of human health effects from exposure to POPs, was first investigated relative to releases of dioxins from incinerators to neighboring residents who claimed to have experienced great rates of cancer compared to the control population (CIES, 2002). Whether the 'increased rate of cancer' in Pyeongtak area has truly occurred was not clear in the following and more comprehensive study (Pyoungtak City, 2003). Even though there was no clear relationship between exposure and adverse outcomes, such as cancer and concentrations of PCDDs/DFs in blood, there was a relationship between proximity to incinerators and the concentrations and patterns of PCDDs/DFs in soils and blood. Elevated CYP 1B1 enzyme activity was observed in individuals living near incinerators. In contrast to acute inhalation exposure, due to the increased consumption rate of fatty food such as fishes and meat in South Korea, another recent concern has been chronic exposure to POPs through consumption of contaminated food. According to a recent food consumption survey, fish/shellfish and meat constitute 13% of the total daily intake of food, which is 1280 g d^{-1} $person^{-1}$. Particularly, the fish/shellfish consumption rate contributes as much as 7% (KREI, 2004) of the total diet. Intake of fish/shellfish and meat in 1980 represented only 1% and 4%, respectively (Lee, 1982). Cereal intake has decreased, while animal food consumption has increased; in which, seafood intake is gradually increasing. Consumption of fish/shellfish is thought to be a dominant factor in human exposure to POPs in South Korea.

2.3.2.2. National strategy for POPs control

Regulatory controls of POPs-containing raw materials or wastes in South Korea are based on eight individual acts (Table 2.1). In 2005, one POPs specific ordinance was presented for registration to effectively enact the use, distribution, emission/discharge, environmental residual levels, and treatment and management over the whole life cycle.

The early regulation was focused on classical POPs, namely, the OCPs (Table 2.1). Like many other developed countries, almost all OCPs were banned from use in South Korea, during the early stages of POPs control in the late 1960s. The AgroChemical Management Act (ACMA) banned the registration of OCPs in 1969, which implies the ban of import, manufacture, and sale. After the ban of other OCPs, heptachlor and toxaphene were widely used as alternatives (see later Fig. 2.9). However, in 1980, these two pesticides were also banned from use in South Korea. HCB and mirex were neither imported nor produced in South Korea as pesticide. Endosulfan, known to affect the central nervous system

(Paul and Subramaniam, 1997; Roberts et al., 2004), has not been banned and is still being used. It is know that OCPs were imported and used illegally for a few years even after the ban. Furthermore, some OCPs are known to have been used as a non-food additive agent. For example, chlordane was used as an adhesive for plywood and DDTs as an intermediate in the production of dicofol. It was not until the 1990s that regulation of OCPs in South Korea was mandated by the Toxic Chemical Control Act (TCCA).

PCBs were imported from abroad and their use was legally regulated for the first time in 1979. The Electricity Business Act (EBA) prohibited the use of electric heaters with PCB-containing dielectic fluids. However, existing PCB-containing articles were allowed to be used for other purposes until 1996 when production, import, and use of articles containing concentrations of PCBs greater than 50 ppm were banned by the TCCA. Waste containing concentrations of PCBs greater than 2 ppm was classified as specific hazardous wastes was treated by special methods listed in the law, and should be reported to and confirmed by the KMOE.

According to the Stockholm Convention, PCB-containing equipments such as capacitors, condensers, and transformers should be forbidden from use by 2025 and are recommended to be treated by environmentally sound methods by 2028 (Stockholm Convention on Persistent Organic Pollutants, 2001). The South Korea Ministry of Environment (KMOE), South Korea Electric Power Corporation (KEPCO) and six electric power companies, and three non-governmental organizations (NGO) reached a cooperative and administrative agreement in 2004 for the removal of PCBs in South Korea by 2015 (KMOE website). An investigation of the domestic status of PCB-containing articles is currently being conducted.

In spite of the regulations, government actions on POPs began practically only after a public concern on the dioxin release in waste incinerators in 1997. Since then, the emission of PCDDs/DFs was included in regulations. Recently, in response to the Stockholm Convention, periodic monitoring has been conducted in South Korea.

The total amount of waste generated in South Korea in 2003 was 300,000 ton day^{-1}. Construction waste, a dominant waste-type in South Korea, has increased from 16% in 1966 to 49% of the total amount of the waste currently. Almost 90% of this waste is recycled and just 1.5% is incinerated. Thus, the proportion of solid waste that is incinerated (6%) is rather small, relative to other countries in Asia (Fig. 2.4). However, the proportion of municipal and industrial waste that contributes to 17% and 34% of the waste that is incinerated has increased continuously. In 1993, the ratio of municipal solid waste (MSW) that was incinerated in South

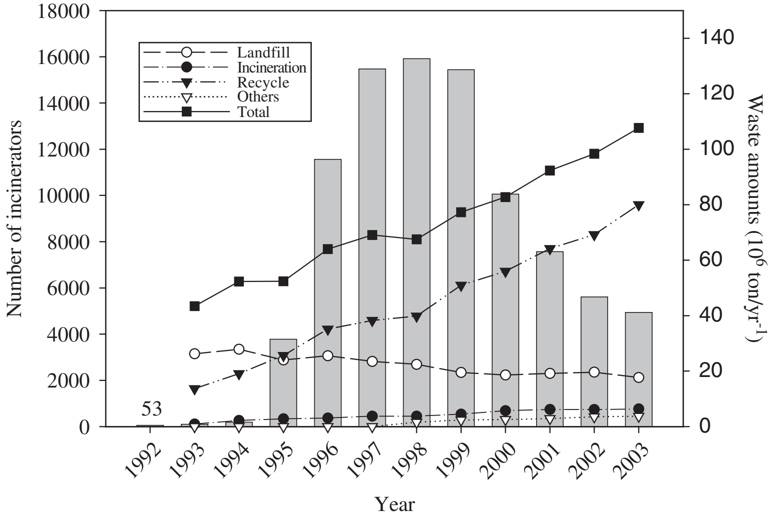


Fig. 2.4. Annual trend of number of all the incinerators in operation (bar plots from Kim et al., 2002d) and waste amounts treated by each method (symbol-line plots from KMOE & NIER, 1997, 1998, 1999, 2000, 2001, 2002, 2003) in Korea.

Korea was about 2.4%, which increased to 14.5% in 2003 (KMOE, 2005b). The proportion of industrial waste that is incinerated has increased from 1.9% to 7.8% during the same period. The proportion of waste that is incinerated is expected to increase in the future as land becomes more and more developed and lesser land is available for landfill.

Waste incineration is a known source of dioxins and other dioxin-like compounds. As a part of change in waste management policy since the early 1990s, many incinerators have been constructed. The number of incinerators in South Korea reached a maximum of about 16,000 in 1998 (from only 100 in 1993). However, it has decreased noticeably to ~5000 in 2003 since an introduction of stringent dioxin emission regulations for the incinerators in 1997 (Fig. 2.4). The majority of these incinerators (more than 90%) are small-scale facilities with a capacity of less than 0.2 ton hr^{-1}. Although the number of large-scale incinerators with capacities of greater than 4 ton hr^{-1} is only 0.2% of the total incinerators, the quantity of wastes treated by these large-scale incinerators is over 70% of the total incernation (Table 2.3). Thus in 1997, the government has started to require emission control of newly installed municipal incinerators with incineration capacities equal to or greater than 50 ton day^{-1} (Table 2.4). Since that time, large-scale incinerators have been required to restrict emission of dioxins to less than 0.1 ng I-TEQ Nm^{-3}. Subsequently,

Table 2.3. Temporal trend of the number of incinerators (unit; *n*) and waste amounts incinerated (unit; 10^3 ton yr^{-1})

	Incinerator size					References
	Year	Small	Medium	Large	Total	
Incinerator facility (*n*)[a]	2000	11,841	394	103	12,338	KMOE, 2001
	2001	7697	362	114	8173	KMOE, 2002a
	2002	5733	309	126	6168	KMOE website
Incineration amount	2000	328	646	2335	3309	KMOE, 2001
	2001	257	848	3481	4586	KMOE, 2002a
	2002	322	751	3899	4972	KMOE website

[a] Data were collected in June every year. Final values are less than these.

medium- and small-scaled incinerators have been included in these regulations (Table 2.4). Now, all the incinerators are required to reduce emissions of dioxins to less than 0.1–10 ng I-TEQ m^{-3}. Under the Waste Control Act (WCA), facilities that incinerate less than 0.025 ton hr^{-1} are no longer allowed (Kim, 2001). Another provision of the WCA is that all incinerators are obliged to conduct regular monitoring for dioxin-like compounds: semiannually, annually, and biannually for large, medium, and small scale, respectively. Since these regulations went into effect, the best available technologies (BAT) such as spray absorber/bag filter (SDA/BF) with lime and activated carbon mixture sprayed into the SDA have been applied to incinerators (Kim et al., 2001a) and the number of smaller, less economically feasible incinerators has greatly decreased.

In addition to regulations on waste incineration, discharge/emission guidelines for dioxins released from industrial sources, such as metallurgical plants, are expected to be established in 2006 (KMOE website). In 2005, an administrative agreement on reduction of dioxin emission through industrial processes was adopted by among KMOE, NGOs, and four industries, including the iron & non-iron metal industry, cement industry, and chemical industry. The groups agreed to reduce dioxin emission to 70% of that estimated for 2001 by 2008 and 50% by 2010. To achieve this goal best environmental practice (BEP) in addition to BAT will be adopted.

Establishment of emission and/or discharge guidelines for each source and environmental quality criteria for each compartment are legal regulations that have been established to reduce environmental exposure to POPs. South Korean guidelines and quality criteria are applied to dioxins from municipal waste incinerators, and waste and environmental quality guideline for PCBs (Table 2.1). The extensive guidelines will be applied following a ministerial ordinance entitled ‘Specific Act on Management of

Table 2.4. Guideline of dioxins release from waste incinerators (ng I-TEQ m^{-3})

Waste type	Incinerator size		Guideline and application date			
			New incinerator		Existing incinerator	
Municipal solid waste	Category	Capacity/application	From Jul./97	To Jun./99	To Jun./03	From Jul./03
	Large	> 50 ton/day	0.1	0.5	0.5	0.1
Other all wastes	Category	Capacity/application	From Jan./01	To Dec./02	To Dec./05	From Jan./06
	Large	≥4 ton/hr	0.1	20	20	1
		2–4 ton/hr	1	40	40	5
	Medium/small	0.025–2 ton/hr	5	40	40	10
Hospital/medical waste	Category	Capacity/application	From Aug./04	To Dec./05	To Jun./06	From Jul./07
	Large	≥4 ton/hr	0.1	0.1[a] (20)[b]	0.1 (1)	0.1 (1)
		2–4 ton/hr	1	1 (40)	1 (5)	1 (5)
	Medium	1–2 ton/hr	1	5 (40)	5 (10)	1 (5)
		0.2–1 ton/hr	5	5 (40)	5 (10)	5 (5)
	Small	0.025–0.2 ton/hr	5	–	10 (10)	10 (10)

[a] For hospital/medical waste incinerators installed between Jan./01 and Jul./04.

[b] For hospital/medical waste incinerators installed before Jan./01.

Persistent Organic Pollutants including Dioxins (Specific Act for POPs control)' that was recently promulgated (KMOE website). This ordinance involves regulation and activities to reduce exposure to POPs including: (1) prohibition and restriction of production, distribution, and use of POPs; (2) establishment of environmental quality guidelines (EQGs) in each compartment, human tolerable daily intake (TDI), standard operation procedure (SOP), and regular monitoring system; (3) emission control including establishment of emission guidelines and emission inventories; (4) management of POPs containing waste; and 5) protection of POPs contamination of soils and restoration of POPs-contaminated soils.

2.3.2.3. National surveillance and monitoring

Beginning in July 1999, several governmental agencies have established 'A 10-year National Research Program for Endocrine Disruptors (1999–2008)' (Choi, 2002). As part of this program, it has been agreed that seven governmental ministries, including the Ministry of Environment (KMOE), Rural Development Administration (RDA), South Korea Food and Drug Administration (KFDA), Ministry of Maritime Affairs and Fisheries (MMAF) and the Ministry of Labor (MOL) should perform various kinds of research and surveillance of EDCs (or POPs). Risk assessments and regular monitoring for POPs exposure from foods and environmental media, and in humans should be conducted and emission inventories developed (Table 2.5).

Nationwide surveillance of POPs is now being performed by a number of governmental agencies. They are establishing emission inventories and regular monitoring of residual levels. National emission inventories are necessary for tracing the life cycle of pollutants, estimating their behavior and fate in environments, and managing and controlling POPs substances by use of BAT in an integrated strategy. Studies of the emissions and/or discharge have focused on unintentionally produced by-products including PCDDs/DFs, coPCBs, PAHs, and HCB because product POPs such as PCBs and OCPs, the uses of which were regulated previously. The earliest emission study was on atmospheric emission of PAHs through pyrolytic processes (MCIE, 1999). This study estimated emission rates by methods developed by the US EPA (US EPA, 1998a). Similar top-down approaches using emission rates and activities of individual sources were applied to estimate preliminary emission inventories for PCDDs/DFs (KMOE, 2001, 2002a) and byproduct PCBs, HCB, and PAHs (KMOE, 2003b) from point sources, and PCDDs/DFs from non-point sources (KMOE, 2004c). The estimates provided by these preliminary studies

Table 2.5. Governmental investigation projects for POPs in Korea (modified from KMOE website (http://www.me.go.kr/dev/board/)

Target medium	Investigation contents	Target POPs[a]	Year[b]	Governmental institution	References
Emission inventory					
Point source	Waste incinerators ($n = 1800$), metallurgical/chemical/energy/mineral production industries ($n = 288$)	PCDDs/DFs, coPCBs	2001–2005	KMOE[c]	KMOE website; NIER, 2000b; KMOE, 2001, 2002a, b, 2003a, 2004b, 2005a
Non-point source	Transport, uncontrolled/residential fuel combustion, fires etc.	PCDDs/DFs, coPCBs, HCB	2004–	KMOE	KMOE, 2004c, 2005a
Products	PCBs product and waste, and OCPs	PCBs, OCPs	2003–2005	KMOE	KMOE, 2004a
By-products	Unintentional PCBs and HCB, and PAHs in point and non-point sources	PCBs, HCB, PAHs	2004–2006	KMOE	MCIE, 1999; KMOE, 2003b; KMOE, 2005a
Monitoring					
Environmental media	Air, freshwater, river/lake sediment, soil, and fresh fishes	67 EDCs	1999–	NIER[d]/KMOE	NIER, 2000a; 2001; 2002; 2003; 2004; 2005a; KMOE website
	Coastal water, sediment, and sentinel organism (i.e., mussel-watch program)	PCDDs/DFs, coPCBs, PCBs, OCPs, PAHs etc.	1999–	MOMAF[e]	Kim et al., 2002b; Oh et al., 2003; Hong et al., 2006
	Agricultural farm land	PCDDs/DFs	–	RDA[f]	–

	Multi-media nearby incinerator (stack gas/ ambient air, discharged/ ambient water, soil, sediment etc.)	PCDDs/DFs	2003–2008	NIER	KMOE website, NIER, 2005b, Kim et al., 2005b
Food	Food items and tolerable daily intake (TDI)	PCDDs/DFs, PCBs, PAHs, PBDEs etc.	2000–	KFDA[g]	KFDA website
	Stock farm products	PCDDs/DFs	–	NVRQS[h]	–
	Seafood	PCDDs/DFs, coPCBs, PCBs, OCPs, PAHs etc.	2001–	MOMAF	Oh et al., 2005a, Yim et al., 2005, Moon and Ok, 2006
	Seafood for export	PCDDs/DFs, PCBs etc.	2005–	NFRQIS[i]	MOMAF website
	Agricultural farm products	PCDDs/DFs	–	RDA	–
Human	Human blood and milk	PCDDs/DFs	2000–	KFDA/NITR[j]	KFDA website
	Resident blood nearby waste incinerators	PCDDs/DFs	Intermittently		–

[a] PCDDs/DFs (Dioxins and Furans), coPCBs (coplanar PCBs), PCBs (polychlorinated biphenyls), HCB (hexachlorobenzene), OCPs (organochlorine pesticides; DDTs, Chlordanes, Dieldrin, Aldrin, Endrin, Heptachlor, Toxaphen, Hexachlorocyclohexane, endosulfan etc.), EDC (Endocrine Disrupting Compounds).

[b] The duration indicates the duration of measurement performances for emission and monitoring.

[c] KMOE (Korea Ministry of Environment).

[d] NIER (National Institute of Environmental Research).

[e] MOMAF (Ministry of Maritime Affairs and Fisheries).

[f] RDA (Rural Development Administration).

[g] KFDA (Korea Food and Drug Administration).

[h] NVRQS (National Veterinary Research Quarantine Service).

[i] NFRQIS (National Fisheries Products Quality Inspection Service).

[j] NITR (National Institute of Toxicological Research).

may have large uncertainties due to use of emission factors developed abroad. Since 2001, extensive measurements have been made to establish actual inventories of PCDDs/DFs, coPCBs, HCB, by-product PCBs, and PAHs (i.e., benzo[*a*]pyrene) for both point and non-point sources (Table 2.5). In 2005, the KMOE announced the first emission inventories with a reference year of 2001 for dioxin-like compounds (KMOE website). Domestic status on usage and waste management of product POPs such as PCBs and OCPs have also been investigated since 2003 (KMOE, 2004a). In particular, during 2003–2004, the NIER investigated the PCB contents of 1237 capacitors. They are now contemplating surveying an additional 3000 capacitors (KMOE website). KMOE plans to investigate PCB-containing capacitors of 130,000 electrical plants between 2005 and 2007 (KMOE website).

Several agencies are responsible for the nationwide monitoring of POPs. Long-term monitoring for environmental media includes inland, marine, and agricultural regions (Table 2.5). In this large-scale monitoring program, the NIER began with the investigation of 37 EDC substances in the inland environment including 43 water sampling stations, 11 river/lake sediment stations, 24 air sites, and 35 soil sites in 1999, The sampling campaign is continuing and the number of target substances and sites has been expanded every year. For example, since 2000, fishes and amphibians were included at 31 sites in five main rivers (Jeong et al., 2001a, b; Kim et al., 2004a). The regular monitoring involves PCDDs/DFs, PCBs, OCPs, and alkylphenols. Marine environments are also monitored annually by MOMAF for sea water, sediment, and bivalves along the coastal area, as mussel watch program (Kim et al., 2002b; Oh et al., 2003; Hong et al., 2006). Fishes from coastal environment and/or markets were also investigated for dioxin-like compounds (Oh et al., 2005a; Moon and Ok, 2006) and organochlorines including PCBs and OCPs (Yim et al., 2005). In addition to the long-term environmental monitoring described above, more targeted, site-specific monitoring is performed for dioxin-like compounds in multi-media (i.e., stack gas, discharged wastewater, and ambient air/water/soil) around 34 waste incinerators from 2003 to 2008. In addition to environmental monitoring, since 2000 foodstuff and human tissues have also been monitored by each responsible governmental institution for stock farm products, seafood, and agricultural farm products. For instance, the KFDA monitors PCDDs/DFs, PCBs, and PAHs in foodstuffs and PCDDs/DFs, PCBs, OCPs, bisphenol A, and PBDEs in human tissues (KFDA website). According to the 'Specific Act for POPs control' the monitoring data from these studies are expected to be integrated into assessments of environmental and human risk, and establish environmental quality criteria and tolerable daily intake on the basis of contamination status and trends in South Korea. While extensive monitoring is being performed by governmental agencies, the reported detection limits are insufficient. Improvements in analytical methods applied in some of the monitoring programs will be necessary to provide information for meaningful risk and fate assessments.

2.4. POPs emission in South Korea

2.4.1. By-product POPs

POPs are generated as waste itself, or during waste treatment, and from synthesis and production of products. Measurements of by-product POP emission began with PCDDs/DFs for waste incinerators in the late 1990s and from 2001 to 2005 have been performed annually at many industrial sources and non-point sources. Other by-product POPs including HCB, BaP, and PCBs were added to these investigations in 2005. The South Korean government is planning to perform long-term measurement for 'emission inventories of by-product POPs including PCDDs/DFs, coPCBs, and HCB' from 2006 and to report the result biennially.

2.4.1.1. Dioxin-like compounds (PCDDs/DFs and coPCBs)

The emission inventory of dioxin-like compounds in South Korea was determined during two preliminary studies (KMOE, 2001, 2002a). For emission factors, the preliminary study (KMOE, 2001) adopted measured values for waste incinerators and the values of UNEP chemicals Toolkit (UNEP Chemicals, 2001) for the other sources. Estimated PCDDs/DFs emission in 1999 ranged from 1163 to 1595 g I-TEQ yr^{-1} due to uncertainties in emission factors and activities (Table 2.6). Besides the preliminary estimate, since the late 1990s extensive measurements of PCDDs/DFs have been performed at waste incinerators and the emission data by 2004 had been compiled for 1800 incinerators. Moreover, nationwide industrial sources have been investigated every year since 2001; 34 ferrous/non-ferrous metal production factories in 2001, 114 non-ferrous metal and mineral production factories in 2002, 73 chemical/energy/landfill factories and crematories in 2003, and 63 municipal wastewater treatment plants and 9 types of vehicles in 2004. By 2005, measurements of total dioxin emissions had been made on 288 industrial sources. Based on these measurements, KMOE made the first official estimate of PCDDs/DFs emission in South Korea. It has been estimated that the total PCDDs/DFs emission was 1021 g I-TEQ yr^{-1} in 2001 (KMOE website) (Table 2.6). This emission was approximately 62% of that

Table 2.6. Summary of annual inventories of PCDDs/Fs emission in Korea (g I-TEQ yr^{-1})

Source category[a]	1998[b]	1999[c]	2001[d]	Conc.[e]
Waste incineration				
Municipal waste (Large, L)	1.47	0.355	163.5	0.02
Municipal waste (Medium, M & Small, S)	105	327		7.15
Industrial furnace	733	429	728.2	25.3
Construction waste		152		
Hazardous waste	126	129–310		6.66
Medical/hospital waste		2.99–7.18		–
Sludge	–	0.398–3.98	–	–
Total (average)	965.5	1040–1230	891.6	–
Ferrous and non-ferrous metal production				
Iron ore sintering	–	9.37–125	96.4	0.043
Coke production	–	2.86		
Iron and steel production plants	–	53.8–173		
Foundries	–	0.049–1.62		
Copper production	–	0.034	15.0	4.234
Aluminum production (all secondary)	–	–		0.25
Lead production	–	0.025–4.00		0.15
Zinc production	–	–		0.036
Brass production	–	–		–
Magnesium production	–	–		–
Thermal non-ferrous metal production	–	–		–
Shredders	–	–		–
Thermal wire reclamation	–	–		–
Total	–	66.1–307	111.4	–
Power generation and heating				
Fossil fuel power plants	–	17.2	9.8	0.019
Biomass power plants	–	–		–
Landfill and biogas combustion	–	–		–
Household heating and cooking (biomass)	–	–	–	–
Domestic heating (fossil fuels)	–	8.39	–	0.074
Total	–	25.6	9.8	–
Production of mineral products				
Cement kilns	–	7.29	3.1	0.095
Lime	–	0.196		0.050
Glass	–	0.023		0.018
Ceramics	–	–		0.223
Asphalt mixing	–	0.190		–
Total	–	7.70	3.1	–
Transport				
4-Stroke engines	–	–	(0.057)[f]	0.138
2-Stroke engines	–	–	(0.187)[f]	
Diesel engines	–	0.591	(0.756)[f]	0.559

Table 2.6. (*Continued*)

Source category[a]	1998[b]	1999[c]	2001[d]	Conc.[e]
Heavy oil fired engines	–	15.2	(13.5)[f]	–
Total	–	15.8	(14.5)[f]	–
Uncontrolled combustion processes				
Fires/burnings (biomass)	–	0.114	–	–
Landfill/industrial fires, waste burning	–	7.32	–	–
Total	–	7.43	–	–
Production of chemicals or consumer goods				
Pulp and paper mills (boilers)	–	0.046	0.6	0.002
Chemical industry	–	–		1.538
Total	–	0.046	0.6	–
Miscellaneous				
Drying of biomass	–	–	–	–
Crematory	–	0.002–0.403	4.1	0.127
Smoke houses	–	0.070–0.704	–	–
Dry cleaning residues	–	–	–	–
Tobacco smoking (pg item^{-1})	–	0.009	–	–
Total	–	0.081–1.12	4.1	–
Total	–	1163–1595	1021 (1036)[f]	–

[a] UNEP Chemicals (2001).

[b] Modified from NIER (2000b) by considering gas amount emitted per unit ton for different incinerator type and size.

[c] KMOE (2001); Emission estimated from top-down approach. Ranges are estimated when varying incinerators' activities (i.e., emission gas amount per ton) or emission factor.

[d] Website of MOE (www.me.go.kr/dev/board/); First emission calculated from measurements for point sources (i.e., up to 2001 for waste incinerator and up to 2005 for others).

[e] Average concentration of stack gas measured at each source since 2000 (ng I-TEQ m^{-3}); Municipal waste (L) from KMOE (2004a), other waste incinerators from KMOE website, ferrous and nonferrous metal industry from Yu et al. (2006), transport from KMOE (2005a), and others from KMOE (2004b).

[f] KMOE (2004c); Results of PCDDs/DFs for non-point sources. Total value in parenthesis includes the non-point emission.

reported for 2001 in Japan, a country that has one of the largest releases worldwide (JMOE website).

A major contributor of PCDDs/DFs release to environments is waste incinerators (77–89% in preliminary study and 86% in follow-up studies) followed by 6–19% from ferrous/non-ferrous metal industry and $<5\%$ from others including power generation and heating, mineral production, chemical industry, and non-point sources. Non-point sources like transportation and uncontrolled burning processes showed a minimal contribution of $<2\%$.

All studies found that more than 70% of PCDDs/DFs released from waste incinerations were from industrial waste incinerations including industrial waste furnace, construction waste incineration, hazardous and medical/hospital waste incineration. In particular, small- and/or medium-sized municipal waste incinerators (~30%) were one of the major contributors with industrial waste furnaces contributing approximately 35–40% of total dioxin emission. In 2002, the number of small incinerators comprised 93% of the total number of incinerators, although the amount of waste treated by smaller incinerators was only 6.5% (Table 2.3). Relatively great amounts of dioxins were emitted from small- and medium-sized incinerators and industrial incinerators, despite the lesser amount of waste treated. This could be due to poor operating conditions, lack of emission control equipments, and ill management practice. The UNEP estimated the emission of gas per unit ton of waste incinerated to be 5000 Nm^3 ton^{-1} when BAT, including activated carbon addition and SCR/DeNOx were applied, while the value was estimated to be 10000 Nm^3 ton^{-1} for incinerators with poor operating conditions (UNEP Chemicals, 2001). In 1999, the amounts of stack gas emissions from domestic incinerators was 3758–8401 (average = 5230 Nm^3 ton^{-1}) for large waste incinerators, 4400–15000 (average = 12000 Nm^3 ton^{-1}) for small/medium-incinerators, and 4400–15000 (average = 12000 Nm^3 ton^{-1}) for industrial furnaces (KMOE, 2001). Thus, improvements in operating conditions for industrial furnaces and small/medium-sized incinerators will be necessary to achieve further reductions in emissions of PCDDs/DFs. In 1998, the Environmental Management Corporation measured dioxins and furans released from selected incinerators, including various types of incinerators and reported an estimate of national emission as 446.5 g I-TEQ yr^{-1}. This value is certainly an underestimated one because of the use of such assumptions as best operating conditions for all incinerators (i.e., 5000 Nm^3 ton^{-1}) (NIER, 2000b). This actual emission rate, based on real operating conditions as in 1999, would be expected to be 965.5 g I-TEQ yr^{-1} (KMOE, 2001). Predicted contributions of individual incinerator types to dioxin emission were similar with that determined by other studies. Overall, the studies indicated that PCDDs/DFs emission from waste incinerators in South Korea was approximately 1000 g I-TEQ yr^{-1} (891.6–1230 g I-TEQ yr^{-1}) between the late 1990s and early 2000s (Table 2.6).

Because of the relatively great contribution of waste incineration to dioxin emission, since 1997 the South Korean government has regulated releases of dioxins from waste incinerators (Table 2.4). Almost all large municipal waste incinerators with BAT reduced the dioxin release to rates that are less than the emission guideline of 0.1 ng I-TEQ Nm^{-3} (Table 2.6). Guidelines have now been established for all types of incinerators. Furthermore, incineration in facilities with capacities below 0.025 ton hr^{-1} is prohibited. As a result of this regulation, the number of incinerators, particularly smaller incinerators, has decreased. In 2003, the smaller incinerations comprise only about 31% as many as were operating in 1998 (see Table 2.3 and Fig. 2.4).

Some PCBs are dioxin-like compounds due to their ability to bind to the arylhydrocarbon receptor (Ah-R). In particular, these are the non- and mono-*ortho*-substituted congeners. Because of their ability to assume a somewhat planar configuration that can result in a molecular size and conformation that is similar to 2,3,7,8-TCDD these congeners are sometimes referred to as co-planar PCBs (coPCBs). The total release of dioxin-like compounds would be underestimated if coplanar PCB congeners were not included. KMOE also reported the emission of dioxin-like compounds including PCDDs, PCDFs, and coPCBs, to be 1247 g WHO-TEQ yr^{-1} for 2001. Here we have corrected the emissions of 1998 and 1999 using the correction factor ($\sim$10%) of I-TEQs to WHO-TEQs for PCDDs/DFs and the ratios of coPCBs to PCDDs/DFs for individual sources presented in the KMOE emission report for 2001 (Table 2.6). When this is done, the contribution of coPCBs to the WHO-TEQs was estimated to be approximately 10% for waste incinerators and 6–26% for industrial sources. Corrected emissions were determined to be 1322 and 1927 g WHO-TEQ yr^{-1}. The conversion factor of I-TEQs (NATO/CCMS, 1988) to WHO-TEQs (van den Berg et al., 1998) is frequently less than 10% for municipal waste incinerators in South Korea; 0.7–18% (average 7%) for gas, ash, and smelted slag (Kim et al., 2005a) and on average 4% for stack gas (Kim et al., 2001b) and fly ash (Shin and Chang, 1999). Thus, the corrected values seem to be a slightly greater than actual expected emission rates.

The South Korean government also reported annual emissions of dioxin-like compounds from waste incineration from 2001 to 2005. During this period the rates of emission of WHO-TEQ in 2004 decreased by 23.5% relative to that in 2001 (Fig. 2.5). Assuming a similar emission as in 2001 for non-waste incineration sources, total atmospheric release of dioxin-like compounds were predicted to decrease 67% between 2001 and 2004, to 410.6 g WHO-TEQ yr^{-1}. The release of dioxins in 2004 is comparable to 401.9 g WHO-TEQ yr^{-1} in Japan in 2003 (Fig. 2.5). The reduction in emissions of dioxin-like compounds from waste incineration seems to reflect the successful regulation for incinerators in South Korea. For instance, the emissions of dioxin-like compounds, expressed as I-TEQ from only 33 incinerators (9.8% of 336 investigated including 243 small- and medium-sized incinerators) exceeded the emission guidelines; so do 12 of 82 municipal incinerators and 21 of 254 industrial incinerators (KMOE website). Furthermore, the average release of TEQ from large municipal waste incinerators decreased from 5.97 ng I-TEQ Nm^{-3} in 1997 to 0.06 ng TEQ Nm^{-3} (Lee et al., 2002).

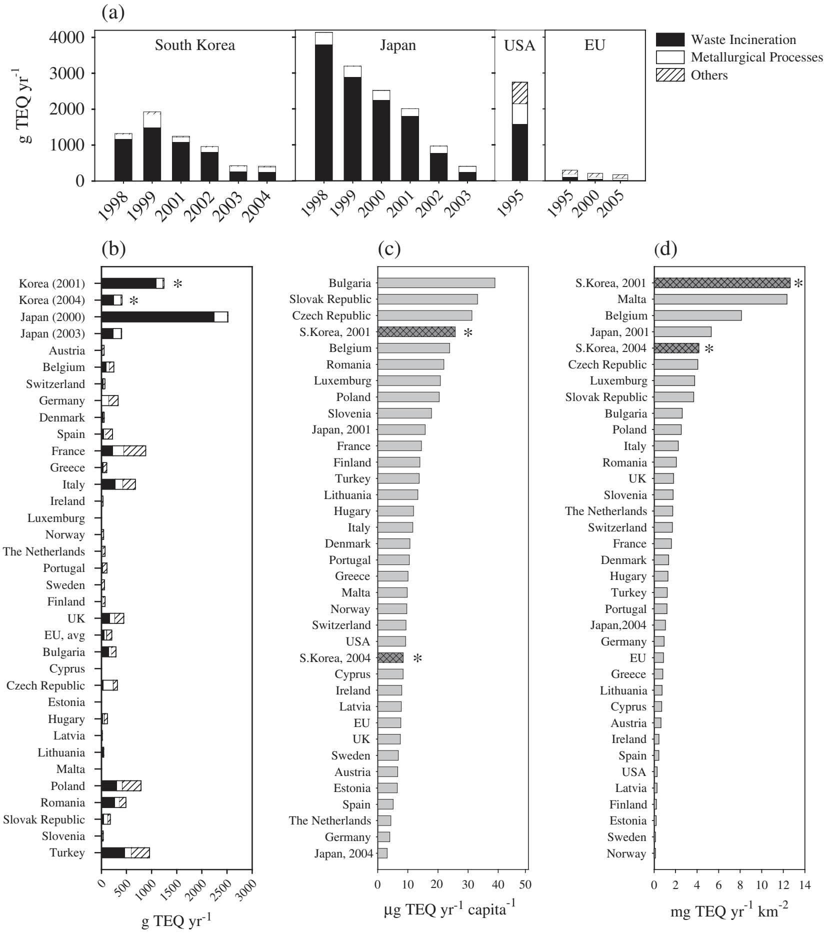


Fig. 2.5. Nationwide annual emission inventories to air of dioxin-like compounds in worldwide countries; (a) Average of emissions of EU countries were used for EU: Korea 1998 and 1999 (recalculated from NIER, 2000b and KMOE, 2001, respectively), Korea 2001–2004 (from KMOE website), Japan (1998–2003) (from (JMOE website), USA 1995 (from US EPA, 1998b), EU 1995 (UNEP, 1999), EU 2000 and 2005 (estimated for 2000 and projected for 2005 from Quaβ et al., 2000), (b) emission inventories of 2000 for EU (Quaβ et al., 2000) and central European countries (Pulles et al., 2005), (c) and (d) calculated from values of (b). The emission of South Korea (S. Korea) and Japan is on basis of WHO-TEQ including PCDDs/DFs and coPCBs, while those of other countries based on I-TEQ of PCDDs/DFs alone. Population and area of each country were quoted from Wikipedia website.

Despite this decrease, in 2004 the emission rates were greater than that of some European countries (Fig. 2.5a, b). Particularly, when emissions of TEQ were normalized by expressing them on a per capita or unit area which was 25.7 μg WHO-TEQ capita^{-1} yr^{-1} and 12.7 mg WHO-TEQ km^{-2} yr^{-1} in 2001 (Fig. 2.5c, d). These values are 1.6 and 2.4 times greater, respectively, than those of Japan in 2001. The emission per unit area remains the greatest in the world, even though the value in 2004 decreased to 4.2 μg WHO-TEQ km^{-2} yr^{-1} (Fig. 2.5d). The relatively great emission rate suggests that the exposure level at least during recent years of South Korean environments and humans has been greater than that for other countries.

In spite of the new introduction of emission regulations, waste incineration is still a major contributor to dioxin emission (greater than 60% of the total emission) in South Korea. In Europe, however, iron ore sintering is the predominant emission source followed by the previous 'No. 1', municipal waste incineration (Quaβ et al., 2004). The South Korean government also plans to regulate the release from industrial sources. For instance, government, NGO and industries have agreed to reduce the release of TEQ from industrial sources to 70% of the 2001 by 2008 and further to 50% by 2010 by establishing release guidelines for the industrial sources. Banning of small-scale incinerators and enforcing the release guideline of 0.1 ng Nm^{-3} for all the waste incinerators is expected to result in a considerable reduction of the emission. According to the emission reduction scenarios (KMOE, 2001), 92% and 68–83% of the emissions are expected to be reduced from waste incineration and from all sources, respectively. With further application of this release guideline to iron ore sinters and steel electric furnaces, total dioxin emission in South Korea are predicted to decrease between 91% and 94%.

Non-point sources are minor contributors (~4% of total emission for 2001, 33.96 g I-TEQ yr^{-1}) (KMOE, 2004c). Among non-point sources, it has been estimated that large ships, using heavy oils, contribute 45% of the total emissions from non-point sources. Major harbors could thus be affected by this source (Cooper, 2005). The releases from landfill leachate, municipal wastewater, and paper/pulp wastewater contribute 2.254 g WHO-TEQ yr^{-1} (KMOE, 2004c). This is comparable to Japanese emission for 2003 (http://www.env.go.jp/en/press/2004/).

2.4.1.2. PCBs

By-product PCB emission from all potential sources was estimated by the 'top–down' approach (KMOE, 2003b). This estimate was made for 2000 by using emission factors from UK National Atmospheric Emissions

Inventory (UK NAEI website) and the Co-operative Program for Monitoring and Evaluation of the Long Range Transmission of Air pollutants in Europe (EMEP) workshop (MSC-E, 2002) and an activity database of individual sources in South Korea. Estimated emission of by-product PCBs was 1085 kg yr^{-1} and is likely to be greater than that for many European countries in 2000 (Fig. 2.6). Considering the greater PCDDs/DFs emission in South Korea than that in European countries, and the similar emission sources of both PCDDs/DFs and PCBs, relatively greater PCBs emission might be reasonable, although the emission estimates are associated with large uncertainties. Among the sources, the ferrous metal industry was a major contributor, 93% (i.e., ~1000 kg yr^{-1}) to the total emissions, followed by fuel combustion (5.9%, 64.2 kg yr^{-1}), waste incineration (1.3%, 14.23 kg yr^{-1}), and others including non-ferrous/mineral production ($<$0.01 kg yr^{-1}). A total of 872 kg PCB yr^{-1} is estimated to be released from electric furnaces producing iron from scrap. This is different from the source profile of Europe where the fuel combustion is a major source. All ferrous steel mills are located in coastal areas in South Korea (see Fig. 2.3), suggesting the possibility of contamination of localized marine environments with by-product PCBs.

2.4.1.3. HCB

HCB was neither imported nor manufactured in South Korea. Domestic emission, therefore, should originate from process such as combustion of organic matters combined with chlorine and from impurities in the production of chemicals and pesticides. HCB emission for 2000 in South Korea was estimated in a preliminary study of emission inventory using 'top-down approach' (KMOE, 2003b). Emissions from some sources in 2005 were determined by measuring concentrations in archived samples originally collected for analysis of PCDDs/DFs in 2001–2003 (KMOE, 2005a).

Domestic HCB emissions have been estimated to be 245 kg yr^{-1} for 2000, which falls approximately in the mid-range of the values reported for EU countries (Fig. 2.6). However, the direct intercomparisons among the countries may be misleading due to the varying uncertainties in emission inventories of these countries. According to the preliminary study (KMOE, 2003b), the source contribution of HCB emission is as follows: waste incineration (62%, 152 kg yr^{-1}) $>$ iron ore sinter (19%, 50 kg yr^{-1}) $>$ fuel combustion (14%, 35 kg yr^{-1}) $>$ non-ferrous metal/mineral production (3.6%, 8.7 kg yr^{-1}) $>$ transport (1%, 2.4 kg yr^{-1}). Emission of the electric furnace for scrap iron was not included in the preliminary study. Thus, the contribution of the ferrous metal manufacturing would

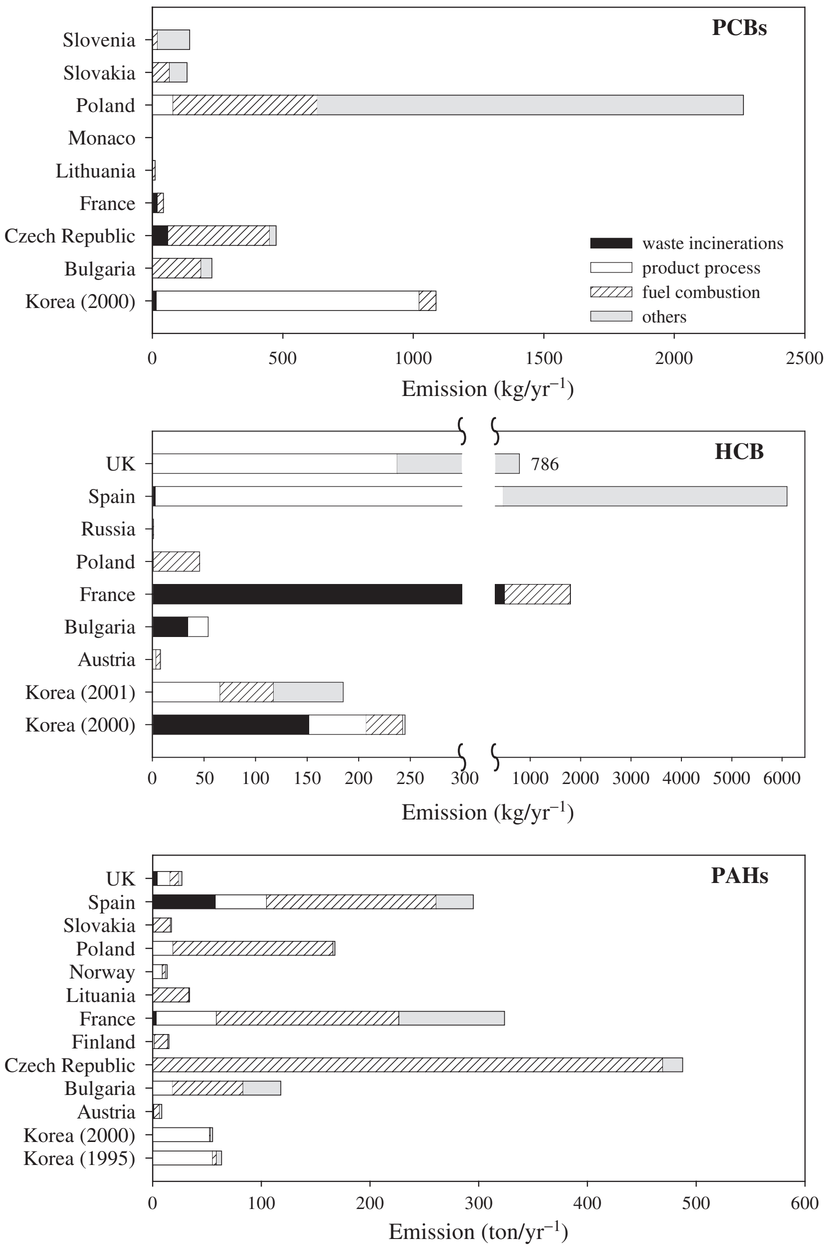


Fig. 2.6. Annual emission of by-product POPs (PCBs, HCB, and PAHs); Korea 1995 (from MCIE, 1999), Korea 2000 (from KMOE, 2003b); Korea 2001 (from KMOE, 2005a); Other countries 2000 (from UNECE/EMEP, 2002). PAHs emissions were based on 7 PAHs for Korea and 6 PAHs for other countries.

be greater if released from electric furnaces are included. KMOE (2005a) measured HCB emission in archived samples from ferrous/non-ferrous metal production, mineral production, chemical and energy production plants from 2001 to 2003, and some additional metal production factories, wastewater treatment plants, and non-point sources such as boiler and uncontrolled incineration in 2005. The measured emission rate was 185 kg yr^{-1} for 2001 as a reference year (Fig. 2.6). In contrast to the preliminary estimate, the individual source categories showed fairly even emission rates; that is, 34% from ferrous/non-ferrous metal production (63 kg yr^{-1}), 28% from fuel combustion (52 kg yr^{-1}), 36% from transportation (68 kg yr^{-1}). Iron ore sinter released four times less HCB than the estimated value for 2000, while the electric furnaces emitted 30 kg yr^{-1}. This discrepancy indicates that the uncertainty of preliminary estimates is still great and warrants further emission measurements. The later study of actual measurements did not include emission from waste incineration. Thus, the total HCB emission observed in 2001 would be greater if waste incineration were included as a source. For instance, total HCB emission would be 337 kg yr^{-1} if estimates of the preliminary study (ca. 152 kg yr^{-1}) are simply added. Based on an assembled list of potential sources for HCB, it was estimated that approximately 23000 kg HCB yr^{-1} (with a range of 12000–92000 kg yr^{-1}) was released in global environments during the mid-1990s (Bailey, 2001). No single major source of HCB was identified. Uniform contribution from pesticide application (28%), manufacturing (41%), and combustion (30%) were estimated. The contribution of South Korea to global HCB emissions was estimated to be approximately 1.3%.

2.4.1.4. PAHs

PAHs are not included in the list of 'dirty dozens POPs' of the Stockholm Convention. However, in addition to 12 existing POPs, UN/ECE (United Unions Economic Commission for Europe) considers PAHs, HCHs, chlorodecone, and hexabromobiphenyl as potential POPs to be restricted based on 'The New Protocol on Persistent Organic Pollutants to the Convention on Long-range Trans-boundary Air Pollution' adopted in 1998. PAHs may be listed as POP in the future Stockholm Convention.

PAHs are released to the environment from a number of sources: pyrogenic sources including fossil fuel combustion and pyrolytic processes of organic matter such as incineration and petrogenic sources such as oils spills. Direct oil spilled from stationary sources and accidents cause contamination of land. Oil spills at US Army bases in South Korea is reported as a source of soil and groundwater contamination to nearby area and it has been suggested that remediation of these sites is required. Oil spills from ship accidents could be a major source of PAH to the marine environment. For example, the supertanker *Sea Prince* was stranded near Sori Island off the South Coast of South Korea. This accident alone released 4160 tons of crude oil and 880 tons of fuel oil into the marine environment (Yim et al., 2002).

Two preliminary studies of atmospheric releases of PAHs in South Korea have been conducted. The top–down approach was adopted to estimate the emission rate of each source by multiplying the emission factor reported by the US EPA (1998a) and the statistics of activities of the each source in South Korea (MCIE, 1999; KMOE, 2003b).

The total emissions of seven PAHs including BaA, CHR, BbF, BkF, BaP, DahA, I123cdP (see Table 2.2 for full names), identified by the International Agency for Research on Cancer (IARC) as animal carcinogens, were 63.4 ton yr^{-1} for 1995 and 55.3 ton yr^{-1} for 2000 (Fig. 2.6). A dominant contributor to PAH emissions was found to be coke oven process for the steel manufacturing, emitting over 60% of the total quantity. Chemical production processes and fuel combustion contributed approximately 10% and 5%, respectively. The total mass of the 16 priority or 'indicator' PAHs suggested by the US EPA, emitted in South Korea during 1995 was estimated to be 768 ton (MCIE, 1999) and 857 ton during 2000 (KMOE, 2003b). In the two preliminary studies, because many sources could not be included due to the lack of information, the total emissions were likely to be underestimated. In contrast to South Korea, fuel combustion was the predominant source of PAHs in EU countries. The discrepancy of national PAH emission profile among countries depends significantly on its industry patterns. One of the important reasons for the large contribution of coke oven process in Korea is the huge scale production of steel in Korea as compared to most European countries. The steel industry is not only a large emitter of an array of pollutants but an energy intensive one, and as a result, it is not blooming in most developed countries. This can be one reason that the inherent emission measurement based on its industrial pattern is required for each country.

2.4.1.5. Comparison of by-product POPs emission inventories

Measurements of emissions of by-product POPs, such as dioxin-like compounds and HCB have been performed and preliminary estimations exist for other POPs. However, due to uncertainty in estimations, comparisons among POPs should be made with caution. Most by-product POPs are likely to be produced from similar sources, principally pyrolytic processes. According to the emission estimates, more than 60% of dioxin-like compounds and HCB were estimated to be emitted from waste incinerators, while substantial portions of PCBs and PAHs were released from metallurgical processes, including electrical furnaces and coke ovens, respectively (Fig. 2.7). These waste incineration and the metal production processes contributed over 80% to the total emission for each of

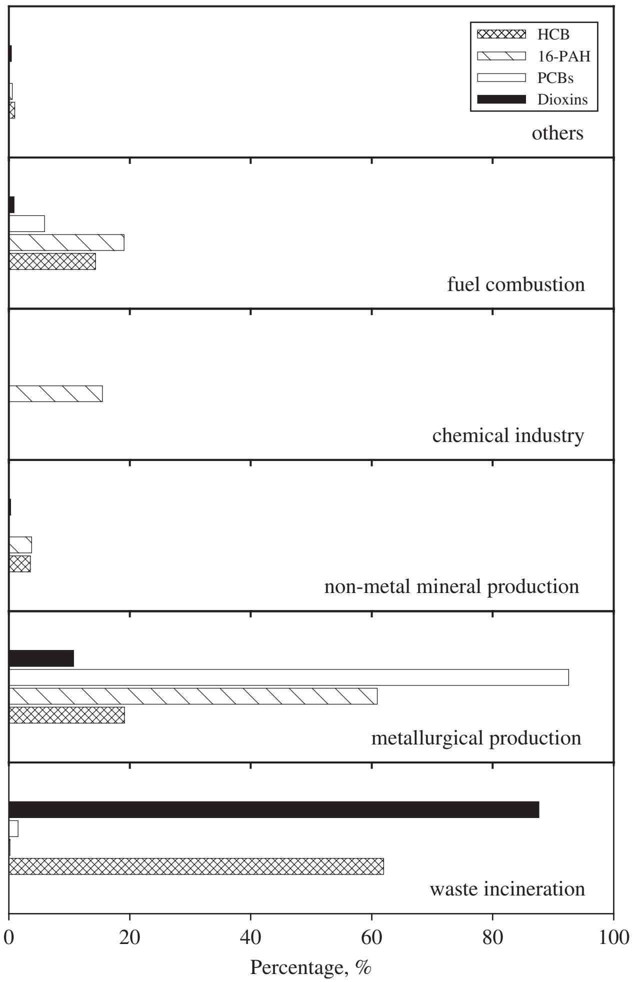


Fig. 2.7. Contribution of each emission source to total emission of by-product POPs in Korea. 'Dioxins' includes PCDDs, PCDFs and coPCBs measured in 2001 (see Table 2.6), and '16-PAHs' means the total emission of EPA priority 16 PAHs. PCBs, HCB, and PAHs emissions were quoted from the preliminary estimation study (KMOE, 2003b).

by-product POPs except for PAHs. For PAHs, the secondary contributors were fuel combustion (19%) and oil refineries (15%). This indicates that the release of by-product POPs in South Korea can be reduced efficiently by focusing the regulation of these two source categories of waste incineration and metallurgical processes.

2.4.2. Product POPs

The governmental works on the emission inventories of product POPs (i.e., PCBs, OCPs, and PBDEs) began only in 2003 as one of the strategies on Stockholm Convention. Preliminary studies (KMOE, 2003b; KMOE, 2004a) and investigation campaigns to determine the domestic status of PCB-containing facilities (KMOE website) are underway. The history of production and use of OCP products and intermediates was recently reviewed (KMOE, 2004a). Domestic use of PBDEs has been reviewed in a report on the use and import of brominated flame retardants (KMOE, 2005c). Distribution and emission of NP as one of APs has been investigated annually by KMOE. However, there is no information on the production and or use of PFAs in South Korea.

2.4.2.1. PCBs

The Stockholm Convention stipulates that, use of PCBs-containing articles should be forbidden after 2025, and it is recommended that PCB stocks (articles and wastes) be destroyed by 2028 by use of environmentally sound methods, and that national efforts for removal of PCBs should be submitted by signatory nations (Stockholm Convention on Persistent Organic Pollutants, 2001). Under an agreement among KMOE, electric power companies, and three NGO for removal of product PCBs in South Korea, the domestic use of PCB-containing transformers is being investigated nationwide and methods of establishing appropriate collection, storage, and treatment implemented.

A governmental investigation on PCB use is in process in South Korea. However, as no report is available yet, we reviewed the estimation of Breivik et al. (2002a), which provided the estimates of consumption of 22 major PCB congeners for 113 individual countries. These estimates are based on reports from PCB manufacturers and information on imports, exports, and consumption as well as restriction on production and imports, and the population and economic status. The total, historical global production of PCBs has been estimated to be approximately 1.3 million tons and Monsanto, the manufacturer of the Aroclors, produced about 50% of the total global production. The estimated cumulative consumption of the 22 predominant PCB congeners in South Korea ranges from 3000 to 6500 tons (default consumption = 4300 tons), which ranks 16th out of 113 countries for which information is available (Fig. 2.8). This quantity is 2% and 20% of the consumption of the USA and Japan, respectively. Products containing PCBs such as Aroclor,

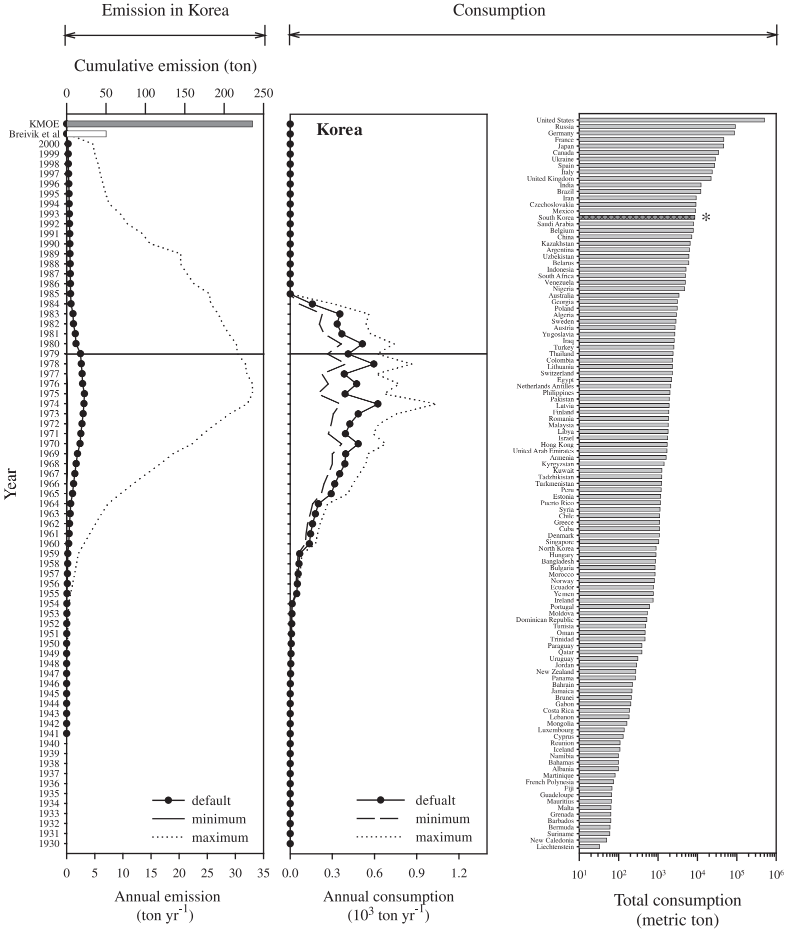


Fig. 2.8. Consumption (total PCBs's consumption modified 22 congener's consumption of Breivik et al., 2002a; *see* the text) and emission (sum of 22 congeners from Breivik et al., 2002b) of PCBs. Two bars in emission plot are the sum of emissions from 1945 to 2000 from Breivik et al., 2002b (white) and KMOE, 2003b (dark gray). Horizontal lines in the plots mean the first legal restriction point in Korea, 1979 (EBA; see Table 2.1). Total consumption of each country (far-right plot) was the sum of annual total PCBs consumption of each country (modified from the default 22 congeners' consumption of Breivik et al., 2002a).

Kaneclor, and Chlophen contain a wide range of congeners. Based on studies of sources of PCB contamination, the South Korean environment appears to be contaminated by a mixture of various products. The predominant product was found to be Aroclor 1254 in Incheon, Aroclor 1242 in Masan, Aroclor 1260 (or Kanechlor-600) in Ulsan, and Aroclor 1242 in the Han River (Kim et al., 2000a, 2002b; Kim, 2004; Hong et al., 2006). Breivik et al.'s 22 congeners comprise of only ~50% in Aroclor mixture (1242:1254:1260 = 1:1:1). Using the fact, we could estimate the total PCBs consumption in South Korea by multiplying a factor of 2 with the inventory for 22 congeners. Based on this estimation, total PCBs consumption in South Korea was estimated to be 6000–14000 tons (default, 9000 tons). When this 2-fold assumption was applied to other countries, the estimated total PCBs consumption was 462000–552000 (default, 500000 tons) for the USA and 30600–62200 (default, 47000 tons) for Japan. Assuming a total production of approximately 680000 tons in the USA (http://www.epa.gov/opptintr/pcb/) with essentially all of the production used domestically, our estimate matched well with the reported value. Furthermore, historical total consumption in Japan was reported to be 54000 tons (JEMCAA, 1997). This value is similar to the consumption estimated in the present study.

Emission of 22 PCB congeners, originating from unintentional use of PCBs-containing product such as accidental releases and disposals including landfill, open burning, waste incinerations, and destruction, has also been estimated (Breivik et al., 2002b). According to their estimation, the historical release of PCBs to the South Korea has been estimated, based on the 22 indicator congeners, to be 2.5–742 tons (default 53 tons). KMOE (2003b) also estimated the total release of product PCBs to the South Korean environment between 1945 and 2000 to be 235 tons by using an emission factor of 0.13 g capita^{-1} yr^{-1} as presented in EMEP/CORINAIR guidebook (EMEP/CORINAIR, 2000).

The primary use of PCBs, over 50%, was in dielectic fluids for transformer and capacitors (UNEP Chemicals, 1999). Moreover, leakage from transformers and capacitors is the major contributor of PCB to the environment (EMEP/CORINAIR, 2000). The South Korean government investigates PCBs-containing transformers nationwide and provides funds for development of PCBs waste treatment technologies. The South Korea Electric Power Corporation (KEPCO), practically the only electricity company in South Korea, has 1.7 million transformers and 540 capacitors (KMOE website). Recent voluntary investigations of electricity companies for 1237 transformers revealed that 22% (i.e., 272 transformers) contained PCBs at concentrations of greater than 2 ppm, which is the threshold to be categorized as a specific waste by the WCA

(KMOE website). The number of transformers containing more than 50 ppm PCBs, which is the guideline for the prohibition of use set by the TCCA, was 19 (i.e., 1.5%). In another study of 90 transformers (KMOE, 2004a), similar results were obtained. That is, 2.2% of transformers contained more than 50 ppm PCBs while 22% contained more than 2 ppm PCBs, while 78% of the transformers contained less than 2 ppm PCBs. The KEPCO reports that 13,610 kl of waste dielectic fluids and 394, 529 waste transformers occurred in South Korea and 643 tons of PCBs-containing waste was exported between 2000 and 2005.

2.4.2.2. OCPs

The classical OCPs have been restricted from use in South Korea since the late 1960s (Table 2.1). OCPs residues currently in the environment are unlikely to have originated from their recent use, they are rather residuals from historical applications. Historical production, distribution, and consumption of seven individual OCPs including DDTs, CHLs, heptachlor, aldrin, endrin, dieldrin, and toxaphene for pesticides and additive agents have been reviewed (KMOE, 2004a). Here, we have compiled the consumption data reported by KMOE for the OCPs and those of other studies for HCHs and Endosulfan (Lee, 1982; Jeong et al., 2001c). There is a large uncertainty in the database for OCPs usage in South Korea. DDTs and toxaphene consumption estimates from individual studies varied by a factor of 2 but those for aldrin and heptachlor estimated varied widely. For instance, heptachlor consumption was reported to be approximately 600 tons in one study (Lee, 1982), which is only 4% of the estimate of KMOE.

Total historical consumption of OCPs in South Korea was 31,000 tons with the following relative proportions: heptachlor (53%) > endosulfan (16%) > aldrin (10%) > DDTs (9%) > HCHs (6%) (Fig. 2.9). DDT, was the first OCP applied in South Korea and was widely used from the late 1940s to the early 1970s. This pesticide was replaced by other OCPs after the toxicity of DDTs to wildlife was known. Use of most OCPs was banned in the late 1960s, but less persistent compounds such as heptachlor and toxaphene were still used until the early 1980s. Endosulfan is still used in large quantities in many parts of the world. Endosulfan has been in use for more than three decades. It was introduced as a replacement for other more persistent OCPs when they were banned. For example, about 1000 tons were consumed in South Korea over five-year periods from 1971 to 1999 (Jeong et al. (2001c). According to KMOE's annual report for distribution and emission of industrial hazardous chemicals, 1144 kg of endosulfan was released to atmospheric from

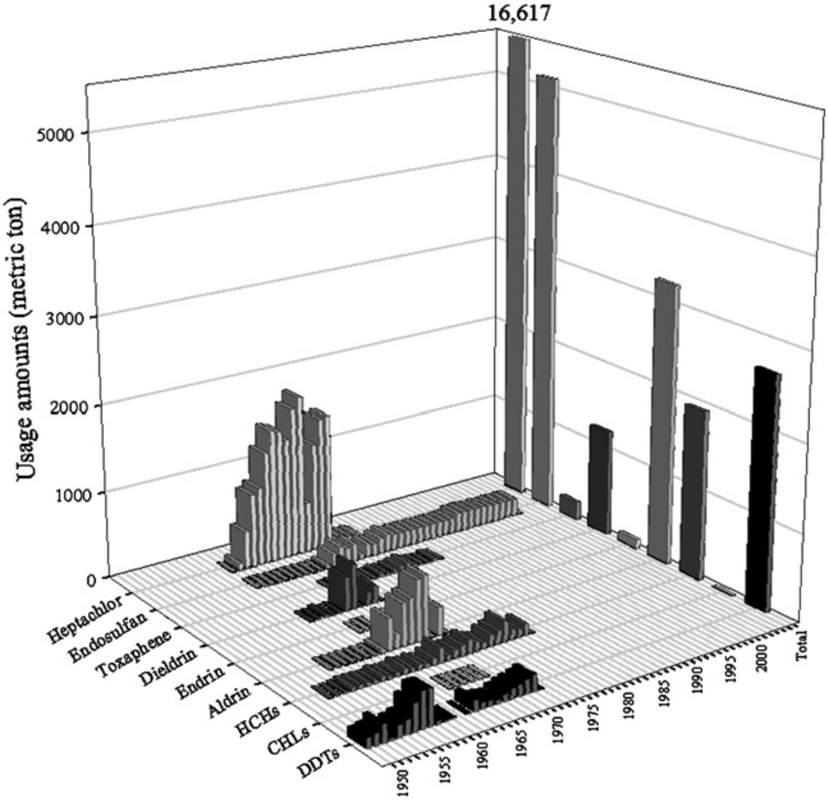


Fig. 2.9. Historical usage amounts of each organochlorine pesticides: DDTs, CHLs, Aldrin, Endrin, Toxaphene, and Heptachlor from KMOE (2004c), HCHs from Lee (1982), and Endosulfan from Lee (1982) by 1980 and modified from Jeong et al. (2001c) since 1981. Total endosulfan use of five years (from Jeong et al. (2001c)) was converted to annual average amount.

chemical processes and/or chemical manufacturing processes in South Korea. But, the amount released varies among years. For instance, 4 kg was estimated to be released in 1999 while 819 kg was estimated to have been released in 2003. These estimates are associated with great uncertainties. Furthermore, it is not certain whether the KMOE report includes releases of endosulfan from agricultural applications.

The order of contributions of OCPs to the total mass of OCPs measured in bivalves (Kim et al., 2002b) and sediment (Hong et al., 2006), was DDTs (63%) > HCHs (21%) > CHLs (11%) > dieldrin (1%). A possible explanation for this observation is the difference in chemical properties among pesticides. The half-lives of DDTs, γ-HCH, and CHLs in soil and sediment are 3–10 times longer than those of heptachlor, aldrin, and endosulfan (Mackay et al., 2000; Ghadiri and Rose, 2001). Furthermore, the vapor pressures of heptachlor and aldrin are 10- to 1000-fold greater than that of DDT, chlordane, and β-HCH. Since the pesticides were applied on land, they may have been volatilized. More volatile pesticides have shorter residence times in soil and aquatic systems. DDTs and CHLs were used as additive agents even after the ban in use as pesticide. For instance, it has been reported that CHLs were used as an adhesive for plywood until 1995 (KMOE, 2004a). DDTs were formed as an impurity during the manufacturing of a pesticide, dicofol. Based on the consumption of dicofol from 1972 to 2002 with the DDT content of 0.1% in dicofol, additional releases of DDTs to the environment during the three decades was estimated to be 578 kg (KMOE, 2004a). This quantity is substantially smaller (0.02%) than its consumption as a pesticide until the early 1970s and does not affect the overall estimates of releases.

HCB is frequently detected in South Korean environments at concentrations that are less than DDTs > HCHs > CHLs. HCB was neither imported nor produced as a pesticide, but is known to be released into the environment at minimal concentrations as a trace contaminant in chlorothalonil. Estimated emission on the basis of HCB content (ca., 0.0219%) in chlorothalonil has been, on average, 77 kg yr^{-1} between 1970 and 2004 (KMOE, 2004a). This amount corresponds to between 20% and 30% of the emission as a by-product.

In the global estimation the usage of HCH in South Korea has been estimated to have been between 10,000 and 100,000 tons (Li, 1999). The great estimate was based on an assumption of very great application rates of 10–40 tons kha^{-1}. However, these estimates appear to be overestimated compared with approximately 2000 tons reported in other studies (Lee, 1982; Jeong et al., 2001c). This inconsistency could be due to false information of usage. Indeed, the concentrations of HCHs in South Korean environments were comparable or less than in many other countries. For instance, residual concentrations in coastal bivalves and sediment ranged from 0.2 to 6.6 (median = 0.1 ng g^{-1} wet wt.) and ND to 5.5 (median = 0.32 ng g^{-1} dry wt.), respectively.

The consumption of OCPs in South Korea can be compared with that of China, which is one of the largest consumers of pesticides in the world. China has used 200,000 ton yr^{-1} of total OCPs every year between 1970s and 1980s (Wang et al., 2005). Three major OCPs including HCHs, DDTs, and toxaphene, collectively accounted for 80.1% of total pesticide use in 1970. The usage of HCHs and DDTs in 1980 corresponded to 70% and 5%, respectively, of gross pesticide usage.

2.4.2.3. APs

APs mainly originate from the degradation of alkylphenol polyethoxylates (APEOs), which are used as nonionic surfactants or detergents in industries and household products for over 40 years (Shang et al., 1999). APEOs are contained in cleaning products, paints, herbicides, and pesticides, and are used to facilitate processes in pulp and paper production and textile manufacturing (Field and Reed, 1996). APs, including NP and bisphenol A (BPA), have endocrine disrupting activity. In the past 40 years, APEOs production was estimated at $>300 \times 10^3$ ton yr^{-1} worldwide (White et al., 1994). Primary degradation of APEOs in wastewater treatment plants or in the environment generates more persistent and toxic shorter-chain APEOs and APs such as NP, OP, and butylphenol (BP) and AP mono- to triethoxylates than the parent substances (Giger et al., 1984).

Nonylphenol is a degradation product of nonylphenol polyethoxylates (NPEOs), which have been the most widely produced APEOs. NPEOs have a worldwide production of $\sim 700 \times 10^3$ tons annually with wide applications such as industrial and institutional (30%) or household (15%) cleaning agents (Ying et al., 2002; Knepper and Berna, 2003; Jonkers et al., 2005), and many other industrial applications including wetting agents, dispersants, emulsifiers, solublizers, foaming agents, and polymer stabilizers. NPEOs have been discharged into surface waters, mostly in wastewater or sewage. Many countries have banned the usage of APEOs surfactants: for instance, the European Union restricted the use of NP and APEOs (Cox and Drys, 2003). Neither inventory efforts nor regulatory action has been taken in South Korea.

BPA is used as an intermediate in the manufacture of epoxy resins and polycarbonate plastics. Global use of BPA is estimated to be more than a million tons per year with 347×10^3 tons yr^{-1} of estimated use in Western Europe in 1993 (BUA, 1997). Although BPA is expected to be released mainly via sewage and industrial wastewater system (Fürhacker et al., 2000), the significant emission is also estimated from combustion sources such as uncontrolled domestic waste burning with $\sim 75 \times 10^3$ kg yr^{-1} in the USA (Sidhu et al., 2005). KMOE reports the emission of hazardous chemicals including BPA annually. According to the report, atmospheric emission of BPA was 4446 kg yr^{-1} in 2002 and 1923 kg yr^{-1} in 2003 (KMOE website).

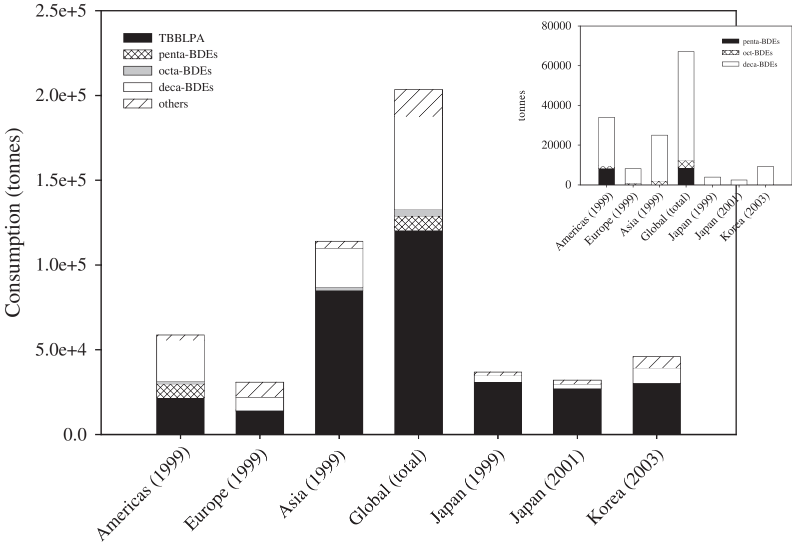


Fig. 2.10. Worldwide Brominated Flame Retardants (BFRs) consumption: Americas, Europe, Asia and Global consumption in 1999 (www.bsef.com), Japan in 1999 and 2001 (Watanabe and Sakai, 2003), and Korea in 2003 (KMOE, 2005c). Korea's values are not consumed but imported amounts. However, the consumption amount is estimated to be similar with this pattern (see the text).

2.4.2.4. PBDEs

The main types of brominated flame retardants (BFRs) are polybrominated biphenyls (PBBs), PBDEs, and tetrabromobisphenol A (TBBPA). PBDEs have replaced PBBs, which are the first brominated organic compounds to be used as flame retardants and were phased out because of environmental issues, but are now being replaced by TBBPA (Renner, 2000). The global consumption of BFRs is estimated to be 203425 tons in 1999 with PBDEs accounting for 33% (Fig. 2.10). Deca-BDEs, 82% of total PBDEs, are the most widely used product. Domestic BFR consumption in South Korea in 2002 was 49050 tons, of which 25% (i.e., 12408 tons) was PBDEs with deca-BDE accounting for 12324 tons and penta- and octa-BDEs accounting for 84 tons (KMOE, 2005c). Imported amounts of each product in 2003 showed a similar distribution to the consumption estimated in 2002 (Fig. 2.10). In BFR market of Western Europe, consumption of PBDEs has declined from 26% in 1996 to 11% in 1998 (DEPA, 1999). Penta-BDEs product has been restricted for over one decade and is now banned within Europe. Furthermore, there has been a trend to substitute PBDEs with other flame retardants in northern Europe since 1996 (Renner, 2000). However, the market of BFRs in South Korea, sharing ~56% of flame retardant market, has increased annually by 13.5% on the average (KMOE, 2005c). In South Korea, PBDEs are regulated under the 'EcoLabelling policy'.

Possible major sources of BFRs are wastewater effluent and flue gases from BFR factories and other facilities processing BFRs (Watanabe and Sakai, 2003). Additives such as PBDEs may leach from the surface of products treated with these compounds, in contrast to TBBPA that are reactive and chemically bound within the material matrices (de Wit, 2002). Based on a model estimate, Danish EPA concluded that PBDE source is evaporation from products in use (DEPA, 1999). Thus, indirect releases from products should also be considered in emission inventories.

PBDEs, one of the major types of brominated flame-retardants, are used as additives in polymetric materials such as polystyrenes, plastics, paints, textiles, machines and household electric appliances such as computer and television, upholstery, and building materials. Commercial PBDE products consist predominantly of penta-BDEs, octa-BDEs, and deca-BDEs products. Each product is composed of several congeners. PBDEs is known to cause various adverse effects including neurobehavioral development (Darnerud, 2003), thyroid system (deBoer et al., 1999), and, some congeners elicit carcinogenicity (McDonald, 2002). Concentrations of PBDEs in environments have been rising in contrast to classical POPs whose levels have been declining markedly during the last 20 years (de Wit, 2002).

2.4.2.5. PFAs

Concern about per- and poly-fluoroalkyl acids (PFAs) including perfluorocarboxylates (PFCA) and perfluoroalkylsulfonates (PFAS) is increasing due to their persistence, bioaccumulation potential and potentially toxicity (i.e., PBT). Due to the presence of the high-energy carbon–fluorine bond, these compounds are resistant to hydrolysis, photolysis, microbial degradation, and metabolism by vertebrates. The PFAs are also bioaccumulated and biomagnified through food chains (Kannan et al., 2005; Sinclair et al., 2006). These anthropogenic compounds reportedly exert various toxic effects, including peroxisome proliferation and potential carcinogenicity (Renner, 2001a), accumulation of triglycerides in liver. These compounds have been routinely and globally measured in environmental matrices; water, wildlife, and human populations (Giesy and Kannan, 2001, Kannan et al., 2004; Yamashita et al., 2005).

The concentrations of PFAs in environments have increased sharply over time (Holmstrom et al., 2005). The sorption/accumulation and fate of PFAs differ from classical chlorinated and brominated POPs in that perfluorinated molecules have surfactant characteristics (i.e., having polar and nonpolar domains) and oleophobic properties. Thus, PFAs is likely to bind to serum protein rather than lipid in tissues (Jones et al., 2003).

Because of their chemical stability, surface tension lowering properties, and ability to create stable foams, PFAs are used in a wide variety of industrial and commercial applications and processes; metal plating and cleaning, coating formulations, fire-fighting foams, polyurethane production, inks, varnishes, vinyl polymerization, lubricants, pesticides, surfactants, gasoline and oil, and water repellents for leather, paper, and textiles (Holzapfel, 1966). Recent studies report that levels of PFAs precursors, degraded to more toxic and persistent metabolites, are greater in indoor than outdoor air due to their application to upholstery and carpets (Shoeib et al., 2004, 2005). The global distribution of PFAs has been hypothesized to be due to volatile neutral precursors of PFCA and PFAS that are distributed via atmosphere, and undergo long-range transport to remote areas, and degrade to yield the free acids (Martin et al., 2002; Renner, 2001b).

Due to their potential PBT properties, the major producer of polyfluorinated sulfonamidoalcohols in the USA and the only major company to use the electrochemical fluorination process, 3M, announced a phasing out of these products beginning in 2001. However, many companies including DuPont (USA), Clariant (Germany), Atofina (France), Asahi Glass (Japan), Daikin (Japan) still produce PFAs such as PFCAs and the products are still in use, worldwide.

The global historical industry-wide emissions of total PFCAs since 1950 are estimated to be 3200–7300 tons from direct (manufacture, use, consumer products) and indirect (PFCA impurities and/or precursors) sources with the majority (~80%) of fluoropolymer manufacture and use (Prevedouros et al., 2006). Total global production of sulfonated PFA is not known but global production by the major manufacturer as a raw material in 2002 was approximately 3700 tons (3M Company, 2000).

Little domestic emission inventory of PFAs has been estimated or investigated. However, according to the personal communication with 3M, total PFAs market in South Korea reached a maximum in 2000 since the stead introduction in the mid-1980s and dropped off recently. Most PFAs were imported from 3M, DuPont, Asahi Glass, Daikin, and others, of which over 90% was used as a water repellant for fiber and leather industries. However, the South Korean 3M stopped import of PFAs after 2004 following the official phase-out announcement of 3M in 2001.

PFCAs produced by telomerization process are likely to be the main PFAs consumed in South Korea. Since the 1950s, a number of textile factories have operated in Daegu and neighboring Kyeongsangbukdo. The 60–80% of PFAs imported is known to be consumed in these areas. Studies are needed for emission inventory and monitoring of PFAs in environments.

2.5. Levels, distribution, and exposure to POPs

2.5.1. Dioxin-like compounds (PCDDs, PCDFs, and coPCBs)

2.5.1.1. Environmental concentrations

Most studies of PCDDs/DFs conducted in South Korea have been focused on air quality (ca. 31%) or human exposure (ca. 28%; residues in human body tissues or food items). Concentrations of dioxin-like compounds in various environmental media are summarized in Table 2.7. We provide information stratified based on location as a source site, background site, or a nationwide indicator site. Concentrations of air ranged from ND to 9.946 pg I-TEQ m^{-3} with median value of 0.124 pg I-TEQ m^{-3}. The levels were in the order of nearby site of waste incinerator > industrial area > urban > rural. Compared with rural air (ND~0.235, median = 0.025 pg I-TEQ m^{-3}), concentrations in air at urban and source sites were, on average, 5 and 10 times greater, respectively. Larger cities tend to show greater contamination (Park and Kim, 2002). For example, in two larger cities with populations of over one million the concentration level was from 0.236 to 0.882 pg WHO-TEQ m^{-3} ($n = 6$, median = 0.882 pg WHO-TEQ m^{-3}) while that of a medium-sized city was 0.103–0.573 pg WHO-TEQ m^{-3} (median = 0.196 pg WHO-TEQ m^{-3}; $n = 8$). For three small-sized cities with populations of less than 0.3 million, the concentration level ranged from 0.017 to 0.18 pg WHO-TEQ m^{-3} ($n = 7$, median = 0.072 pg WHO-TEQ m^{-3}). Greater contaminations were also observed in pine needles from larger cities, where concentrations of PCDDs/DFs were 10-fold greater in the second largest city in South Korea, Busan, than that of Jeju, a remote island (Ok et al., 2002). Air of industrial cities ($n = 102$) was more contaminated (twice on average), relative to ambient air of eight major cities with a population over one million but with less industrialization ($n = 235$) (NIER, 2000a, 2001, 2002, 2003, 2004, 2005a). For instance concentrations of 0.006–8.450 pg I-TEQ m^{-3} (median = 0.255) were reported for more industrial cities while a range of 0.008–2.478 pg I-TEQ m^{-3} (median = 0.121) for cities with

Table 2.7. Concentrations of PCDDs/DFs in various ambient environmental media in Korea

Sampling			Total PCDDs/DFs				References[a]
Sample type	Year	*n*	Min	Max	Mean	Median	
Air			pg I-TEQ m^{-3}				
Near incinerators (or in industrial complex)	1999–2004	50	nd	9.95	0.56	0.29	(1), (2)
Urban area	1999–2004	408	nd	8.45	0.31	0.13	(3)–(8)
Rural area	1999–2004	42	nd	0.24	0.04	0.03	(2)
Nationwide (NIER)	1999–2004	386	nd	8.45	0.30	0.12	(2)
Soil			pg I-TEQ g^{-1}, dw				
Near incinerators (< 500 m)	2000–2004	162	0.01	130	13.6	5.37	(2), (9)–(12)
Near incinerators (> 500 m)	2000–2004	119	nd	56.45	3.72	1.48	(2), (9)–(12)
Industrial area	1999–2000	18	1.52	120	18.0	9.14	(8)
Nationwide (NIER)	1999–2004	251	nd	65.4	1.08	0.02	(7)
Water			pg I-TEQ L^{-1}				
Land-fill leachate	1998–2003	33	nd	175	18.4	4.02	(13)–(17)
Industrial/municipal wastewater	1999–2004	78	nd	50.5	1.60	0.006	(2), (18)–(20)
Liver/lake water	1998–2004	298	nd	3.35	0.066	0.007	(7), (15)
Coastal water	2002	5	0.127	0.996	0.377	0.207	(21)
Sediment			pg I-TEQ g^{-1}, dw				
Freshwater sediment							
Outlet of incinerator	2002–2004	9	nd	410	46.8	0.008	(2), (22)
River and lake	1998–2004	94	nd	15.1	0.222	0.009	(23), (24)
Marine sediment							
Masan bay	1992	11	0.554	73.7	11.1	2.92	(25)
Pohang bay	2000–2002	20	2.09	15.5	7.89	7.44	(26)
Ulsan bay	2000–2002	22	1.63	5.50	3.45	3.41	(26)
Busan bay	2000–2002	41	1.50	22.1	6.57	5.04	(26)
Jinhae bay	2000–2002	26	1.21	39.6	7.08	3.93	(26)

Gwangwang bay	2000–2002	35	0.569	2.12	1.37	1.38	(26)
Pohang bay (coPCBs)	2000–2002	20	0.324	2.67	0.615	0.463	(26)
Ulsan bay (coPCBs)	2000–2002	22	0.667	27.7	6.77	3.55	(26)
Busan bay (coPCBs)	2000–2002	41	0.273	24.0	2.99	1.71	(26)
Jinhae bay (coPCBs)	2000–2002	26	0.139	1.718	0.453	0.299	(26)
Gwangwang bay (coPCBs)	2000–2002	35	0.069	0.278	0.145	0.139	(26)
Organism			pg I-TEQ g^{-1}, ww				
Freshwater fishes							
Han River	1998–2001	20	nd	0.740	0.255	0.205	(15), (27)
Nakdong River	1998–2001	21	0.018	4.10	0.814	0.475	(15), (27)
Kum River	1998–2001	13	nd	0.740	0.152	0.100	(15), (27)
Youngsan River	1998–2001	15	nd	0.430	0.122	0.079	(15), (27)
Other river/stream/wetland	1998–2001	44	nd	3.405	0.514	0.283	(15), (23), (27)
Freshwater frog							
Han River	2001	6	0.150	0.615	0.327	0.273	(27)
Nakdong River	2001	6	0.180	1.26	0.682	0.705	(27)
Kum River	2001	4	0.030	0.375	0.201	0.200	(27)
Youngsan River	2001	3	0.220	0.760	0.427	0.300	(27)
Other river/stream/wetland	2001	8	0.010	0.680	0.279	0.205	(27)
Saltwater fish							
Masan Bay and Shihwa lake	1991–2000	8	0.027	0.637	0.302	0.348	(4), (28)
Saltwater Bivalvia							
Total coast	1996–2002	79	0.019	2.74	0.330	0.217	(26), (29), (30)
West coast	1999	9	0.043	0.760	0.175	0.077	(30)
South coast	1999	9	0.052	1.37	0.295	0.115	(30)
East coast	1999	9	0.026	2.74	0.648	0.239	(30)
Water birds			pg I-TEQ g^{-1}, fat				
Nakdong River estuary	1992–1994	42	15.8	899	–	–	(31)

[a] (1) Oh et al., 2001, (2) NIER, 2005b, (3) Eem et al., 2003, (4) Im et al., 2004, (5) Park & Kim, 2002, (6) Kim et al., 2001a, (7) NIER, 2000a; 2001, 2002, 2003, 2004, 2005a, (8) Oh, 2001, (9) Kim et al., 2002c, (10) Park et al., 2004, (11) Kim et al., 2005b, (12) Kim et al., 2005d, (13) Lee et al., 2000, (14) Kim et al., 2001d, (15) Jeong et al., 2001a, (16) Choi et al., 2004, (17) KMOE, 2003a, (18) Shin & Jang, 2001, (19) Chung et al., 2001, (20) KMOE, 2005a, (21) MOMAF, 2003, (22) Pyoungtak City, 2003, (23) Kim & Hong, 2000, (24) Ryoo et al., 2005, (25) Im et al., 2002b, (26) Moon, 2003, (27) Kim et al., 2004a, (28) MOMAF, 2001, (29) Hashimoto et al., 1998, (30) Oh et al., 2003, (31) Choi et al., 2001a.

larger populations, but less industrialized. The population of South Korea tends to be concentrated in urban areas, with 90% of the people living in cities. Fifty percent of the total national population lives in eight major cities that occupy only 5.5% of the land area. That results in a population density of approximately 1875 people km^{-2} for these cities. The population density and industry of these largest cities generates a patchy distribution of contamination. Thus, human and ecological exposure may be more serious in these areas.

A concentration in soil, 3720 pg I-TEQ g^{-1} dw, was found in 1994 near an open burning site of industrial waste in the Masan Industrial area (Im et al., 2002a). Concentrations of PCDDs/DFs in 569 ambient soils measured since 1999 ranged from less than the limit of quantification to 130.4 pg I-TEQ g^{-1} (average = 5.84 and median = 0.61 pg I-TEQ g^{-1}). Recent monitoring of soils around waste incinerators has revealed that a strong source signature appeared only within a few hundred meters of incinerators when based on spatial distribution of the concentration (Park et al., 2004; Kim et al., 2005b; NIER, 2005b). Soils from 149 sites within 500 m from incinerators had concentrations of TEQ that were 5-fold and 14-fold greater than concentrations in soils from more distant locations; in that study, 124 soils from far sites between 500 m and 5 km from incinerators and 281 soils from random sites of non-incinerator measured nationwide were compared with those close to incinerators, respectively (Table 2.7). When concentrations in the areas near to incinerators were excluded, the eight major cities (0.045 pg I-TEQ g^{-1}) contained in soils average 4-fold greater concentration of PCDDs/DFs than other cities (median = 0.018 pg I-TEQ g^{-1}). The impact of incinerators on PCDDs/DFs soil contamination will be described in more detail (see part Section 2.6.1).

As mentioned earlier, direct release of PCDDs/DFs into aquatic systems (2.3 g WHO-TEQ yr^{-1}) is 0.6% of atmospheric release of 401.9 g WHO-TEQ yr^{-1} in 2004. The release of PCDDs/DFs into water occurs via landfill leachate or discharge of industrial and/or municipal wastewater, particularly paper-mill wastewater. PCDDs/DFs investigated in 413 samples ranged from ND to 175 pg I-TEQ L^{-1}. Although concentrations in some wastewaters discharged from paper-mills or waste incinerators exceeded 10 pg I-TEQ L^{-1} (Japanese standard for effluents), generally wastewaters discharged from incinerators or industrial and/or municipal waste treatment plants did not contain concentrations of PCDDs/DFs that were significantly greater than those of ambient water (two-tailed t-test, $p = 0.07$). Alternatively, leachates of waste landfill, contained significantly greater concentrations of PCDDs/DFs, relative to wastewater and ambient water (one-tailed t-test, $p < 0.01$). Particularly, leachates contained concentrations of PCDDs/DFs that were more than 100-fold greater (median $= 4.02$ pg I-TEQ L^{-1}, $n = 33$) than those in ambient water (median $= 0.007$ pg I-TEQ L^{-1}, $n = 295$). This observation indicates that more studies should focus on the landfill leachates. No statistically significant difference was found among five major river systems (ANOVA, $p = 0.40$). However, it is important to note that the greatest concentrations were measured in the Han River and the Nakdong River, two of the longest rivers in South Korea. The river and sea water sampled at the Nakdong River estuary in 2003 contained the greatest concentrations measured in ambient waters (i.e., ~0.3 and 0.996 pg I-TEQ L^{-1}, respectively) (MOMAF, 2003). Additionally, samples collected at 31 national monitoring sites for freshwater showed a relative greater concentration in the Han River (median $= 0.34$ pg I-TEQ g^{-1} ww) and the Nakdong River (median $= 0.43$ pg I-TEQ g^{-1} ww) than other river (median $= 0.19$ pg I-TEQ g^{-1} ww) (Kim et al., 2004a).

Concentrations of PCDDs/DFs in sediments have been measured in three areas, including sediment at the wastewater discharge from waste incinerators, ambient freshwater sediments, and seawater sediments along the coast (Table 2.7). Sediments at the incinerators' wastewater discharge exhibited the greatest range of concentrations with concentrations ranging from below the limit of quantification to a maximum of 409.6 pg I-TEQ g^{-1} dw. Due to the small number of samples ($n = 9$), it is impossible to determine whether the concentrations were significantly greater in sediment at incinerator wastewater discharge. Approximately 77% of the concentrations of PCDDs/DFs in freshwater sediments ($n = 80$) were less than 0.1 pg I-TEQ g^{-1}. Relatively great concentrations were measured in inland sediment from waterways, into which wastewater from industrial areas is discharged. In particular, a few hundreds of pg I-TEQ g^{-1} were measured in sediment from the Hyungsan River in the vicinity of POSCO I.C. in Pohang city (Koh et al., 2004). This is the largest steel production facility in South Korea. Concentrations of PCDDs/DFs in marine sediments from major bays (Pohang, Ulsan, Busan, Jinhae, and Gwangyang) were greater than 1 pg I-TEQ g^{-1} (Moon, 2003). Concentrations of PCDDs/DFs in sediments from these five bays were: Pohang (7.24 pg I-TEQ g^{-1}) > Busan (6.55 pg I-TEQ g^{-1}) > Masan (3.88 pg I-TEQ g^{-1}) > Ulsan (3.18 pg I-TEQ g^{-1}) > Gwangyang (1.33 pg I-TEQ g^{-1}) on basis of median value (Moon, 2003). However, contamination of sediments from Ulsan Bay is as serious as Pohang and Busan with median concentrations of 7–8 pg I-TEQ g^{-1}, if coPCBs are included (Table 2.7). Co-planar PCBs accounted for about 55% and 27% of the total TEQs in surface sediments from Ulsan and Busan Bays, respectively. These relatively greater contributions of coPCBs, compared with $< 10\%$ for the other bays, indicate that PCDDs/DFs contamination may be caused by commercial PCBs formulations at these two bays. The average contamination level for marine sediment along the entire coastal area is likely to be lower because the five bays are sort of hot spots of POPs contamination in Korea.

coPCBs contributed $>90\%$ to total TEQs of dioxin-like compounds in most PCBs products such as Aroclor, Kanechlor, and Clophen (Wakimoto et al., 1988). Major 'hot spots' of PCDDs/DFs in coastal areas such as big harbor can be influenced by releases of PCBs products. This conclusion is based on the relative contribution of coPCBs to total TEQs or PCDDs/DFs pattern relative concentrations of congeners measured in the costal areas samples. Homologue compositions of PCDFs in the more contaminated sediments, such as those from Masan Bay were similar to that of commercial PCB products, KC-300 or KC-400 (Im et al., 2002b). Additionally, according to the results of the mussel watch programs from 1987 to 1999 (Oh et al., 2003), bivalves collected along the entire coastal area showed a clear difference in coPCB contribution to total TEQs between 1987–1990 and 1996–1999, and between the larger harbor areas and others. On average 82% of the TEQ was contributed by coPCBs in the earlier years' samples ($n = 13$) but only 32% in more recently collected sediments ($n = 38$). This indicates that concentrations of PCBs have decreased in these areas, instead of concentrations of PCDDs/DFs increasing over time. In more recently deposited sediments there is a greater contribution from coPCBs relative to PCDDs/DFs in larger harbors, such as Incheon, Ulsan, Masan, and Busan (see the map in Fig. 2.3). In contrast, mussels from the vicinity near the POSCO facility contained relatively less contribution (7%) by coPCBs to total TEQs. It has been suggested that PCB contamination in larger harbors could be ascribed to commercial formulations used in ship-painting (Hong et al. 2005). Consequently, contamination of larger harbors with dioxin-like compounds could be caused by commercial PCBs products, whereas impact of combustion sources seem to be greater in other areas.

There are relatively few reports of concentrations of PCDDs/DFs in wildlife from South Korea. The few available studies are comprised of monitoring for: (1) fishes and amphibian in inland rivers and lakes; (2) shellfishes and fishes in coastal region; and (3) birds and pine needles (Table 2.7). Little difference in concentrations of PCDDs/DFs was observed between inland fishes and marine shellfishes (two-tailed t-test, $p = 0.99$). Nevertheless, coastal environments are expected to be more heavily contaminated considering the possibility that fishes at higher tropic levels can bioaccumulate these residues to a greater extent. For instance, concentrations of PCBs in shellfishes for 1999 (Kim et al., 2002b) and fishes for 1997 (Yim et al., 2005) sampled along the entire coastal area can be compared. Concentrations in fishes were, on average, two-fold greater than those in shellfishes, even though PCBs in fishes were measured for major 22 congeners while 104 congeners were analyzed in shellfishes. That is, 4.5–96 ng g^{-1} ww (average = 23 ng g^{-1} ww) for fishes vs. 0.27–84.6 ng g^{-1} ww (average = 12.6 ng g^{-1} ww) for shellfishes. Among coastal regions, concentrations of PCDDs/DFs greater than 0.5 pg I-TEQ g^{-1} ww was found in bivalves around larger industrial complexes such as Incheon, Yeochun, Ulsan, and Pohang (Oh et al., 2003). Together with these areas, bivalves from Masan and Busan exceeded 1 pg WHO-TEQ g^{-1} ww when including coPCBs TEQs (Oh et al., 2003). Concentrations of TEQs (i.e., PCDDs/DFs TEQs + coPCBs TEQs) in the other coastal regions were less than 0.5 pg WHO-TEQ g^{-1} ww in bivalves (Oh et al., 2003).

Monitoring of residues in fish and amphibians has been performed by the NIER at 31 sites along major Rivers (Jeong et al., 2001a; Kim et al., 2004a). In two extensive monitoring programs, concentrations of PCDDs/DFs were generally greater in rivers flowing through larger cities and industrial areas. The order of decreasing concentrations is: Nakdong River > Han River > other rivers and wetlands. Mountain frogs from the Nakdodng River contained the greatest concentrations among amphibians from rivers and wetlands investigated (Kim et al., 2004a). Furthermore, in the period from 1992 to 1994, concentrations of PCDDs/DFs as great as 100 pg WHO-TEQ g^{-1} fat were measured in the subcutaneous fat of water birds from Nakdong River estuary (Choi et al., 2001a).

There was little correlation between PCDDs/DFs (Jeong et al., 2001a) and total PCBs (Jeong et al., 2001b) in the fish samples from 31 inland sites. Based on the composition of coplanar PCBs congeners, it was proposed that contamination of the atmosphere with PCBs could be caused by waste incinerators (Kim et al., 2003b; Kim et al., 2005c). However, the contribution of waste incinerators to environmental release of byproduct PCBs is trivial. Net gaseous exchange of PCBs occurs from water to air and PCB profiles in river sediments resemble that of commercial PCBs products (Kim, 2004). Moreover, concentrations of PCB in South Korean air vary with temperature (Yeo et al., 2004a). Based on these observations, concentrations of PCB in South Korean air are unlikely to be controlled by atmospheric emission (see the part Section 2.6.2.1 for more discussion). Consequently, concentrations of PCBs in aquatic environments are less dependent on atmospheric concentrations, but more likely due to direct releases into water. In contrast to PCBs, the major source of PCDDs/DFs in South Korea is airborne releases, particularly from waste incinerators. Therefore, the discrepancy between PCBs and PCDDs/DFs residues in inland fishes could be due to the difference in their sources.

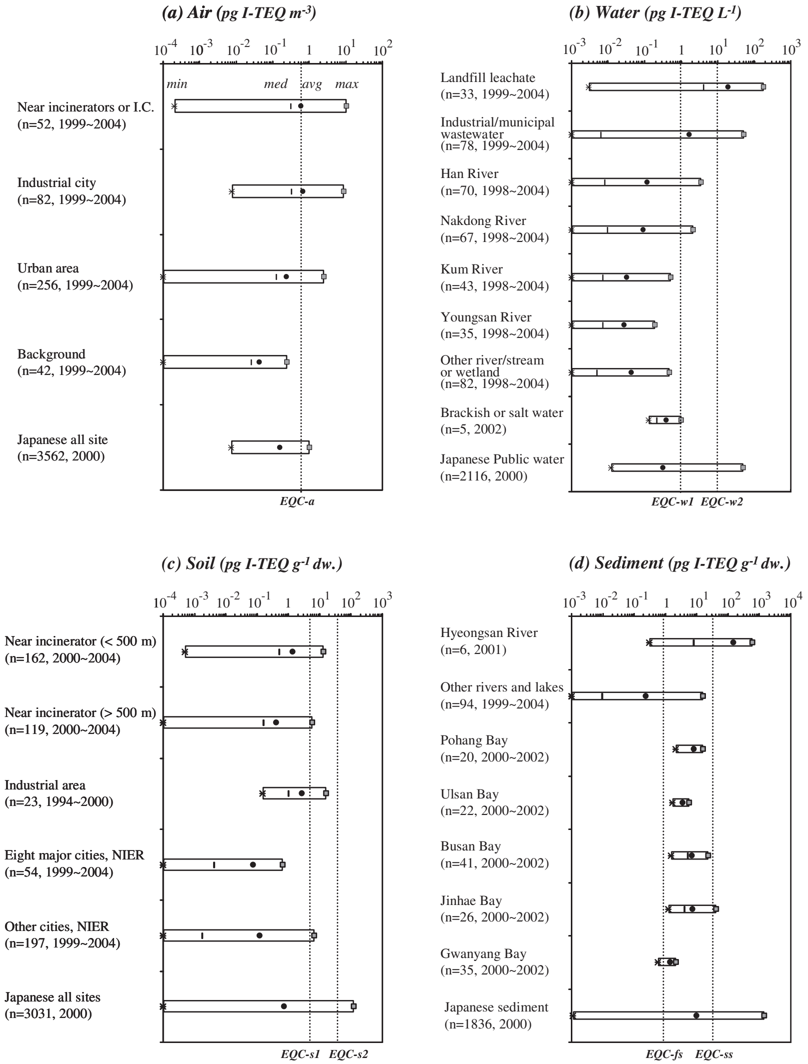


Fig. 2.11. Comparison of PCDDs/DFs levels in Korean environments with environmental quality criteria proposed worldwide. Range indicates minimum (min), maximum (max), median (med), and arithmetic mean (avg). Dotted lines indicate environmental quality criteria: 0.6 pg TEQ m^{-3} for ambient air (EQC-a), 1 pg TEQ L^{-1} for ambient water (EQC-w1) and 10 pg TEQ L^{-1} (EQC-w2) for wastewater, 5 (EQC-s1) and 40 (EQC-s2) pg TEQ g^{-1} dw for soil, and 0.85 (EQC-fs) and 21.5 (EQC-ss) pg TEQ g^{-1} dw for sediment. Japanese data is based on WHO-TEQs including PCDDs/DFs and coPCBs (JMOE, 2002).

2.5.1.2. Comparison of environmental levels with EQCs

Since the early 1990s, the Japanese government has conducted extensive surveys of both sources and environmental concentrations of dioxin-like compounds nationwide (JMOE, 2002). Comparison of concentrations of residues between South Korea and Japan suggests that concentrations in air are greater in South Korea than in Japan (Fig. 2.11). However, for other media, concentrations are similar or less in South Korea than in Japan. Intake rates of PCDDs/DFs, expressed as TEQ, by people in South Korea is similar to or less than those of people in other countries (see Section 2.5.1.5). As presented earlier, environmental emissions of dioxin-like compounds per unit area is greater in South Korea than other countries. Thus, relatively lesser concentrations in the South Korean environment except air seem to be inconsistent with emissions. One possible explanation for the inconsistency may be associated with the short history of waste incineration. The mass balance of PCDDs/DFs has not yet been thoroughly evaluated. However, according to multi-media modeling, it is evaluated that it takes more than a decade for POPs to reach steady state in soil or sediment (Lee et al., 2004). Waste incineration in South Korea became significant only after mid-1990s (Fig. 2.4). Furthermore, since 1997, releases from waste incinerators have been regulated. This suggests that their levels in soil or sediment may increase with time in the future unless emission level decreases significantly. Another reason could originate from the possibility that the number and location of the monitoring sites may not be representative.

In South Korea, no environmental quality criteria (EQCs) have been proposed to protect human health and wildlife from dioxin-like compounds. Thus, we compared concentrations of TEQ measured in individual media with EQCs or benchmarks for PCDDs/DFs proposed by other governments worldwide (Fig. 2.11). Japan proposes EQCs for ambient air and water of 0.6 pg WHO-TEQ m^{-3} for air, 1 pg WHO-TEQ L^{-1} for public water and 10 pg WHO-TEQ L^{-1} for wastewater (JMOE, 2002). Since 1999, concentrations of TEQ measured in air from within 1 km of waste incinerators and/or industrial area and sites in industrial cities, have exceeded the EQCs established by Japan (0.6 pg WHO-TEQ m-3) 22% and 29%, respectively. Alternatively, only 7% of air samples from urban and background sites exceeded the EQCs (Fig. 2.11a). This indicates that air quality is poorer in South Korea than in Japan where only 1.1% of 920 air samples collected in Japan during 2000 exceeded EQC (Shibata, 2002). The EQC values are applied differently, depending on the objective. Generally, landfill leachates exceeded the EQC (10 pg WHO-TEQ L^{-1}) more frequently (30%) than the wastewaters discharged from treatment plants or industrial areas (3.8%). Only two samples of 302 fresh and salt waters measured contained concentrations of TEQ that exceeded the 1 pg WHO-TEQ L^{-1}, which is less than 3.9% of 2116 sites for Japanese waters were over the EQC. However, it should be noted that TEQs contributed by coPCBs were included for Japanese TEQ values but not for those from South Korea.

EQCs for soils vary among countries from 4 to 1000 pg TEQ g^{-1} dw. For instance, 1000 pg TEQ g^{-1} was suggested as the limit for residential soils in Japan and the USA but 500 pg TEQ g^{-1} has been proposed as the criterion in Finland, 10 pg TEQ g^{-1} in Sweden, and 4 pg TEQ g^{-1} in Canada (Schulz, 1993; JMOE, 2002; CCME website). Of the countries, Germany adopts specialized soil EQCs to protect the human health and the environment for different soil uses (Schulz, 1993). According to the EQCs, no restrictions are placed on use of soils containing less than 5 pg TEQ g^{-1} dw, precautious use and identification of PCDDs/DFs contamination source are required for soils containing between 5 and 40 pg TEQ g^{-1}, and, for soils containing more than 40 pg TEQ g^{-1}, use for cultivation of fruits, legumes, or forage plants is prohibited. Furthermore, soils containing more than 100 pg TEQ g^{-1} should be removed in playgrounds and, for soils over 1000 pg TEQ g^{-1}, measure should be taken to reduce contact with soil. Since 1999, 10 (ca. 4%) of 251 samples measured in non-source areas of South Korea exceeded the 5 pg TEQ g^{-1} criterion. Only two concentrations exceeded 40 pg TEQ g^{-1}. On the contrary, soils in the vicinity of sources like incinerators or industrial complex frequently exceeded 5 pg TEQ g^{-1} and, to a less degree, exceeded 40 pg TEQ g^{-1}. For instance, 49.4% of soils within 500 m of incinerators, 21% of soils more than 500 m from incinerators, and 69.6% of soils in industrial areas (as in Masan/Changwon I.C. in 1994 and Gwangyang/Yeocheon I.C. in 1999 and 2000) were greater than 5 pg TEQ g^{-1}. Soils with greater than 40 pg TEQ g^{-1} over which cultivation is prohibited account for 11.7% for within-500 m of waste incinerators and 13% for industrial origin as compared to only 0.8% of the soils beyond 500 m from the incinerators. Two samples were found to exceed 100 pg TEQ g^{-1} for both near-incinerator and industrial area. Only one sample near incinerator was measured to be 3720 pg TEQ g^{-1} in 1994. Based on this observation, ambient soils in non-source areas require no restrictions on use. For soils in the vicinity of sources such as waste incinerators and in industrial complexes, however further investigation and regulations are needed.

Various sediment quality guidelines (SQGs) and benchmark values have been proposed by several states and federal agencies in the USA and other countries. However, none of these benchmarks have been adopted for widespread regulatory applications. Concentrations of TEQ in sediments of South Korea measured since 1999 were compared with SQGs for PCDDs/DFs proposed by Canadian Council of Ministers of the Environment (CCME) to protect human health and wildlife (CCME, 1999). CCME proposed 0.85 pg TEQ g^{-1} dw as an interim guideline and 21.5 pg TEQ g^{-1} as probable effect level for both freshwater and saltwater sediment. Except for sediment from the Hyeongsan River (Koh et al., 2004), none of the concentrations of TEQ in 94 freshwater sediments exceeded the probable effect level, over which an incidence of adverse biological effects of 46% would be predicted. Concentrations of TEQ in only three samples were in the range of 0.85–21.5 pg TEQ g^{-1}, indicating 24% incidence of adverse biological effects. Most of the 144 marine sediments from industrialized or urbanized bays contained concentrations of TEQ that ranged from 0.85 to 21.5 pg TEQ g^{-1}. The proportion of TEQ contributed by coplanar PCB was not included for sedimentary TEQ values in the present study. While concentrations of PCDDs/DFs in South Korean environments are generally less than proposed quality criteria for ambient environments, but more control is needed for environments in the immediate vicinity of sources.

2.5.1.3. Source identification of PCDDs/DFs in environmental media

For appropriate and cautious use of soils, sources of PCDDs/DFs contamination and their impacts should be evaluated. One way to differentiate source from ambient sample is the fraction of total PCDDs are greater in ambient samples than in the source. The ratios of PCDDs are on average 0.59($\pm$0.20) and 0.80($\pm$0.19) for landfill leachate and ambient water, respectively. The ratios are 0.53 and 0.81($\pm$0.36) for sediment at incinerator wastewater discharge and ambient river/lake sediments, respectively. This trend was also observed for soils. The proportion of the PCDDs fraction of TEQ increases with increasing distance from incinerators with the following proportions: 0.58($\pm$0.16) for ashes; 0.58($\pm$0.17) for soils within 500 m from incinerator; 0.74($\pm$0.15) for soils beyond 500 m from incinerator; and 0.91($\pm$0.18) for ambient soils. The dramatic increase in the proportion of the TEQ attributed to PCDD in the ambient environment results from the phase out of PCDF congeners and persistence of OCDD (Fig. 2.12). For all environmental media, lesser chlorinated PCDDs/DF congeners are uniformly detected in source samples. However, the less chlorinated congeners are distinctly depleted in ambient samples while OCDD is enriched. The transition of the relative proportions of PCDDs/DFs from the initial source to remote areas will be discussed in detail (see Section 2.6.1).

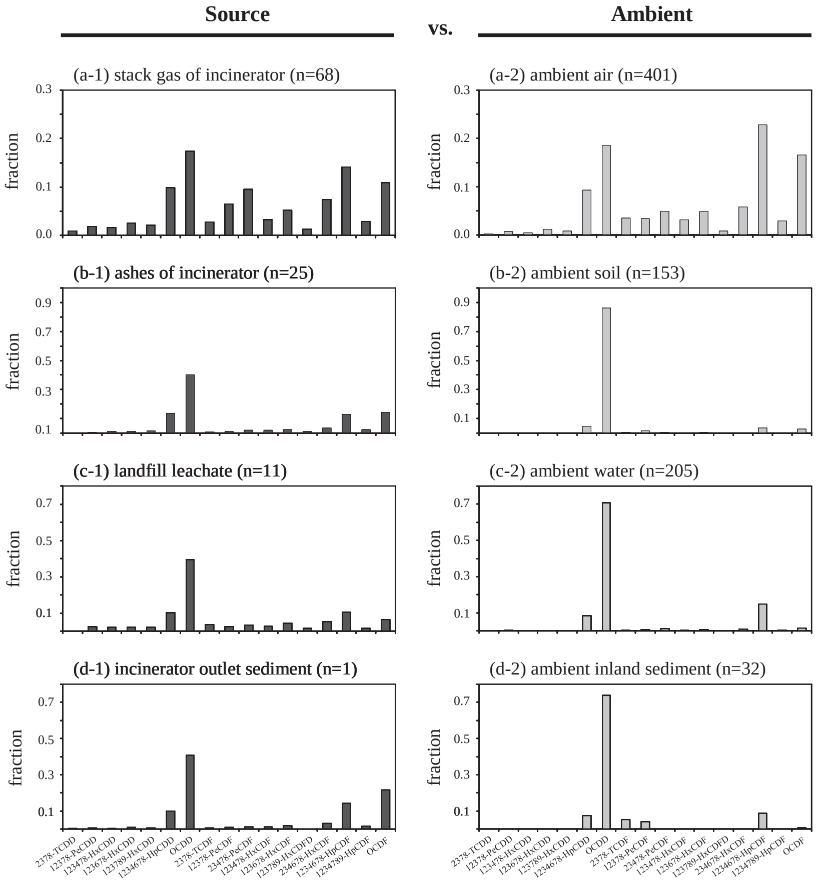


Fig. 2.12. Comparison of average fraction profiles in individual media between source and ambient environments; Data were collected from references in Table 2.7.

2.5.1.4. Temporal distribution

The decrease in concentrations of PCBs in coastal bivalves, between 1987–1990 and 1996–1999 was observed more clearly than that of PCDDs/DFs (Oh et al., 2003). However, it is not possible to assess temporal trend of PCDDs/DFs, because there is little information about PCDDs/DFs contamination level for environmental media before the late 1990s.

Emission of dioxin-like compounds has decreased progressively since the regulation with a 67% decrease between 2001 and 2004 (see Fig. 2.5).

Thus, it is important to assess whether the decline of emission has resulted in decreases in concentrations in the various environmental compartments. The NIER, a principal research organization for environmental residue monitoring of POPs in South Korea, has been annually conducting a regular monitoring at 130 sites for ambient media including air, water, sediment, and soil since 1999 (NIER, 2000a, 2001, 2002, 2003, 2004, 2005a). There is little available concentration data for temperal variation of other POPs (i.e., 'not detected' for lots of measurements reported or 'detected' in only a specific media) because the detection limits were relatively great. Meanwhile, enough monitoring data has been reported for PCDDs/DFs due to the use of standard operation procedure (SOP) with the state-of-the art analysis technique such as HRGC/HRMS and administrative notification for the Certified Laboratory for PCDDs/DFs analysis since the late 1990s.

In general, concentrations of PCDDs/DFs have decreased in all media (Fig. 2.13). Decrease in ambient air was significant with annual incremental decreases observed. For instance, the declines in all of arithmetic mean, median, and maximum concentrations were significantly correlated with those in annual emission of individual years presented in Fig. 2.5a ($r > 0.7$, $p < 0.05$). An eight-fold decrease was observed over a period of 6 yr. This decline in concentrations of PCDDs/DFs is related to regulation of emissions in South Korea. Because most of environmental release occurs primarily into air, residues in other media would also be expected to follow the same declining trend observed in air.

It seems, however, less clear if decreases in concentrations of PCDDs/DFs have occurred in soils or water. The responding point at which the concentration in soil begins to decrease is known to be delayed by a few years (typically ~3–5 years) depending on the emission scenario. According to the model performance (Lee, 2005), concentrations in soils continues to increase gradually even after regulation, then reaches a maximum in 3rd year after regulation and thereafter decreases. This may be because of overall atmospheric input (i.e., dry/wet deposition and sorption) to soil is still greater than total output from soil including volatilization, run-off, and degradation. It is not until the reversal phase occurs between input and output that residue in soil is expected to decrease. This means that atmospheric concentrations should be reduced up to the level that can result in a decrease in concentrations in the soil. Furthermore, it has been determined that concentrations in soil decrease slowly due to its strong sorption capacity. Thus, it takes decades for concentrations to decrease to the half of the original steady state level in realistic emission reduction conditions (Lee, 2005). It should also be

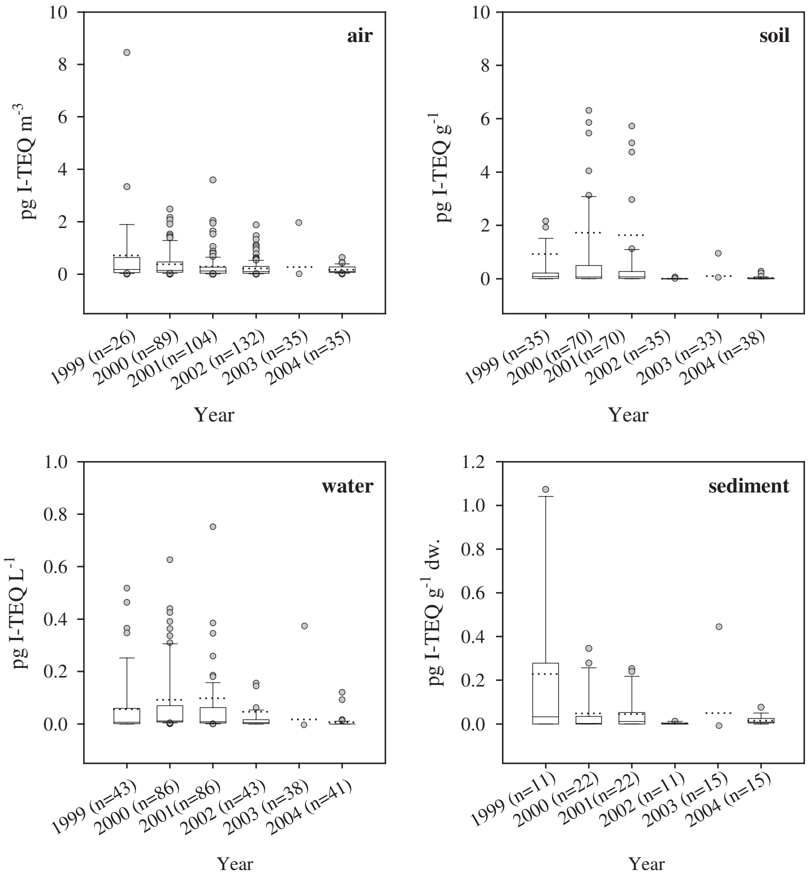


Fig. 2.13. Temporal trend of PCDDs/DFs concentration in individual environmental ambient media (NIER, 2000a, 2001, 2002, 2003, 2004, 2005a). The boundary of the box indicates the 25th and 75th percentile, and a line within the box marks the median. Whiskers above and below the box indicate the 90th and 10th percentiles. Dotted lines and points are the arithmetic mean and outlying points, respectively. Values in the parenthesis are the number of samples. Two points and a dotted line of individual media for 2003 indicate maximum (upper) and minimum (below), and arithmetic mean, respectively. Outliers in early years (i.e., four for water (1–4 pg I-TEQ L^{-1}) and five for soil (20–70 pg I-TEQ g^{-1})) were excluded.

noticed that concentrations of PCDDs/DFs in air cannot decrease dramatically, even after regulation because soil plays a secondary source for air contamination after regulation. Therefore, residues in both soil and air need to be monitored continuously. In brief, considering the temporal trend of the residues in the media, the distribution and fate of

PCDDs/DFs in South Korean environments seems to be strongly influenced by emissions to the atmosphere (see Section 2.6.2.1).

2.5.1.5. Human exposure

Concentrations of PCDDs/DFs in human blood, adipose and breast milk have been monitored in the South Korean population. Concentrations of PCDDs/DFs in tissues of the South Korean population ranged from 0.1 to 105 pg I-TEQ g^{-1} lipid. In spite of the great variation, the average exposure was 10–20 pg I-TEQ g^{-1} lipid (Fig. 2.14). This level is within the average human background range, 10–30 pg I-TEQ g^{-1}, as suggested by WHO in 1998 (WHO, 1998). The difference in the average exposure between workers and residents living near waste incinerators seems not clear in many cases (Fig. 2.14). However, the exposure may vary with the nature of the work within an incinerator. According to the study of Kim et al. (2005d), the body level was over 60 pg I-TEQ g^{-1} lipid for incinerator workers, handling fly ash, or operating and maintaining the incinerators for more than 6 years whereas that of new employee or office worker was about 10 pg I-TEQ g^{-1} lipid. This suggests that exposure via inhalation could be significant for incinerator workers. The residents in urban and industrial cities showed the body level 2–5 times higher than that of the residents in remote areas ($\sim$4 pg I-TEQ g^{-1} lipid) (Fig. 2.14). TEQ contributed by dioxin-like PCBs (coPCBs) in human blood accounted for $\sim$70% of PCDDs/DFs TEQs for both workers and the general population (Kim et al., 2005e). Thus, when coPCBs are included, the total TEQ concentration could be approximately two-fold greater.

When excluding accidental or occupational exposure, over 90% of human background exposure to dioxin-like compounds is estimated to occur through the diet, with food of animal origin being the predominance source (US EPA, 2004). Residues of dioxin-like compounds in various food items collected from South Korean markets are summarized in Table 2.8. Fishes and shellfishes bore the greatest concentrations of TEQ, followed by meat/poultry > dairy product > other non-animal food-items. Considering the gradual increase in animal food consumption from 7% of the diet in the late 1970s to 20% in the 2000s, exposure of humans to these toxic compounds would be expected to be greater in more recent years. In contrast to those in other food-items, contribution of coPCBs to total TEQ in seafood appeared to be substantial, accounting for $71 \pm 26\%$ (average ± standard deviation). Thus, coPCBs need to be included to assess human exposure of dioxin-like compounds.

Average Daily Intake (ADI) via dietary exposure to dioxin-like compounds was estimated by multiplying residue concentrations and

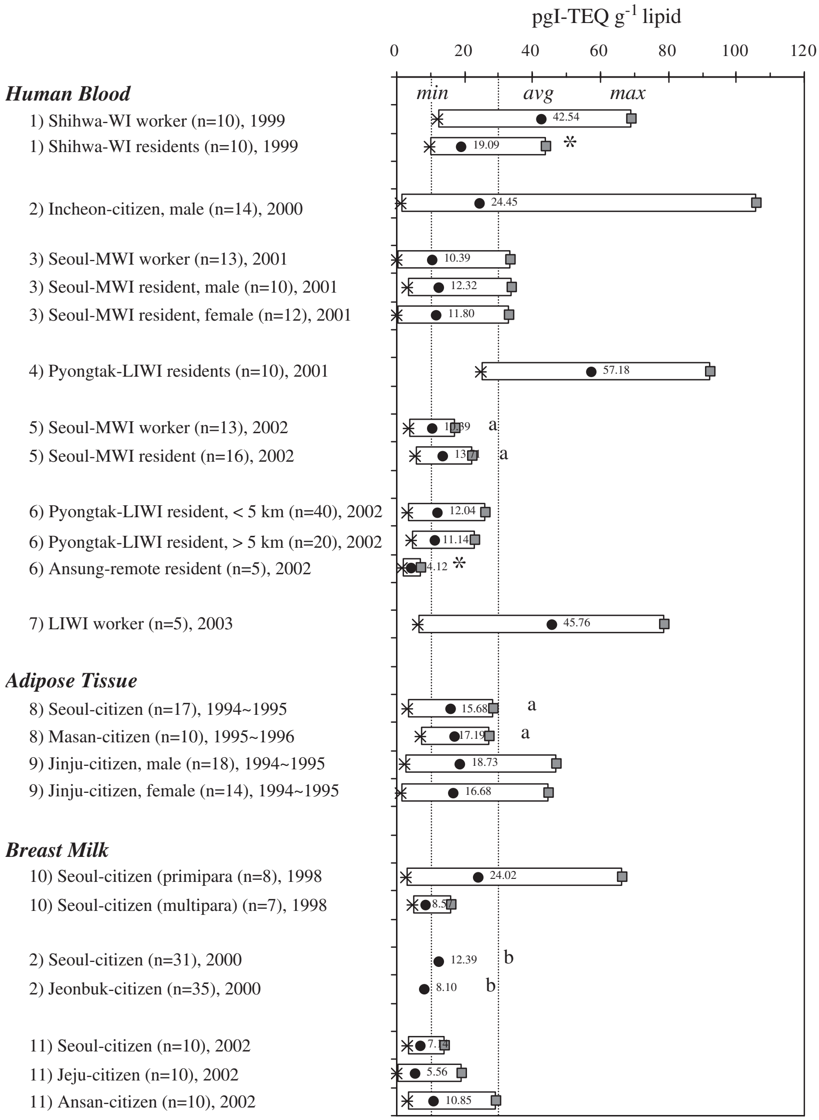


Fig. 2.14. PCDDs/DFs residues in Korean human body. The upper- and down-side of bars indicates minimum and maximum, respectively, and black circles in the center of bars indicate arithmetic means. Exceptionally, the upper- and down-side in 'a' bars indicate 'arithmetic mean ± 1 standard deviation' and the arithmetic means alone were presented for 'b'. '*' means the significant difference PCDDs/DFs residues in between residents around waste incinerator and incinerator workers (paired t-test, $p < 0.01$). Two dotted lines indicate average human background level suggested by WHO. (1) Yang et al. (2001), (2) Kim et al. (2000b), (3) Kim et al. (2005e), (4) CIES (2002), (5) Leem et al. (2003), (6) Pyoungtak City, 2003, (7) Kim et al. (2005d), (8) Kang et al. (2002), (9) Kang et al. (1997), (10) Yang et al. (2002), (11) Kang et al. (2003).

Table 2.8. Residual levels of dioxin-like compounds in various food-items from South Korea since 1999

Food items	Sample number (*n*)	PCDDs/DFs (pg WHO-TEQ g^{-1}, ww)	coPCBs (pg WHO-TEQ g^{-1}, ww)	Total TEQs (pg WHO-TEQ g^{-1}, ww)	References[a]
Cereals	74	ND–0.358[b] (0.0123, 0.0005)[c]	ND–0.005 (0.0005, 0)	ND–0.358 (0.0141, 0.0025)	(4)–(6), (9)–(11)
Vegetables	23	ND–0.046 (0.0037, 0.0010)	ND–0.004 (0.0007, 0)	ND–0.006 (0.0020, 0.0010)	(6), (9)
Fruits	15	ND–0.008 (0.0042, 0.0048)	ND–0.002 (0.0004, 0)	ND–0.008 (0.0045, 0.0048)	(6), (9)
Meat/poultry	147	ND–0.454 (0.0375, 0.0060)	ND–1.065 (0.0325, 0.0035)	ND–1.519 (0.0696, 0.0155)	(2)–(11)
Fish/shellfish	276	ND–7.235 (0.2300, 0.0350)	ND–19.037 (0.7888, 0.2199)	ND–19.441 (0.9757, 0.2902)	(1)–(6), (8)–(12)
Dairy products	55	ND–0.080 (0.0142, 0.0050)	ND–0.195 (0.0280, 0.0070)	ND–0.239 (0.0351, 0.0120)	(2), (4)–(6), (8)–(11)

[a] (1) Oh et al. (2005a), (2) Choi et al. (2002), (3) Kim et al. (2001e), (4) Chae et al. (2004), (5) Kim et al. (2004b), (6) Kim et al. (1999a), (7) Choi et al. (2001b), (8) Won et al. (2000), (9) Won et al. (2001), (10) Hong et al. (2002), (11) Hong et al. (2003a), (12) Moon and Ok (2006).

[b] Range (minimum–maximum).

[c] Average value (arithmetic mean, median).

Table 2.9. Average daily intakes (ADIs) investigated for market food-items

Food group assessed	Collected year	Percentage of food-items assessed (%)[a]		ADI (pg WHO-TEQ kg(bw)^{-1} day^{-1})			References
		Of total	Of fish/shellfish	PCDDs/DFs	coPCBs	Total TEQs	
31 Items in 6 food-groups (cereals, vegetables, fruits, meat/poultry, dairy products, fishes/shellfishes)	1999	72.7	26.1	0.63[b]	–[c]	–[c]	Kim et al., 2000c
13 Items in 3 food-groups (cereals, meat/poultry, fishes/shellfishes)	1999[d]	28	20	0.26	0.39	0.64	Won et al., 2000
23 Items in 6 food-groups (cereals, vegetables, fruits, meat/poultry, dairy products, fishes/shellfishes)	2000[d]	52	23.4	0.08	0.23	0.31	Won et al., 2001
23 Items in 3 food-groups (meat/poultry, dairy products, fishes/shellfishes)	2001[d]	34	37.3	0.14	0.78	0.92	Hong et al., 2002
17 Items in 4 food-groups (cereals, meat/poultry, dairy products, fishes/shellfishes)	2002[d]	30	15.3	0.06	0.13	0.19	Hong et al., 2003a

40 Fishes/shellfishes	2002–2003	3.6	54.1	0.28	0.4	0.68	Moon & Ok, 2006
32 fishes/shellfishes	2003	5.2	76.7	0.26	0.67	0.93	Lee et al., 2007
14 Items in 4 imported food-groups (cereals, meat/poultry, dairy products, fishes/shellfishes)	2003[d]	25.3	10	0.04	–[c]	–[c]	Chae et al., 2004
17 Items in 4 food-groups (cereals, meat/poultry, dairy products, fishes/shellfishes)	2003[d]	29	20.2	0.12	0.29	0.41	Kim et al., 2004b
Average food-items (cereals, vegetables, fruits, meat/poultry, dairy products, fishes/shellfishes)	1999–2003	82.1	100	0.08–10.95 (0.42)	0.26–22.6 (0.96)	0.39–25.7 (1.32)	This study[e]

[a] Average daily consumption rate of total food and fishes/shellfishes are 1280 and 86 g capita^{-1} day^{-1}.

[b] pg I-TEQ kg(bw)$^{-1}$ day^{-1}.

[c] Not analyzed.

[d] Estimated year from ‘published date minus one year’ because of not presented.

[e] Minimum–maximum (arithmetic mean) which were estimated by assuming as representative residues of individual food groups median, maximum, and arithmetic mean, respectively, of residual levels in individual food groups presented in Table 2.7.

consumption rate of individual food items. The estimated ADI for South Korean people since 1999 ranged from 0.19 to 0.93 pg WHO-TEQ kg bw^{-1} day^{-1} (Table 2.9). There existed great uncertainties in these estimates because the assessments did not include all food items that South Koreans consume daily or did not represent average composition of individual items in food consumption. Most studies involved ~30% (~400 g $capita^{-1}$ day^{-1}) of average daily food consumption rate, ca. 1280 g $capita^{-1}$ day^{-1}. Fishes/shellfishes, containing the greatest concentrations of dioxin-like compounds among food-groups, were assessed for 20% (~17 g $capita^{-1}$ day^{-1}) of average daily consumption rate, ca. 86 g $capita^{-1}$ day^{-1}, in most studies (Table 2.9). Thus, true ADI is likely to be greater than previous estimates. For instance, Lee et al. (2007) estimated that ADI was 0.93 pg WHO-TEQ $kg(bw)^{-1}$ day^{-1} from fishes/shellfishes alone in which 77% of daily fishes/shellfishes consumption rate was included. This corresponds to 1.2 pg WHO-TEQ $kg(bw)^{-1}$ day^{-1} for all food items. We also estimated ADI using median, maximum, and arithmetic mean values observed for individual food groups. Assuming that a South Korean is exposed to the observed maximum levels for all individual food groups, ADI would be 25.7 pg WHO-TEQ $kg(bw)^{-1}$ day^{-1}. Although this exposure rate seems unrealistically great since it might represent a worst-case scenario. If it is assumed that individuals are exposed to the arithmetic mean concentration of each residue for all individual food groups, the ADI is estimated to be 1.32 pg WHO-TEQ $kg(bw)^{-1}$ day^{-1}. Since values less than the limit of quantification were included in the database as 'zero', ADI calculated using median residues would underestimate the actual ADI.

Fishes/shellfishes contributed 82% of the ADI, followed by cereals (6.2%), meat/poultry (6.1%), dairy products (3.9%), fruits (1.1%), and vegetables (0.7%). Again, coPCBs accounted for 70% of the total TEQs, implying the significant contribution by seafood. A similar contribution from fishes/shellfishes (>70% of total TEQs) and coPCBs (>60% of total TEQs) was also observed in ADI assessments of the Japanese population (Tsutsumi et al., 2001; Sasamoto et al., 2006). The contribution of seafood to total TEQs worldwide varies from a value of less than 6% for the USA (Charnley and Doull, 2005) and Egypt (Loutfy et al., 2006) to more than 70% for South Korea, Finland (Kiviranta et al., 2004), and Japan. Major contributors are determined depending on specific consumption style in individual nations. For instance, meats and dairy products are a major contributor in the diet of people in the USA and Egypt. In South Korea, it is notable that fishes/shellfishes, account for only 6.7% of daily food ingestion, but account for about 80% of total TEQs. Dried anchovy alone accounted for 0.62 pg WHO-TEQ $capita^{-1}$ day^{-1}

(Lee et al., 2007). To reduce exposure to dioxin-like compounds, therefore a change in food consumption pattern may be helpful, together with control of environmental release. In some previous studies (Kim et al., 2000b; Yang et al., 2001; Lee, 2002), the role of fishes/shellfishes was underestimated as 37–55% of total TEQs. This is because the co-planar PCBs were excluded from the analysis and many kinds of fishes/shellfishes were not included from their estimation.

Besides dietary exposure, the daily dioxins intake rate can be also predicted on the basis of its level in breast milk, blood, and adipose tissue as shown in Eq. (1) (WHO, 1998; US EPA, 2000).

$$\mathrm{EDI} = \frac{C_{\mathrm{tissue}} \times 0.693 \times f_2}{h_{12} \times f_1} \tag{1}$$

In this calculation the EDI is an average daily intake estimated (pg TEQ kg(bw)$^{-1}$ day^{-1}), $h_{1/2}$ is the half-life of dioxins in human body (day), f_1 is the fraction of dioxins absorbed (dimensionless), and f_2 is the proportion of body fat to weight (dimensionless). These constants were assumed to be 7 yrs, 0.9, and 0.3 for $h_{1/2}$, f_1, and f_2, respectively. We estimated EDIs from body residues presented in Fig. 2.14. These EDIs for the general population except incinerator workers were less than 4 pg WHO-TEQ kg(bw)$^{-1}$ day^{-1} (Fig. 2.15). In particular, average EDIs for individuals of general population ranged from 0.37 pg TEQ kg(bw)$^{-1}$ day^{-1} to 2.21 pg TEQ kg(bw)$^{-1}$ day^{-1} with a mean of 1.21 pg TEQ kg(bw)$^{-1}$ day^{-1}. These EDIs were predicted using PCDDs/DFs residues alone and I-TEQ basis. Considering that coPCB can contribute as much as 70% of the concentration of PCDDs/DFs observed in South Korean human tissues, average EDI is expected to be about 2 pg WHO-TEQ kg(bw)$^{-1}$ day^{-1}. This is greater than the average ADI (i.e., 1.32 pg WHO-TEQ kg(bw)$^{-1}$ day^{-1}) of dietary intake that had been estimated previously. However, if longer half-lives ($h_{1/2}$) are applied in the Eq. (1), the average EDI including coPCBs will would be less than 2 pg WHO-TEQ kg(bw)$^{-1}$ day^{-1}. Half-life of the TCDD (ca., 7 yr) was used in the present study but those of other congeners are generally 2- to 100-fold longer than TCDD (Geyer et al., 2002). Based on the ADIs and EDIs estimated here, the general South Korean population with an average body weight of 60 kg is expected to ingest dioxin-like compounds of between 60 and 120 pg WHO-TEQ per day which is equivalent to the WHO limit of 1–2 pg WHO-TEQ kg(bw)$^{-1}$ day^{-1}. This exposure rate is within the range of other countries (Fig. 2.15).

Although the contribution of coPCBs to the ADI was greater than of that of PCDDs/DFs, concentrations in humans were relatively small. The likely reasons for this include relatively rapid excretion of coPCBs and

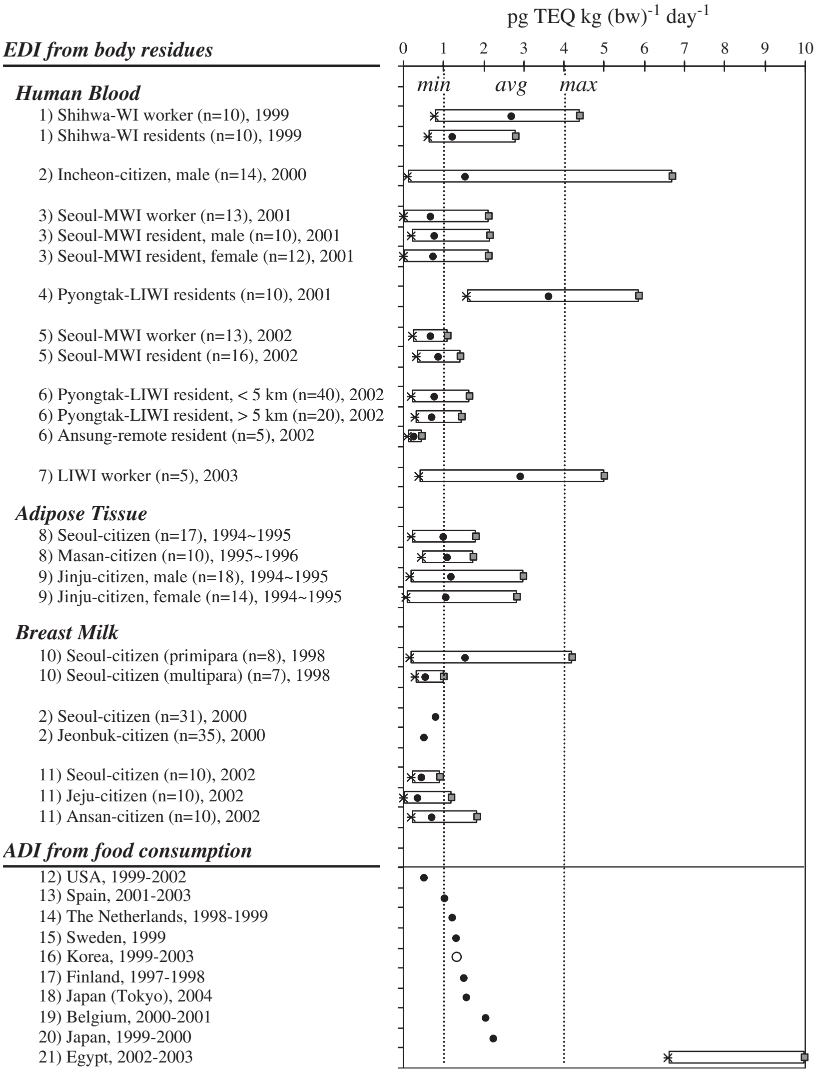


Fig. 2.15. EDI (Estimated Daily Intake) predicted from human body residues in Fig. 2.14 and ADI (Average Daily Intake) reported worldwide. ADI for Korean was predicted from average residues of individual food-groups in Table 2.7: (1)–(11) in Fig. 2.14, (12) Charnley and Doull (2005), (13) Bocio and Domingo (2005), (14) Baars et al. (2004), (15) Darnerud et al. (2006), (16) this study, (17) Kiviranta et al. (2004), (18) Sasamoto et al. (2006), (19) Focant et al. (2002), (20) Tsutsumi et al. (2001), (21) Loutfy et al. (2006). Two dotted lines indicate tolerable daily intake (TDI) guidelines of WHO.

change of chemical status during cooking. In 1997 the KFDA established 4 pg I-TEQ kg(bw)$^{-1}$ day^{-1} as a guideline for the TDI. In 2005, the committee for dioxin risk assessment, joined by five governmental ministries (Ministry of Environment, Ministry of Agriculture and Forestry, Ministry of Maritime Affairs and Fishery, Rural Development Administration, and South Korea Food and Drug Administration), set a plan to establish EQGs for individual environmental compartment and a new TDI on the basis of domestic contamination and exposure levels. Through this plan, uncertainties in exposure assessment are expected to decrease.

2.5.2. PCBs

Among the POPs reviewed, the PCBs were found to be one of the most intensively studied compounds following PCDDs/DFs. PCBs are one of the classical POPs and have been detected in various environmental media for over the last 30 years worldwide. In South Korea, despite the ban in 1970s on the use of PCBs, these compounds were detected in various environmental samples including air, sediment, and aquatic organisms (Table 2.10). In the earlier stages (viz. mid-1990s) of POPs study, efforts had been focused on the coastal contamination (mainly coastal sediments) (Khim et al., 1999b; Lee et al., 2001a). However, later studies have monitored air, water, freshwater-, brackish-, marine-sediments, and aquatic organisms.

2.5.2.1. Environmental levels

Compared to sediment and aquatic organisms, little is known about concentrations of PCBs in the atmosphere of South Korea. Concentrations of total PCBs (gas + particle phase) in the air of Ansung City ranged from 0.02 to 0.26 ng m^{-3}, with a mean of 0.07 ng m^{-3}. Gas phase PCBs accounted for approximately 90% of the total concentration of PCBs, showing that atmospheric PCBs predominantly existed in the gas phase.

As for sediment, various sites from the inland rivers, lakes, and bays have been investigated since the mid-1990s (Table 2.10). Total PCBs concentrations measured in freshwater sediments ($n = 64$) ranged from less than 1.0 to 141 ng g^{-1} dw, with a mean range of between 10.5 and 38.5 ng g^{-1} dw for individual regions. Brackish sediment collected from Lake Shihwa contained detectable concentration of PCBs in the survey of 1996 (mean = 12.5 ng g^{-1}, dw; $n = 4$) and 1998 (mean = 4.37 ng g^{-1}, dw; $n = 11$). Lake Shihwa is an artificial lake created by the construction of 12.7 km of sea dike in 1994. In contrast to the limited reports on PCBs in

Table 2.10. Concentrations of total PCBs in the various environmental media in South Korea

Sampling				No. of isomers	Total PCBs			References
Samples	From	Year	*n*		Min	Max	Mean	
Air					ng m^{-3}			
Gas/particles								
Inland (gas)	Ansung (rural)	2001–2002	28	24	0.02	0.23	0.06	Yeo et al., 2003
Inland (particle)	Ansung (rural)	2001–2002	28	24	0.0004	0.03	0.01	Yeo et al., 2003
Soil					ng g^{-1}, dw			
Urban soil	Seoul	2001	6	20	6.5	12.4	9.8	Kim, 2004
Water					ng L^{-1}			
Freshwater	Han River, Seoul	2001–2003	15	105	0.427	3.27	1.353	Kim, 2004
	Wastewater, Incheon	1998	1	105	–	–	27.18	Kim et al., 2000a
	Saltwater, Incheon	1998	3	105	0.89	11.11	6.16	Kim et al., 2000a
Sediment					ng g^{-1}, dw			
Freshwater sediment								
Westward	2 Rivers, Shihwa	2000	8	98	9.00	122	30.3	Koh et al., 2005
	1 River, Han river	2001–2002	25	104	1.76	68	17.3	Kim, 2004
Southward	3 Rivers, Masan	2000	8	98	8.49	92.0	38.5	Koh et al., 2005
	1 River, Busan	1999	18	43	1.10	141	18.7	Jeong et al., 2001d
Eastward	2 Rivers, Onsan	1999	8	98	1.00	56.2	15.2	Koh et al., 2002
	3 Rivers, Ulsan	1999	14	98	0.56	52.2	10.5	Khim et al., 2001
	1 River, Pohang	2000	8	98	1.00	141	31.7	Koh et al., 2004
Brackish sediment								
West coast	Shihwa lake	1996	4	101	2.71	27.9	12.5	Lee et al., 2001a
	Shihwa lake	1998	11	98	1.00	12.3	4.37	Khim et al., 1999a

Marine sediment								
West coast	Incheon Harbor	1995	7	101	10.7	580	146	Lee et al., 2001a
	Incheon Harbor	1998	21	95	0.35	1093	133	Kim et al., 2000a
	Gyeonggi Bay	1995	47	101	0.39	10.2	3.12	Lee et al., 2001a
	Namyang Bay	1996	5	101	0.99	2.45	1.45	Lee et al., 2001a
South coast	Masan Bay	1997	20	22	1.24	41.4	15.0	Hong et al., 2003b
	Masan Bay	1998	28	98	6.94	148	36.0	Khim et al., 1999b
	Gwangyang Bay	2001	11	98	1.00	4.53	1.32	Koh et al., 2005
East coast	Onsan Bay	1999	14	98	1.00	13.0	3.31	Koh et al., 2002
	Ulsan Bay	1999	16	98	1.00	76.7	17.6	Khim et al., 2001
	Yeongil Bay	2000	26	98	1.00	32.3	3.93	Koh et al., 2006
Korean coasts	3 Coastal bays	1996–1998	6	134	10.0	140	40.8	Oh et al., 2003
	27 Coastal areas	2000	138	22	0.09	199	9.17	Hong et al., 2006
Open sea	Yellow Sea	2000	23	21	0.17	1.37	0.69	Oh et al., 2005b
Organism					ng g^{-1}, dw			
Freshwater fish								
Korean coasts	10 Rivers	2002	20	28	0.37	20.0	5.84	Moon et al., 2006
Saltwater fish								
Korean coasts	19 Coastal areas	1997	33	22	31.0	630	85.2	Yim et al., 2005
Bivalvia								
West coast	Incheon harbor	1998	12	95	49.0	422	228	Kim et al., 2002e
	10 Coastal areas	1990–1999	12	134	7.78	394	56.5	Oh et al., 2003
	17 Coastal areas	1997–1999	34	104	4.40	422	94.1	Kim et al., 2002b
South coast	Gwangyang bay	1998	9	98	32.3	162	72.7	Khim et al., 2000
	Masan bay	1998	9	98	64.2	313	134	Khim et al., 2000
	Busan bay	1998	5	98	63.6	407	185	Khim et al., 2000
	7 Coastal areas	1987–1999	21	134	2.83	389	93.9	Oh et al., 2003
	10 Coastal areas	1999	19	104	7.30	184	67.5	Kim et al., 2002b
East coast	Ulsan bay	1998	11	98	60.6	547	176	Khim et al., 2000
	6 Coastal areas	1999	13	104	5.30	170	54.2	Kim et al., 2002b
	10 Coastal areas	1990–1999	24	134	3.67	456	79.1	Oh et al., 2003

freshwater ($n = 64$) and brackish sediments ($n = 15$), a relatively large number of samples of coastal marine sediment ($n = 362$) have been analyzed. The maximum concentration of total PCBs in marine sediment was detected in Incheon Harbor, which had a concentration of 1090 ng g^{-1} dw in 1998 (Kim et al., 2000a). A recent study by Hong et al. (2006) reported total PCBs concentrations at 138 sites along the South Korean coasts to range from 0.09 to 199 ng g^{-1} dw (mean = 9.17). Overall, mean concentrations of total PCBs in coastal marine sediments in South Korea ranged from several to several tens of ng g^{-1} dw. Considering the detectable concentrations of total PCBs (0.17–1.37 ng g^{-1} dw) at the offshore sites in the Yellow Sea, widespread contamination is evident even in open seas.

Several studies have reported concentrations of PCBs in aquatic organisms such as freshwater fish ($n = 20$), saltwater fish ($n = 33$), and bivalves ($n = 169$) (Table 2.10). Total PCBs concentrations in aquatic organisms were generally within the range of those in sediments, with a mean of 5.84–228 ng g^{-1} dw. Among the biota samples analyzed from various sites, Incheon Harbor contained the greatest total PCBs (228ng g^{-1} dw), where a highest level of PCBs was also detected in the sediment in 1998 (Kim et al., 2000a). Overall, total PCBs concentrations in aquatic organisms in South Korea were comparable to or greater than those (mostly several ng g^{-1} dw levels) reported for developing countries in Asia (Monirith et al., 2003).

2.5.2.2. Sources and distribution

The homologue pattern of PCBs found in sediment from the various sites in South Korea suggests the source is technical mixtures such as Aroclors 1016, 1242, 1254, and 1260 or corresponding Kanechlor products. Lesser chlorinated CBs such as tri-, tetra-, and penta-CBs were the major PCB congeners found in freshwater sediments ($n = 64$) accounting for about 21%, 24%, and 20% of total PCBs, on average, respectively (Fig. 2.16). The predominant CBs shifted to more chlorinated congeners in marine sediments ($n = 195$); 27% penta-, 22% tetra- and 20% hexa-CBs (Fig. 2.16). This indicates that different sources could influence freshwater and marine environments. Based on a study of sources of PCBs, that the South Korean environment is contaminated by mixtures of products with various chlorine contents dominated by Aroclor 1254 in Incheon, Aroclor 1242 in Masan, Aroclor 1260 (or Kanechlor-600) in Ulsan, and Aroclor 1242 in the Han River (Kim et al., 2000a, 2002b; Kim, 2004; Hong et al., 2006). Thus, the type of PCBs that contaminated the marine environments is likely to depend on specific activities in the individual

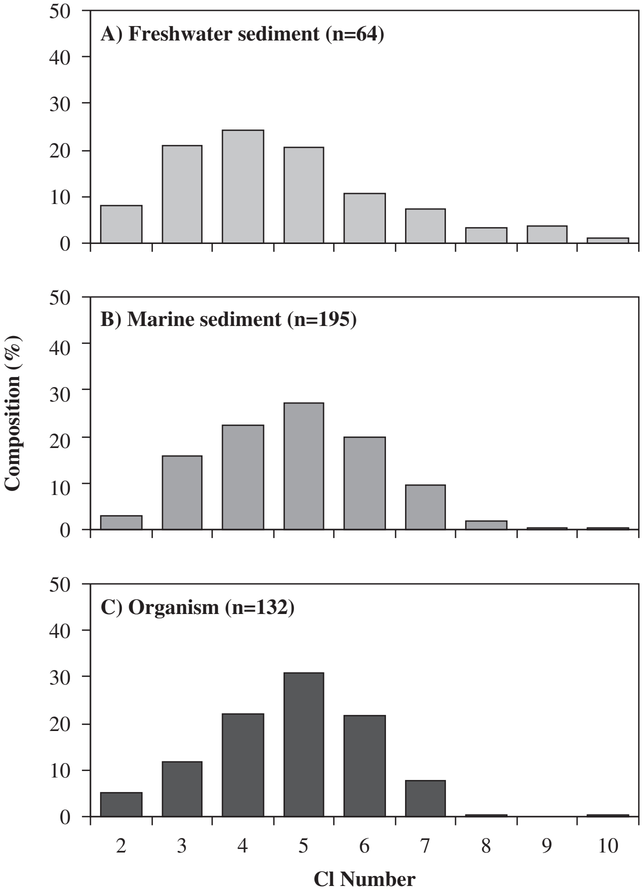


Fig. 2.16. Homolog composition (mean%) of polychlorinated biphenyls (PCBs) in (A) freshwater sediment ($n = 64$), (B) marine sediment ($n = 195$), and (C) organism ($n = 132$), from South Korea.

coastal area. CBs homologue of biota samples showed very strong correlation ($r^2 = 0.96$, $p < 0.05$) with that of sediment, reflecting bioaccumulation of sedimentary PCBs into aquatic organisms (Fig. 2.16).

Among 21 published reports of concentrations of PCBs in sediments (Table 2.10), Masan inland (mean = 38.5 ng g^{-1} dw, $n = 8$, 2000) and Incheon Harbor (mean = 146 ng g^{-1} dw, $n = 7$, 1995) were identified as the most contaminated areas for freshwater and marine sediments, respectively. PCBs in freshwater sediments from six areas exceeded ERL for total PCBs (22.7 ng g^{-1}, dw). However, the concentrations of sediment

PCBs from any of the stations ($n = 65$) did not exceed the ERM (180 ng g^{-1}, dw). PCBs were reported to be mostly less than ERL for total PCBs in the brackish sediments from the Shihwa lake in 1996 ($n = 4$) and 1998 ($n = 11$). PCBs in marine sediments reported from the South Korean coasts showed relatively great variations in terms of concentration and congener distribution (Fig. 2.17). Along the South Korean coasts, several hot spots were found in which concentrations were greater than the ERM for total PCBs. This was particularly true in Incheon Harbor, near the capital city of Seoul. However, the contamination level in several bays including the Onsan, Gyeonggi, Gwangyang, Namyang bays, and Yellow Sea did not contained concentrations that exceeded ERL for total PCBs. Overall, the concentrations of sedimentary PCBs in the inland rivers and bay areas were comparable. Their spatial distribution indicated the presence of the localized zones of extremely great concentrations (hot spots).

2.5.3. OC pesticides

During the past several decades, contamination of the environment by OCPs has been of great concern worldwide, due to their persistent, ubiquitous, and biologically harmful properties. Although their production and use had mostly been banned since the 1970s (Fig. 2.9), OCPs are still found in various environmental samples and widely distributed along the coasts of South Korea (Table 2.11). Studies investigating the environmental concentrations and distribution of OCPs have increased in the last 10 years, for both inland areas and coastal environment. In these studies, the environmental concentrations of OCPs (HCB, HCHs, CHLs, and DDTs) were reported for various environmental samples including air ($n = 36$), soil ($n = 10$), sediment ($n = 397$), and aquatic organism ($n = 133$) in South Korea.

2.5.3.1. Environmental concentrations

Little is known about concentrations of OCPs in the atmosphere over South Korea. Two studies reported concentrations of HCHs, CHLs, and DDTs in air over the cities of Seoul ($n = 19$) and Ansung ($n = 17$) in 1990–2000 (Yeo et al., 2004b). The mean concentration of total OCPs in air from Ansung (2.00 ng m^{-3}) was approximately three times greater than that in Seoul (0.71 ng m^{-3}). Among the atmospheric OCPs, HCHs were the greatest level, accounting for $>80\%$ of the total OCPs.

Total OCPs detected in soil ($n = 10$) from Jeonbuk province ranged from 1.57 to 52.9 ng g^{-1} dw, with a mean concentration of 27.8 ng g^{-1} dw (Kim and Smith, 2001). OCPs in sediments were reported for various sites

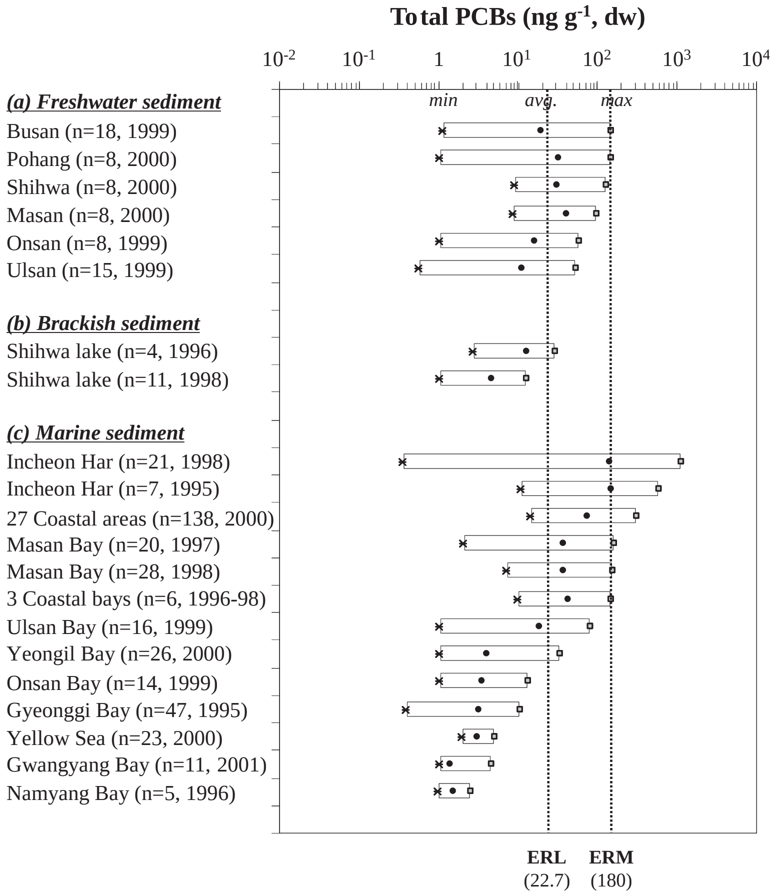


Fig. 2.17. Comparison of measured levels and sediment quality guidelines (SQGs) for total polychlorinated biphenyls (PCBs) in sediments from the various sites, in South Korea; (a) freshwater ($n = 64$), (b) brackish ($n = 15$), and (c) marine sediments ($n = 362$). Range indicates minimum (min), maximum (max), and arithmetic mean (avg.). Dotted lines represent SQGs of effect range low (ERL) and effect range median (ERM) for total PCBs (Long et al., 1995).

in inland ($n = 47$), lake ($n = 15$), and coastal bay ($n = 335$) areas since 1995 (Table 2.11). Total OCPs concentrations measured in freshwater sediments ($n = 47$) ranged from 0.04 to 47.0 ng g^{-1} dw, with a regional mean of 1.24–12.7 ng g^{-1} dw. Concentrations of OCPs such as HCB, HCHs, CHLs, and DDTs in 1996 ($n = 4$) and 1998 ($n = 11$) were measured in 15 sediment samples from Lake Shihwa. Mean concentrations of total OCPs in Lake Shihwa were comparable between 1996

Table 2.11. Concentrations of organochlorine pesticides (OCPs) in various environmental media in Korea

Sampling				HCB	HCHs	CHLs	DDTs	Total OCPs			References
Samples	From	Year	*n*	Mean				Min	Max	Mean	
Air				ng m^{-3}				ng m^{-3}			
Gas/particles											
Inland (*G*+*P*)	Seoul (urban)	1999–2000	19	–	0.27	0.01	0.04	0.05	4.14	0.71	Yeo et al., 2004b
Inland (*G*+*P*)	Ansung (rural)	1999–2000	17	–	0.22	0.04	0.06	0.04	15.7	2.00	Yeo et al., 2004b
Soil and sediment				ng g^{-1}, dw				ng g^{-1}, dw			
Soil											
Inland	Jeonbuk	1996	10	–	1.49	25.6	0.09	1.57	52.9	27.8	Kim and Smith, 2001
Freshwater sediment											
Westward	2 Rivers, Shihwa	2000	8	1.13	2.74	0.06	0.55	0.89	16.6	4.49	Koh et al., 2005
Southward	3 Rivers, Masan	2000	8	0.30	11.2	0.09	1.09	0.36	46.9	12.7	Koh et al., 2005
Eastward	2 Rivers, Onsan	1999	8	1.00	0.62	0.17	1.61	0.09	6.44	3.28	Koh et al., 2002
	3 Rivers, Ulsan	1999	15	0.23	0.28	0.17	0.21	0.04	5.81	1.24	Khim et al., 2001
	1 River, Pohang	2000	8	0.50	6.36	0.04	0.43	0.35	47.0	7.32	Koh et al., 2004
Brackish sediment											
West coast	Shihwa lake	1996	4	0.18	1.07	0.37	1.34	0.88	6.55	2.96	Lee et al., 2001a
	Shihwa lake	1998	11	1.31	0.18	0.02	1.28	1.04	5.47	2.80	Khim et al., 1999a

Marine sediment											
West coast	Incheon harbor	1995	7	1.52	0.67	29.6	12.4	3.68	167	44.2	Lee et al., 2001b
	Gyeonggi bay	1995	47	0.05	0.44	0.25	0.82	0.10	6.75	1.56	Lee et al., 2001b
	Namyang bay	1996	5	0.02	0.46	0.25	0.34	0.14	1.72	1.07	Lee et al., 2001b
South coast	Gwangyang bay	2001	11	0.08	0.25	0.01	0.07	0.10	0.99	0.42	Koh et al., 2005
	Masan bay	1997	20	0.13	0.26	0.65	16.0	0.84	97.9	18.1	Hong et al., 2003b
	Masan bay	1998	28	0.62	0.30	0.09	3.45	1.14	14.6	4.46	Khim et al., 1999b
East coast	Onsan bay	1999	14	0.15	0.21	0.02	0.43	0.07	2.81	0.78	Koh et al., 2002
	Ulsan bay	1999	16	0.05	0.35	0.08	2.99	0.14	20.2	4.21	Khim et al., 2001
	Yeongil bay	2000	26	0.03	1.07	0.08	0.52	0.05	13.8	1.70	Koh et al., 2006
Korean coasts	27 Coastal areas	2000	138	0.14	0.65	0.37	6.64	0.06	161	8.31	Hong et al., 2006
Open sea	Yellow Sea	2000	23	0.16	1.17	0.06	0.48	0.38	7.75	1.97	Oh et al., 2005
Organism				ng g^{-1}, dw				ng g^{-1}, dw			
Saltwater fish											
Korean coasts	19 Coastal areas	1997–2001	33	1.19	3.48	4.07	33.2	6.96	129	41.9	Yim et al., 2005
Bivalvia											
West coast	17 Coastal areas	1997–1999	34	–	7.09	8.49	33.0	9.59	128	48.6	Kim et al., 2002b
South coast	Yeosu	1998	9	0.46	1.80	0.31	23.5	10.0	64.3	26.0	Khim et al., 2000
	Masan	1998	9	1.44	1.99	1.69	46.0	16.7	114	51.1	Khim et al., 2000
	Pusan	1998	5	0.77	2.71	1.91	59.4	26.9	112	64.8	Khim et al., 2000
	10 Coastal areas	1999	19	–	5.29	2.52	19.1	8.81	61.8	26.9	Kim et al., 2002b
East coast	Ulsan	1998	11	3.28	2.83	1.69	23.5	12.0	101	31.4	Khim et al., 2000
	6 Coastal areas	1999	13	–	5.56	5.70	29.3	12.8	97.4	40.6	Kim et al., 2002b

(2.96 ng g^{-1} dw) and 1998 (2.80 ng g^{-1} dw), suggesting persistence of OCPs in environments. In contrast to the small number of reports on OCPs in inland and lake areas ($n = 62$), since 1995 there has been a large number of sites that have been investigated for concentrations of OCPs in sediments of bays ($n = 335$) along the South Korean coasts as well as the open sea. Concentrations of total OCPs varied greatly among locations, depending on sampling stations and/or areas ranging from 0.42 to 44.2 ng g^{-1} dw of regional mean concentrations. Total OCPs concentrations in marine sediments were comparable to those detected in freshwater and brackish sediments, however, the composition of HCB, HCHs, CHLs, and DDTs to total OCPs varied greatly among samples.

Several studies have reported OCPs concentrations in aquatic organisms such as saltwater fishes ($n = 33$) and bivalves ($n = 100$) along the South Korean coasts since 1997 (Table 2.11). Total OCPs concentrations in aquatic organisms were found to range from 26.0 to 64.8 ng g^{-1} dw, and the mean concentrations of OCPs were generally 10-fold greater than those in sediments. In sediments, DDTs represented the greatest portion (52%) of the total OCPs in sediment. Similarly, in aquatic organisms the DDTs were the prevalent measured. Overall, total OCPs detected in aquatic organisms in South Korea were within the range of OCPs reported from the developing countries in Asia (Monirith et al., 2003).

2.5.3.2. Sources and distribution

The contribution of individual OCPs to the total OCPs varied among environmental media (air, soil, sediment, and organism) (Fig. 2.18). The relative abundance of OCPs in air samples was found to be in the order of endosulfan (77%) > HCHs (18%) > DDTs (3.7%) > CHLs (1.6%). The large abundance of endosulfan in air samples could be explained by its usage, duration used in the past and chemical properties (Yeo et al., 2004b). The composition of OCPs in soil, freshwater, and coastal marine sediment samples were predominated by CHLs (92%), HCHs (72%), and DDTs (> 50%), respectively. The OCPs composition of soil was significantly different from that of sediment. The disparity indicates that OCPs contamination in marine environments is likely to be contaminated by potential coastal sources themselves rather than by transport of contaminants from inland sources. It should be noted that the relative composition of OCPs in aquatic organisms was similar to that found in marine sediment, which indicates the accumulation of contaminants in the body of organisms and sediment from water column via similar mechanisms (Fig. 2.18).

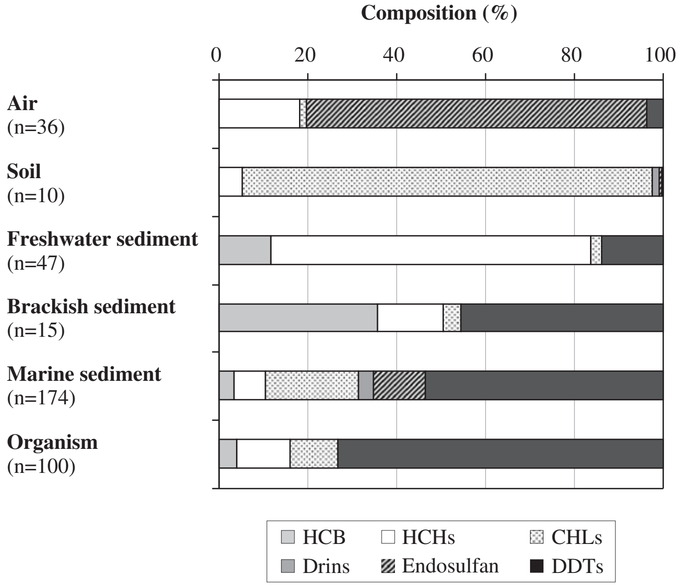


Fig. 2.18. Composition (mean%) of individual organochlorine pesticides (OCPs; HCB, HCHs, CHLs, Drins, Endosulfan, and DDTs) relative to total OCPs, detected in the various environmental media (air, soil, freshwater, brackish, marine sediments, and organism; no. of samples are in parenthesis) from the South Korea.

Inland soil collected from Jeonbuk province showed the OCPs concentrations as great as 52.9 ng g^{-1}, with a mean of 27.8 ng g^{-1}. The mean concentration was significantly greater than that in sediment (6.76 ng g^{-1}). Among 18 datasets concentrations of OCPs in sediments of South Korea (Table 2.11), Masan inland (mean = 12.7 ng g^{-1} dw, $n = 8$, 2000) and Incheon Harbor (mean = 44.2 ng g^{-1} dw, $n = 7$, 1995) were identified as the most contaminated areas with total OCPs for freshwater and marine sediments, respectively. These areas were found to be the most contaminated areas by PCBs as well, indicating a close relationship between PCBs and OCPs sources in Masan and Incheon areas. A correlation of the spatial distribution was frequently observed between the concentrations of PCBs and major OCPs such as DDTs and CHLs (Kim et al., 2002b; Hong et al., 2006). Intensive industrial and municipal activities near the cities of Masan and Incheon would cause the level of contamination by classical POPs such as PCBs and OCPs. Relatively low OCPs contamination has been found in the areas of Gwangyang (steel manufacturing, mean = 0.42 ng g^{-1}, $n = 11$, 2001) and Onsan Bay (non-ferrous metal manufacturing, mean = 0.78 ng g^{-1}, $n = 14$, 1999). The degree

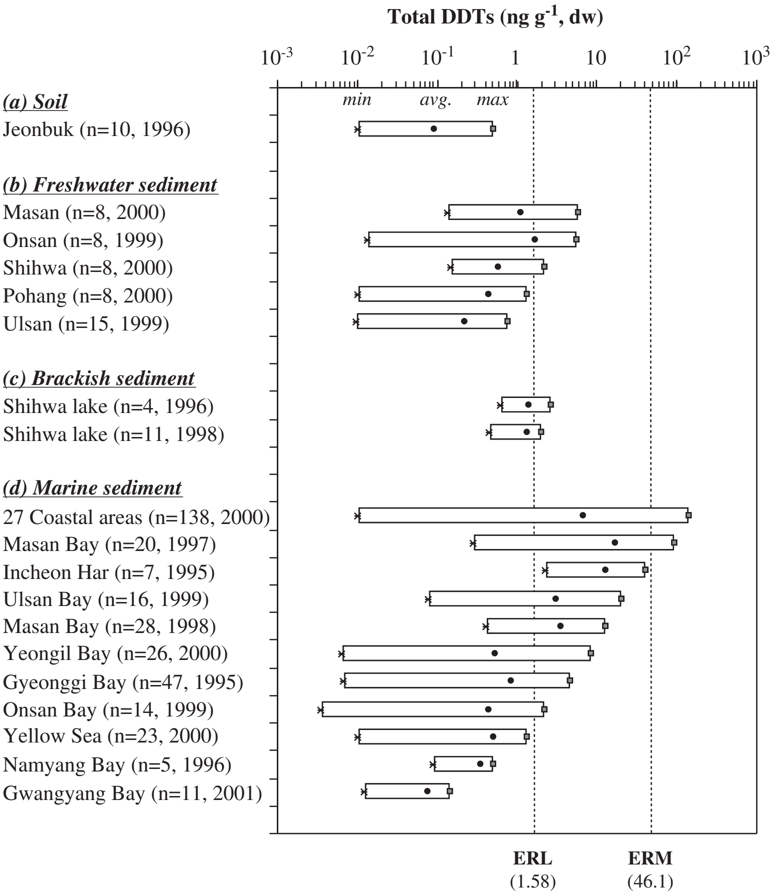


Fig. 2.19. Comparison of measured levels and sediment quality guidelines (SQGs) for total DDTs in soil and sediments from the various sites, in South Korea; (a) soil ($n = 10$), (b) freshwater ($n = 47$), (c) brackish ($n = 15$), and (d) marine sediments ($n = 335$). Range indicates minimum (min), maximum (max), and arithmetic mean (avg.). Dotted lines represent SQGs of effect range low (ERL) and effect range median (ERM) for total DDTs (Long et al., 1995).

of contamination of the South Korean coastal environment showed an existence of the clear but localized sources and distribution.

Among the OCPs, DDTs, CHLs, and γ-HCH (lindane) were found to be the most contaminated OCPs present in Korean sediments (Fig. 2.19). Out of 18 datasets examined ($n = 407$), 13, 10, and 9 of the total sites contained the concentration that exceeded the corresponding threshold effect concentrations such as ERL or TEL for total DDTs, total CHLs, and γ-HCH, respectively. DDTs were found to be widespread OCPs contaminants across the inland and coastal-marine areas, accounting for $>50\%$ of the total OCPs both in sediment and aquatic organisms. Inland soils and sediments contained relatively low total DDTs over ERL (1.58 ng g^{-1}) at some stations but mostly below ERM (46.1 ng g^{-1}). Contrarily, in most coastal bay areas (8 out of 11 areas), the contamination level exceeded the ERL for total DDTs and even the ERM was exceeded at some sites. In spite of lower level than DDTs, CHLs showed the similar distribution spatially with DDTs. By contrast, γ-HCH was the most contaminated OCPs in the inland areas and distributed relatively evenly in marine areas. None of the site exceeded the SQGs of low apparent effects threshold (22 ng/g, dw) for HCB. Overall, the concentration and distribution of OCPs in Korean sediments reflected the widespread distribution with some localized hot spots of considerably great concentrations.

2.5.4. PAHs

Many of PAHs are known to be mutagenic and/or carcinogenic (Neff, 1979). Coke production, combustion of fossil fuels, chemical production, and oil spills are the potential sources of PAHs. In recent studies on PAHs, these compounds were found to be one of the prevalent organic contaminants in South Korean sediments (Kim et al., 1999b; Koh et al., 2002). However, compared to the reports on the classical POPs such as PCBs and OCPs, little is known about the degree of PAHs contamination in the South Korean environment, except for soil and sediments (Table 2.12). A total of 28 datasets reporting total concentrations of PAHs in South Korean samples, by sampling area, were found in the literature where total PAHs in air ($n = 70$), soil ($n = 232$), water ($n = 25$), and sediment ($n = 281$) were reported.

2.5.4.1. Environmental levels

A few studies reported total PAHs (gas + particle phase) in air in Seoul City during 1999–2002 and found concentrations between 9.10 and 350 ng m^{-3}, with a regional mean of 35.6–89.3 ng m^{-3} (Park et al., 2002b; Kim, 2004). Relatively great concentrations of atmospheric PAHs during winter were ascribed to increased fuel consumption, the lower mixing height and low air temperature.

A comprehensive study on total PAHs in soil from inland areas have been reported by Nam et al. (2003) through a survey of 226 sites in South Korea. Mean concentrations of total PAHs in soil from 6-areas were

Table 2.12. Concentrations of total PAHs detected in the various environmental media in South Korea

Sampling				No. of PAHs	Total PAHs			References
Samples	From	Year	*n*		Min	Max	Mean	
Air						ng m^{-3}		
Gas/particles								
Inland (*G*+*P*)	Seoul (urban)	1999	24	12	11.3	350	89.3	Park et al., 2002b
Inland (*G*+*P*)	Seoul (urban)	2001–02	5	24	11.4	81.0	44.3	Kim, 2004
Inland (*G*+*P*)	Seoul (suburban)	2001–02	5	24	9.10	70.3	35.6	Kim, 2004
Inland (P alone)	Seoul	1992–94	36	20	7.74	265	61.1	Panther et al., 1999
Water						ng g^{-1}, dw		
Freshwater								
Inland	Han River, Seoul	2001–03	15	15	13.44	75.73	43.03	Kim, 2004
Soil and sediment						ng g^{-1}, dw		
Soil								
Inland	Seoul (urban)	2001	3	24	791	1729	1175	Kim, 2004
	Seoul (suburban)	2001	3	24	874	1073	999	Kim, 2004
	Seoul-Gyeonggi	$<$2002	61	16	32.0	1057	257	Nam et al., 2003

	Gwangwon	<2002	50	16	43.0	1852	271	Nam et al., 2003
	Gyeongbuk	<2002	24	16	43.0	623	199	Nam et al., 2003
	Gyeongnam	<2002	31	16	41.0	336	171	Nam et al., 2003
	Jeolla	<2002	45	16	23.0	303	118	Nam et al., 2003
	Pohang	<2002	15	16	105	2833	578	Nam et al., 2003
Freshwater sediment								
Westward	2 Rivers, Shihwa	2000	8	16	8.61	643	224	Koh et al., 2005
	1 River, Seoul	2001–02	25	24	173	1721	858	Kim, 2004
Southward	3 Rivers, Masan	2000	8	16	16.3	481	212	Koh et al., 2005
Eastward	2 Rivers, Onsan	1999	8	16	1.00	573	128	Koh et al., 2002
	3 Rivers, Ulsan	1999	14	16	9.46	1373	265	Khim et al., 2001
	1 River, Pohang	2000	8	16	5.88	7685	1282	Koh et al., 2004
Brackish sediment								
West coast	Shihwa lake	1998	11	16	<1.00	31.4	11.4	Khim et al., 1999a
Marine sediment								
West coast	Han River mouth	1995	16	24	28.8	229	86.5	Kim et al., 1999b
	Incheon Harbor	1995	19	24	13.1	1430	272	Kim et al., 1999b
	Gyeonggi Bay	1995	31	24	9.54	167	53.1	Kim et al., 1999b
South coast	Gwangyang Bay	2001	11	16	10.5	105	36.8	Koh et al., 2005
	Masan Bay	1998	28	16	41.5	1102	353	Khim et al., 1999b
East coast	Onsan Bay	1999	12	16	1.00	50.6	21.6	Koh et al., 2002
	Ulsan Bay	1999	16	16	19.7	3095	409	Khim et al., 2001
	Yeongil Bay	2000	26	16	1.00	1872	227	Koh et al., 2006

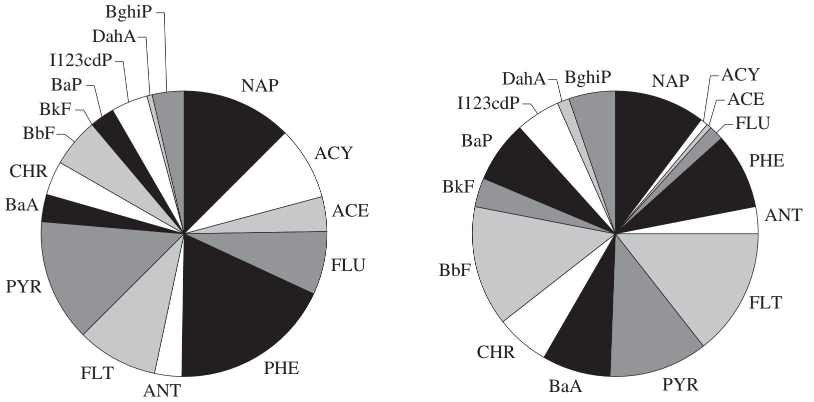
found to be 257 (Seoul-Gyeonggi, $n = 61$), 271 (Gwangwon, $n = 50$), 199 (Gyeongbuk, $n = 24$), 171 (Gyeongnam, $n = 31$), 118 (Jeolla, $n = 45$), and 578 ng g^{-1} dw (Pohang, $n = 15$), respectively. The greatest concentration (2833 ng g^{-1} dw) of total PAHs in soil was found in the Pohang area near a large scale steel manufacturing plant. This spatial distribution is consistent with information of emission sources of PAHs described earlier that a major source of PAHs is coke oven from metal industries. The distribution of total PAHs found in soil samples were primarily of pyrogenic origins such as heavy industry emission and motor vehicle exhaust in South Korea.

Since 1995, concentrations of PAHs have been reported for various sites along the South Korean coasts. Concentrations of total PAHs measured in freshwater sediment ($n = 71$) varied greatly with sampling station, ranging from 1.00 to 7685 ng g^{-1} dw, with regional means of 128–1282 ng g^{-1} dw at the sites. Relatively small concentrations have been found in Lake Shihwa sediment with a mean of 11 ng g^{-1} dw of total PAHs. Many studies reported the sedimentary PAHs in coastal bay areas, and their total PAHs (mean = 266 ng g^{-1}, dw, $n = 226$) were similar to those measured in soil samples (mean = 255 ng g^{-1}, dw, $n = 216$). The maximum concentration (3095 ng g^{-1} dw) of total PAHs in marine sediments was found in Ulsan Bay near a shipbuilding area.

2.5.4.2. Sources and distribution

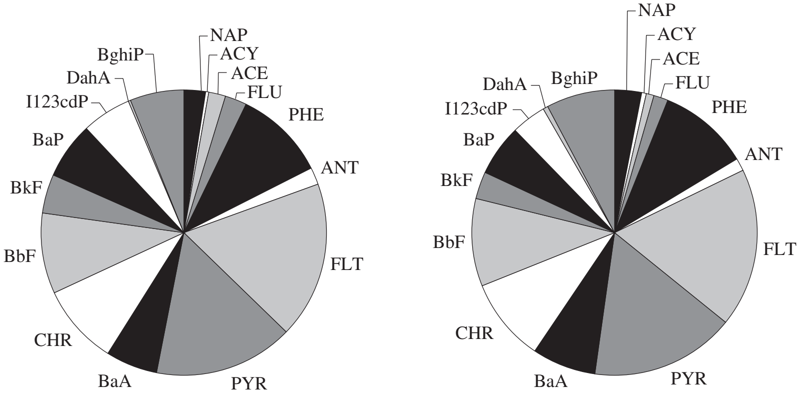
The relative contributions of the 16 individual indicator PAHs to the total concentration of PAHs in air samples significantly differed from soil or sediment samples (Fig. 2.20). Low molecular weight PAHs (L-PAHs) such as 2-3 ring aromatic hydrocarbons (NAP, ACY, ACE, FLU, PHE, and ANT) were predominant in air samples, accounting for >50% of total PAHs. This is attributable to the contribution of gaseous L-PAHs of greater volatilities. Particle-associated PAH composition is similar to those of soil and sediment. This is not only because their low volatility but dry/wet deposition of particulate PAHs plays a significant role as source to underlying soils. H-PAHs such as 4-5 ring aromatic hydrocarbons (FLT, PYR, BaA, CHR, BbK, BkF, BaP, and DahA) accounted for ca. 70% of total PAHs detected in soil and sediment samples. A significant relationship in composition of PAHs was found between soil and river- ($r^2 = 0.65$, $p < 0.05$) or marine-sediments ($r^2 = 0.71$, $p < 0.05$), indicating their sources are closely related with each other. Furthermore, the strong correlation ($r^2 = 0.97$, $p < 0.05$) between river and marine sediments

Composition (%)



(a) Air
(n=24)

(b) Soil
(n=226)



(c) Freshwater sediment
(n=46)

(d) Marine sediment
(n=159)

Fig. 2.20. Composition (mean%) of 16 individual polycyclic aromatic hydrocarbons (PAHs) to total PAHs detected in various environmental media; in (a) air (*n* = 24), (b) soil (*n* = 226), (c) freshwater (*n* = 46), and (d) marine sediment (*n* = 159), from the South Korea. Naphthalene; NAP, Acenaphthylene; ACY, Acenaphthene; ACE, Fluorine; FLU, Phenanthrene; PHE, Anthracene; ANT, Fluoranthene; FLT, Pyrene; PYR, Benz[*a*]anthracene; BaA, Chrysene; CHR, Benzo[*b*]fluoranthene; BbF, Benzo[*k*]fluoranthene; BkF, Benzo[*a*]pyrene; BaP, Indeno[1,2,3,*c*,*d*]pyrene; I123cdP, Dibenz[*a*,*h*]anthracene; DahA, Benzo[*g*,*h*,*i*]perylene; BghiP.

reflected their widespread distribution from similar origins across the inland and coastal bay areas.

Because PAHs can originate from pyrogenic sources (combustion) as well as petrogenic origins (petroleum), the concentrations, distribution, and fate of PAHs in environment would vary with their sources. Several molecular ratios of specific hydrocarbons such as PHE/ANT, FLU/PYR, FLU/(FLU + PYR), CHR/BaA, and L-/H-PAHs have been used to characterize sources and origins (Budzinski et al., 1997; Baumard et al., 1998; Dickhut et al., 2000; Yunker et al., 2002). Analysis of such ratios for air, soil, and sediment samples in South Korea suggested that airborne and soil PAHs were mainly pyrogenic while the sources for sediment were from both pyrogenic and petrogenic origins. It is also noteworthy that the sites near urban and industrial areas received more pyrolytic inputs whereas the bay areas or downstream of rivers close to harbor places and/or shipping yards could be influenced by more of petrogenic inputs (not presented).

The distribution of total PAHs in soil and sediment samples was dependent on the land use types (Fig. 2.21). Among the six areas investigated for total PAHs in soil from South Korea, the industrial area such as that at Pohang showed the greatest concentrations of PAHs and the west plain area in Jeolla province where agricultural activities are dominant tended to show lower concentrations of PAHs. The greater concentrations of PAHs in freshwater sediment have been found in the inland area near Pohang, further supporting the conclusion that there are direct sources of PAHs input to this area. Only in the Pohang area existed a site of contamination exceeding the ERL for total PAHs (4022 ng g^{-1} dw). In no stations of other five areas, Seoul, Ulsan, Shihwa, Onsan, and Masan did exceed the corresponding ERL. Meanwhile, total PAHs in brackish sediment measured from Lake Shihwa contained the least concentrations of PAHs in South Korea. Although the contamination of PAHs in marine sediments showed a wide spatial variability, at none of the stations exceeded the ERL for total PAHs. Overall, distribution for PAHs in soil (266 ng g^{-1}, dw, $n = 226$), freshwater (514 ng g^{-1}, dw, $n = 81$), and marine sediment (182 ng g^{-1}, dw, $n = 159$) suggested the widespread contamination of PAHs across the inland and coastal bay areas in South Korea.

2.5.5. APs and BPA

Distributions of APs and BPA in South Korea have been studied since the late 1990s. Concentrations of APs and BPA have been measured in

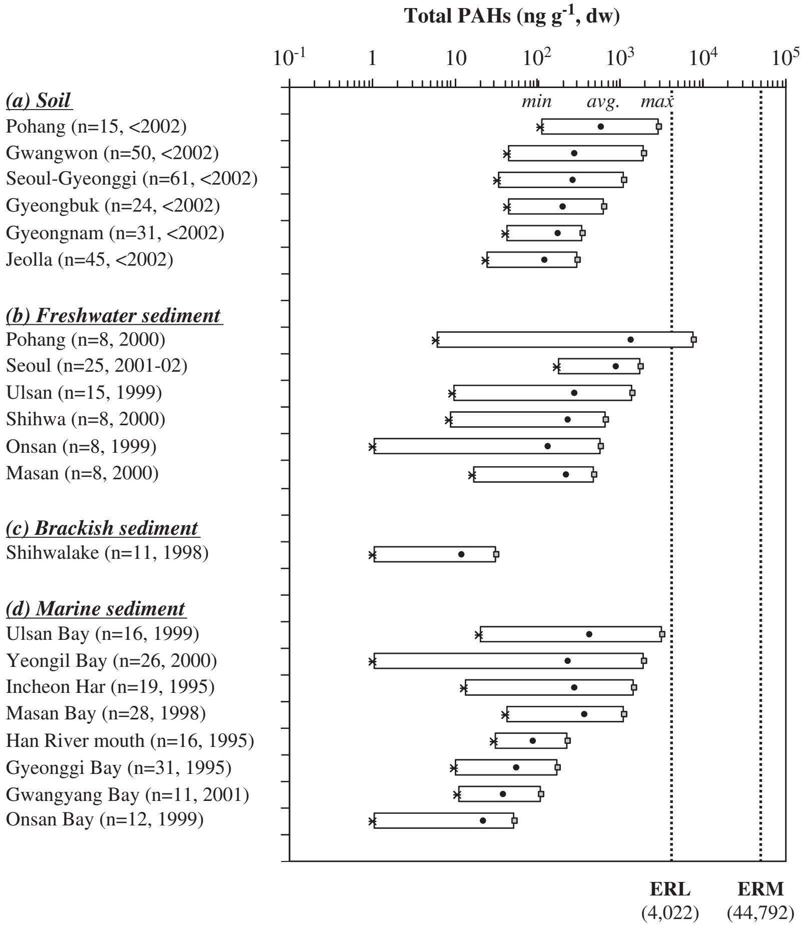


Fig. 2.21. Comparison of measured levels and sediment quality guidelines (SQGs) for total polycyclic aromatic hydrocarbons (PAHs) in soil and sediments from the various sites, in South Korea; (a) soil ($n = 226$), (b) freshwater ($n = 81$), (c) brackish ($n = 11$), and (d) marine sediments ($n = 159$). Range indicates minimum (min), maximum (max), and arithmetic mean (avg.). Dotted lines represent SQGs of effect range low (ERL) and effect range median (ERM) for total PAHs (Long et al., 1995).

water, suspended solids, and sediments in South Korea (Khim et al., 1999a, b, 2001; NIER, 2000a, 2001, 2002, 2003; Koh et al., 2002, 2005; Li et al., 2004a–c, 2005). NP was frequently detected and well reported compared to OP, BP, and BPA. Data available for these compounds are summarized in Table 2.13.

Table 2.13. Concentrations of alkylphenols (APs) and bisphenol A (BPA) in various environmental media in Korea

Sampling				Compounds measured	Total APs and BPA			References
Samples	From	Year	*n*		Min	Max	Mean	
Water						ng L^{-1}		
Freshwater								
Westward	Han river	1999	10	NP + OP + HP + PP + BPA	116	984	429	NIER, 2000a
		2000	10	NP + OP + BPA	30	1266	294	NIER, 2001
		2001	10	NP + BPA	<10	1203	298	NIER, 2002
		2002	13	NP + BPA	<10	432	96	NIER, 2003
Southward	Nakdong river	1999	10	NP + OP + HP + PP + BPA	190	874	367	NIER, 2000a
		2000	10	NP + OP + BPA	30	488	211	NIER, 2001
		2001	10	NP + BPA	<10	871	528	NIER, 2002
		2002	9	NP + BPA	<10	298	73	NIER, 2003
Westward	Geum river	1999	12	NP + OP + HP + PP + BPA	212	646	342	NIER, 2000a
		2000	6	NP + OP + BPA	38	87	67	NIER, 2001
		2001	6	NP + BPA	10	818	422	NIER, 2002
	.	2002	6	NP + BPA	<10	380	94	NIER, 2003
Southward	Yeongsan river	2000	6	NP + OP + BPA	20	377	187	NIER, 2001
		2001	6	NP + BPA	47	687	392	NIER, 2002
		2002	4	NP + BPA	<10	110	51	NIER, 2003
	Other rivers of lakes	1999	11	NP + OP + HP + PP + BPA	55	6340	1133	NIER, 2000a
		2000	11	NP + OP + BPA	20	1169	300	NIER, 2001
		2001	11	NP + BPA	<10	1742	511	NIER, 2002
		2002	11	NP + BPA	<10	432	104	NIER, 2003
Westward	Han river	Aug–2001	10	NP	71	188	103	Li et al., 2004(a)
	Han river	Oct–2001	10	NP	42	84	60	Li et al., 2004(a)
	Han river	Dec–2001	10	NP	17	72	43	Li et al., 2004(a)
	6 Creeks, Shihwa	Apr–2000	18	NP	46	41,300	3580	Li et al., 2004(b)
	6 Creeks, Shihwa	Aug–2002	6	NP	90	15,821	3010	Li et al., 2004(c)
	6 Creeks, Shihwa	Oct–2002	6	NP	118	4324	2309	Li et al., 2004(c)
	6 Creeks, Shihwa	Dec–2002	6	NP	131	5239	1339	Li et al., 2004(c)

Brackish								
West coast	Shihwa lake	Apr–2000	12	NP	37	770	183	Li et al., 2004(b)
	Shihwa lake	Aug–2002	10	NP	35	1533	280	Li et al., 2004(c)
	Shihwa lake	Oct–2002	10	NP	17	140	92	Li et al., 2004(c)
	Shihwa lake	Dec–2002	10	NP	31	87	61	Li et al., 2004(c)
Saltwater								
West coast	Saemangeum Bay	May–2002	18	NP	4.5	52	20	Li et al., 2005
	Saemangeum Bay	Aug–2002	18	NP	23	48	30	Li et al., 2005
	Saemangeum Bay	Nov–2002	18	NP	3.1	22	12	Li et al., 2005
	Saemangeum Bay	Feb–2002	18	NP	7.1	79	21	Li et al., 2005
	Saemangeum Bay	May–2003	18	NP	17	129	34	Li et al., 2005
	Saemangeum Bay	Aug–2003	18	NP	28	247	76	Li et al., 2005
Suspended solid						ng g^{-1}, dw		
Freshwater								
Westward	Han river	Aug–2001	10	NP	3.8	17	8.7	Li et al., 2004(a)
	Han river	Oct–2001	10	NP	1.1	9.3	3.6	Li et al., 2004(a)
	Han river	Feb–2001	10	NP	1.0	6.9	3.1	Li et al., 2004(a)
	6 Creeks, Shihwa	Apr–2000	18	NP	600	116,700	14,400	Li et al., 2004(b)
	6 Creeks, Shihwa	Aug–2002	6	NP	69	10,183	2136	Li et al., 2004(c)
	6 Creeks, Shihwa	Oct–2002	6	NP	120	3836	1323	Li et al., 2004(c)
	6 Creeks, Shihwa	Dec–2002	6	NP	8.3	3487	742	Li et al., 2004(c)
Brackish								
West coast	Shihwa lake	Apr–2000	12	NP	93	859	445	Li et al., 2004(b)
	Shihwa lake	Aug–2002	10	NP	31	87	61	Li et al., 2004(c)
	Shihwa lake	Oct–2002	10	NP	19	831	149	Li et al., 2004(c)
	Shihwa lake	Dec–2002	10	NP	15	38	26	Li et al., 2004(c)
Soil						ng g^{-1}, dw		
	Country wide	1999	35	BPA	<0.5	54	7	NIER, 2000a
	Country wide	2000	35	NP + OP + BPA	<0.5	14	3	NIER, 2001
	Country wide	2001	35	NP + BPA	<0.5	8	2	NIER, 2002
	Country wide	2002	35	NP + BPA	<0.5	6	2	NIER, 2003

Table 2.13. (*Continued*)

Sampling				Compounds measured	Total APs and BPA			References
Samples	From	Year	*n*		Min	Max	Mean	
Sediment					ng g^{-1}, dw			
Freshwater								
Westward	Han river	1999	5	NP + OP + HP + PP + BPA	7	61	26	NIER, 2000a
		2001	5	NP + BPA	2	5	3	NIER, 2002
		2002	4	NP + BPA	1	2	1	NIER, 2003
Southward	Nakdong river	1999	3	NP + OP + HP + PP + BPA	88	124	101	NIER, 2000a
		2000	1	NP + OP + BPA	28	28	28	NIER, 2001
		2001	3	NP + BPA	<0.5	5	3	NIER, 2002
		2002	2	NP + BPA	1	2	1	NIER, 2003
Westward	Geum river	1999	1	NP + OP + HP + PP + BPA	104	104	104	NIER, 2000a
		2000	1	NP + OP + BPA	31	31	31	NIER, 2001
		2001	1	NP + BPA	6	6	6	NIER, 2002
		2002	3	NP + BPA	<0.5	2	1	NIER, 2003
Southward	Yeongsan river	1999	2	NP + OP + HP + PP + BPA	31	80	55	NIER, 2000a
		2001	2	NP + BPA	<0.5	2	1	NIER, 2002
		2002	1	NP + BPA	1	1	1	NIER, 2003
	Other rivers or lakes	2000	9	NP + OP + BPA	6	38	15	NIER, 2001
		2002	1	NP + BPA	1	1	1	NIER, 2003
Westward	2 Creeks, Shihwa	Oct–2000	8	NP + OP + BP + BPA	308	5124	1736	Koh et al., 2005
	6 Creeks, Shihwa	Apr–2000	18	NP	1.0	31,700	3008	Li et al., 2004(b)
	Han river	Aug–2001	10	NP	11	624	251	Li et al., 2004(a)
	Han river	Oct–2001	10	NP	56	357	157	Li et al., 2004(a)
	Han river	Dec–2001	10	NP	35	550	192	Li et al., 2004(a)

Southward	3 Rivers, Masan	Nov–2000	8	NP + OP + BP + BPA	158	1114	479	Koh et al., 2005
Eastward	2 Rivers, Onsan	Apr–1999	13	NP + OP + BPA	3.0	1074	168	Koh et al., 2002
	3 Rivers, Ulsan	Apr–1999	15	NP + OP + BPA	3.0	1161	180	Khim et al., 2001
Brackish								
West coast	Shihwa lake	Jan–1998	11	NP + OP + BP	37	1783	637	Khim et al., 1999a
	Shihwa lake	Apr–2000	12	NP	11	624	235	Li et al., 2004b
	Shihwa lake	Oct–2002	12	NP	10	5054	826	Li et al., 2004c
	Shihwa lake	Dec–2002	12	NP	16	2513	772	Li et al., 2004c
Marine								
South coast	Masan Bay	May–1998	28	NP + OP + BP + BPA	129	4168	547	Koh et al., 2002
	Gwangyang Bay	Feb–2001	11	NP + OP + BP + BPA	13	43	24	Koh et al., 2005
East coast	Onsan Bay	Apr–1999	13	NP + OP + BPA	3.0	6.3	3.9	Koh et al., 2002
	Ulsan Bay	Apr–1999	15	NP + OP + BPA	3.0	22	7.4	Khim et al., 2001
	Yeongil Bay	Mar–2000	26	NP + OP + BP + BPA	4.0	3199	194	Koh et al., 2006

2.5.5.1. *Environmental levels*

Based on the data from 1999 through 2003, concentrations of APs and BPA were relatively greater in creeks in industrial areas than in rivers and lakes (Table 2.13). Among APs and BPA, NP was the predominant chemical species in water and sediment both from inland and coastal areas. Most sites were contaminated with NP where other APs and BPA were generally low.

In a case study of the Shihwa-Banweol, creeks in this area were highly contaminated with NP (10- to 1000-fold greater than those in the Han River and Saemangeum Bay). The maximum concentration of NP observed was as great as 41300 ng L^{-1} in creeks with the average concentrations of from 1339 to 3580, depending upon sampling years. Concentrations of NP in Lake Shihwa ranged from 61 to 280 ng L^{-1}. These concentrations were similar to those of the Han River with 43–103 ng L^{-1} whereas, NP in coastal seawater from Saemangeum Bay were in the range of 12–76 ng L^{-1}.

The AP concentrations in sediments were also greater in creeks than in the brackish and marine environment. The average concentrations of NP, OP, and BP in sediment from Lake Shihwa were 609, 18, and 10 ng g^{-1} dw, respectively (Khim et al., 1999a). The NP concentration was detected up to 116700 ng g^{-1} dw in suspended solids, and 32000 n g^{-1} dw in sediments. The concentrations of APs and BPA in soil samples from the national monitoring sites of NIER were at a few ppb levels, implying that little APs and BPA were introduced into soil.

2.5.5.2. *Temporal and spatial distribution*

Concentrations of APs and BPA in South Korea appear to decrease with time. Based on the national monitoring data from NIER, the average concentrations of NP and BPA were 446 and 52 ng L^{-1} in 1999, 171 and 60 ng L^{-1} in 2000, 416 and 116 ng L^{-1} in 2001, and 79 and 67 ng L^{-1} in 2002. In the Shihwa-Banweol area, the concentration of NP might be decreasing with time. The greatest concentration of NP (41300 ng L^{-1}) measured in the tributaries to Lake Shihwa in April 2000 was reduced to almost one-third (15821 ng L^{-1}) in August 2002, and continuously decreased to 4000–5000 ng/L in October and December 2002. Concentrations of NP in suspended solids in the Lake Shihwa area was also observed to decrease. The average NP concentration in suspended solids reduced from 4744 to 151 ng g^{-1} dw during the period from 2000 to 2002. This is presumably due to the expansion of wastewater treatment plants (WWTP) and solid treatment plants (STP) in the Shihwa-Banweol industrial area. However, concentrations of NP in sediments from Lake Shihwa did not show such a rapid reduction, indicating the persistence of NP in sediment. Half-life of NP and OP is known to be in the order of years in sediments (Ying et al., 2002).

2.5.5.3. Comparison with EQCs

To evaluate the risks by water-borne NP exposure, the concentrations of NP in water and sediments were compared to acute and chronic water

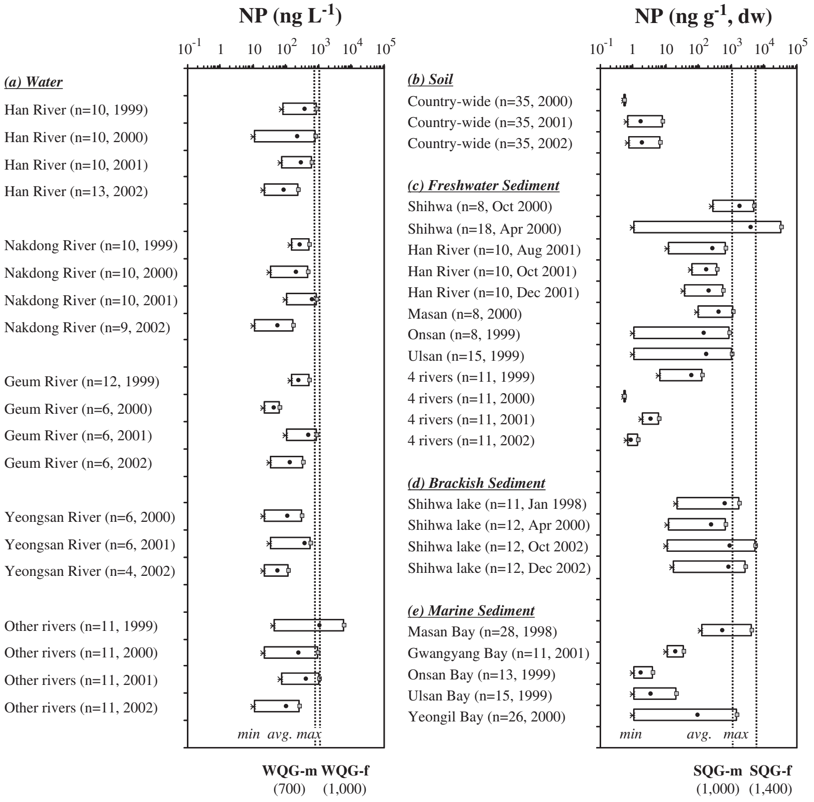


Fig. 2.22. Comparison of measured levels and environmental quality criteria (EQCs) for nonylphenol (NP) in water, soil and sediments from the various sites, in South Korea; (a) water ($n = 172$), (b) soil ($n = 105$), (c) freshwater sediment ($n = 131$), (d) brakish sediment ($n = 47$), (e) marine sediment ($n = 93$). Range indicates minimum (min), maximum (max), and arithmetic mean (avg.). Dotted lines represent Canadian EQCs proposed for marine water (WQC-m) and freshwater (WQC-f), and marine sediment (SQG-m) and freshwater sediment (SQG-f) (see the text).

quality criteria (WQC) and sediment quality guideline (SQG). In this evaluation, we used a final WQC and SQG for NP suggested by the USA and Canada (Environment Canada, 2001; US EPA, 2005). The acute criterion of 28000 ng L^{-1} and chronic criterion of 6600 ng L^{-1} were proposed for freshwater, while acute criterion of 7000 ng L^{-1} and chronic criterion of 1700 ng L^{-1} were proposed for salt water. These values are the concentrations of NP in water at which aquatic life is protected from acute and chronic adverse effects. In only 0.5% of the freshwater samples from South Korea the concentration was over the EPA's proposed chronic WQC of 6600 ng L^{-1} (Fig. 2.22). This is similar to the report that 99% of the detectable levels of APs/APEs and their biodegradation intermediates in US surface waters are below the chronic WQC (only four data among database exceeded chronic WQC). Canadian water quality guidelines (WQGs) for NP and its ethoxylates were proposed in 2002 and the guidelines were lower than USA chronic WQG. Based on the Canadian WQG for NP (1000 ng L^{-1}), 5.1% of water samples exceeded the WQG whereas 1.3% of salt water samples were over the guideline in salt water (700 ng L^{-1}). The fractions of the samples exceeding the Canadian sediment quality guidelines for NP in fresh water (1400 ng g^{-1}) and salt water (1000 ng g^{-1}) were 3.6% and 6.6%, respectively (Fig. 2.22). The percentages of sediment samples over SQG are larger than in water sample, indicating NP contamination in sediment might be more serious than that in water.

United States and Canada have water quality guidelines and European countries banned the use of alkylphenol polyethoxylates. To date, there is no standard available for regulating APs in the environmental media of South Korea. Most of the sites investigated throughout the South Korean peninsula are not expected to be sufficiently contaminated with APs or BPA to cause adverse effects. However, NP concentrations in some waters and sediments were over the guidelines of the USA and Canada. This means that aquatic organisms can be adversely affected by NP exposure in some aquatic systems. Therefore, actions should be taken to implement the regulations of NP to protect the aquatic ecosystems in South Korea.

2.5.6. PBDEs

Although the use of PBBs in South Korea was banned in 1999 the total use of BFRs including PBDEs has increased during the last decade (Park and Jeong, 2001). Concentrations of PBDEs in South Korea have only recently been measured. There are three peer-reviewed papers available, which reported the concentrations of PBDEs in air, sediments and bivalves. One report was available focusing on the PBDEs in human blood. A few reports on environmental policy of PBDE management were also published (Park and Jeong, 2001; Kim et al., 2002f; KMOE, 2005c).

2.5.6.1. Environmental levels

PBDEs have been detected in air at the sites of Busan, Masan, and Jinhae cities (Moon et al., 2007a), in sediment and bivalve from coastal regions (Moon et al., 2001, 2007b), and in human blood samples from workers and general population in Seoul (Kim et al., 2005e). The predominant PBDE congener in all atmospheric deposition samples was deca-BDE (BDE 209), which accounted for $>93\%$ of the total PBDE concentrations, indicating that deca-BDE was mainly used for industrial applications in South Korea. This observation is consistent with domestic consumption history of PBDEs in South Korea. The depositional fluxes of PBDEs from air varied from 10.1 to 89.0 μg m^{-2} year^{-1}. The total PBDE concentrations ranged from 0.45 to 494 ng g^{-1} dw (average 27.8 ng g^{-1} dw) in sediments, and from 0.38 to 9.19 ng g^{-1} ww (average 2.94 ng g^{-1} ww) in bivalves. The predominant PBDE congener in sediments and bivalves was deca-BDE, which accounted for $>90\%$ and $>60\%$ of the total PBDE concentrations in sediment and bivalves, respectively. The relatively great contribution of deca-BDE in sediments may be due to large quantity of industrial use and chemically stable property of deca-BDE. However, relatively great accumulation of deca-BDE in organisms was not consistent with other studies reporting that penta-BDE was more persistent and accumulative in organisms than octa-BDE and deca-BDE, or could be formed from debromination process of heavier molecules (de Wit, 2002).

Specific accumulation of PBDEs in organisms may vary with the source and the organisms' diets and metabolic capacities. Laboratory studies of PBDEs using aquatic organisms showed high potential of bioaccumulation up to the bioconcentration factor of 1,400,000 (Gustafsson et al., 1999). In the Baltic Sea, strong biomagnification in different tropic levels was observed (Martin et al., 2004). As PBDE contamination appear to be an emerging problem, further studies on the distribution, fate and bioaccumulation of PBDEs should be conducted in future in South Korea.

2.5.7. PFAs

Only a few reports of concentrations of PFAs in South Korea have been published (Kannan et al., 2002; So et al., 2004; Rostkowski et al., 2006). The distribution, fate and exposure level of PFAs should be intensively investigated in South Korea because the very great concentrations of PFAs from water bodies and human blood in South Korea have been reported and the single greatest concentration of perfluorooctanesulfonate (PFOS) was reported for water in Lake Shihwa.

2.5.7.1. Environmental levels

PFAs concentrations in 11 seawater samples collected from west and south coasts of South Korea in 2003 were measured (So et al., 2004). Concentrations of PFOS ranged from 40 to 730000 pg L^{-1} and the average concentrations of west and south coasts were 147000 and 748 pg L^{-1}, respectively. The greatest concentration, 730000 pg L^{-1}, was observed in the vicinity of Shihwa-Banweol industrial complex of west coast, which was thousands of times greater than those reported in open oceans such as the Pacific Ocean, Atlantic Ocean, Zulu Sea, South China Sea, and two orders of magnitude greater than those reported in coastal regions of Japan, Hong Kong and China. The average concentration of PFOA for overall South Korean waters was similar to that in Tokyo Bay, and 3–50 times lower than in Ai River from Japan, but 1–100 times greater than those reported for the open ocean (Table 2.14).

A detailed survey was conducted in the vicinity of the Shihwa-Banweol industrial complex in 2004 (Rostkowski et al., 2006). Concentrations in seawater in 2004 were 100-fold less than what had been in 2003. However, the average (range) PFOS concentration in water from the inland areas near Shihwa was as great as 89000 (8000–651000) pg L^{-1}. The concentration decreased to 12900 (7330–18300) pg L^{-1} in Shihwa Lake, and to 5210 (2240–8260) pg L^{-1} in coastal regions with increasing distance from the source area. The distribution of PFOA in this region was similar to PFOS with an average concentration of 19220 pg L^{-1} in inland area, 6140 pg L^{-1} in Shihwa Lake, and 2200 pg L^{-1} in bay area. The distribution pattern of PFNA in this region was similar but the concentrations of PFHxS, PFBS, PFOSA, PFDA, PFNA, and PFHxAha were one order of magnitude lower than those of PFOS and PFOA. This means that there is a continuous input of PFOS from Shihwa-Banweol inland area.

The concentrations of PFAs were reported for 43 individuals of 10 water bird species collected from Hongdo in the vicinity of Nakdong River, and Nando, west coast of South Korea, between 1993 and 1994 (Kannan et al., 2002). PFOS, PFOSA, PFOA and PFHS were analyzed in this study, but only PFOS was found in bird samples. The greatest and average concentration of PFOS in these bird liver samples from South Korea were 500 and 80 ng g^{-1} ww, respectively, while those in Japan were 650 and 215 ng g^{-1} ww, respectively. PFOS was detected in all bird

Table 2.14. Concentrations (pg L^{-1}) of PFAs in water from various regions

Sampling			PFOS			PFOA			PFHS			PFNA			References
Area	Year	*n*	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Korea															
River (Shihwa-Banweol)	12–04	17	8030	651,350	89,110	5210	61,690	19,220	1940	84,610	10,700	830	6950	3260	Rostkowski et al., 2006
Lake Shihwa	12–04	5	7330	18,320	12,850	1670	10,860	6140	630	2040	1310	630	2100	1320	Rostkowski et al., 2006
Gyeonggi bay	12–04	5	2240	8260	5210	940	3290	2200	550	990	720	510	830	680	Rostkowski et al., 2006
South coast of Korea	01–03	6	40	2300	748	240	11,000	4840	30	460	240	40	590	242	So et al., 2004
West coast of Korea	01–03	5	620	730,000	147,028	1300	320,000	65,680	160	52,000	10,898	50	13,000	2662	So et al., 2004
Japan															
Ai river	03–04	5	2900	12,300	46,300	16,700	87,100,000	236,017	–	–	–	–	–	–	Morikawa et al., 2006
Tokyo bay	02–04	8	338	57,700	–	1800	192,000	–	17	5600	–	163	71,000	–	Yamashita et al., 2005
Offshore of Japan	02–04	4	40	75	–	137	1060	–	3	6.1	–	–	–	–	Yamashita et al., 2005
China															
Coastal area of Hong Kong	02–04	12	70	2600	–	673	5450	–	5	311	–	22	207	–	Yamashita et al., 2005
Coastal area of China	02–04	14	23	9680	–	243	15,300	–	5	1360	–	2	692	–	Yamashita et al., 2005
Open ocean															
Sulu sea	02–04	3	17	109	–	88	510	–	0.2	0.2	–	–	–	–	Yamashita et al., 2005
South China sea	02–04	2	8	113	–	160	420	–	0.2	0.2	–	–	–	–	Yamashita et al., 2005
Western Pacific ocean	02–04	2	54	78	–	136	142	–	2.2	2.8	–	–	–	–	Yamashita et al., 2005
Central-Eastern Pacific ocean	02–04	12	1.1	20	–	15	62	–	0.1	1.6	–	1	16	–	Yamashita et al., 2005
North Atlantic ocean	02–04	9	8.6	36	–	160	338	–	4.1	6.1	–	15	36	–	Yamashita et al., 2005
Mid Atlantic ocean	02–04	7	37	73	–	100	439	–	2.6	12	–	–	–	–	Yamashita et al., 2005

samples collected from South Korea and Japan, indicating that it is one of the most persistent and accumulative PFAs. PFOS has a great potential for bioaccumulation relative to other PFAs including PFOA. The persistence and bioaccumulative potential of PFOS in organisms have been reported in other studies (Martin et al., 2003; Morikawa et al., 2006). The average concentration of PFOS in human blood in Daegu, South Korea, was similar to that in Japan, 5–7 times greater than that in Indian and Italian samples, and two times less than in American and Polish samples (Kannan et al., 2004). The average PFOA concentration in human blood was 62 ng ml^{-1} in South Korea. The level is three times greater than in American and Polish, six times greater than in Japanese and Malaysians, and over 10 times greater than in other general populations in other countries. It is noteworthy that: (1) most of imported PFAs might be used as water-repellant for textile and leather industries; (2) PFCAs produced by telomerization process are likely to be the main PFAs source in South Korea after phase out for perflurosulforamide products of 3 M; and (3) over 50% of PFAs imported from abroad might have been used in Daegu and neighboring Kyeongsangbukdo where a large number of textile plants have been in operation since the 1950s.

Although classical POPs such as PCBs, DDTs and CHLs in environmental media from South Korea were relatively less compared to other industrialized countries, the emerging pollutants including PBDEs, and PFAs in South Korea were relatively great. Great concentrations of PFOS and PFOA in human serum were also reported in recent studies in some areas of South Korea. Therefore, it is necessary that the source, distribution, and fate of emerging pollutants in environmental media should be investigated nationwide and that the contamination levels and the exposure routes of pollutants to human and wild life should be assessed. Additionally, establishment of toxic release inventory, source control and management, and ecological/human risk assessment should be performed. Especially, human exposure from the consumption of fishes and shellfishes in South Korea should be assessed for these emerging POPs.

2.6. Fate and transport of POPs in South Korea

2.6.1. Sources of PCDDs/DFs in environmental media

Relatively great concentrations of PCDDs/DFs ranging from 22.15 to 92.99 pg I-TEQ g^{-1} fat wt (with an average concentration of 53.42 pg I-TEQ g^{-1} (fat wt)) were reported in the blood of residents near a large scale industrial waste incinerator (CIES, 2002). Furthermore, more incidences of glycosuria and cancer were reported in the population near the incinerator facility than those in the distant areas. However, more epidemiological investigation would be required to accurately assess the effects of PCDDs/DFs. Extensive measurements of residues in soils, sediment at the wastewater discharging sites, agricultural products (including poultry), and human blood were performed from 2002 to 2003 (Pyoungtak City, 2003). These efforts were focused on revealing the health effects from exposure to point sources (i.e., waste incinerator) of PCDDs/DFs in the environment. Although no clear difference was found in the extent of contamination of human blood or environmental media between sites near and away from incinerators, the influence of incinerator on dioxin exposure was clearly shown by the congener patterns of PCDDs/DFs that changed with distance from the incinerator in soil and human blood (Park et al., 2004). Furthermore, concentrations of PCDDs/DFs in soils decreased as a function of distance from the incinerator over the first few hundred meters. However, no clear trend was found beyond 200 m (for instance, ~60 pg WHO-TEQ g^{-1} near incinerator; ~15 pg WHO-TEQ g^{-1} for 20 m; and ~3 pg WHO-TEQ g^{-1} for most samples over 200 m). Soils 200 m away from the incinerators had similar TEQs with an average of 2.32 pg WHO-TEQ g^{-1} (geomean, $n = 3$) detected at 7 km away from the incinerator. Thus, there is a characteristic spatial distribution of concentration with a clear decrease near the source followed by a fairly even distribution.

In contrast to the total concentration, a gradual transition was found for the relative composition of PCDDs/DFs congeners with distance from the incinerator. The proportion of PCDFs, particularly 1,2,3,4,6,7,8-HpCDF and OCDF, which were the dominant congeners in soils near sources such as stack gas and fly ash decreased progressively with distance while OCDD enriched with distance. A similar trend in patterns of relative concentrations of congeners was observed in blood of residents in the area. The composition of PCDF congeners among 2,3,7,8-substituted PCDDs/DFs was significantly greater in blood of residents living near incinerators than in blood of those living farther away from incinerators. Based on the congener composition together with concentration gradient, the exposure and effect zones were determined to be within 1–1.5 km of the incinerator (Park et al., 2004). Several other studies have also reported point sources of dioxins and their effects, i.e., the impact of sources to the surrounding environment. In the late 1990s, Kim et al. (2002c) and Oh (2001) compared concentrations and composition profiles in soils near incinerators used to combust solid wastes from paper mills or municipal solid waste incinerators with those of stack gas. In order to obtain information on the emissions of industrial waste incinerators (IWI) to their surrounding environment, Kim et al. (2005d) determined the concentrations of PCDDs/DFs in various samples such as stack gas, fly ash, ambient air, soil, pine needles, rice plants, IWI worker blood collected from different distances in the vicinity of IWI. Recently, Kim et al. (2005b) and NIER (2005b) reported the results of a five year project conducted between 2003 and 2008 to measure concentrations of PCDDs/DFs in stack gas, wastewater, sediment, and soil around incinerators. Based on a meta-analysis of the data collected from these studies, it was concluded that there was a common composition pattern which changes gradually from the source while the concentrations decreased more rapidly before reaching a relatively uniform pattern (Fig. 2.23). At the same distance from incinerator, similar concentrations were detected in rice fields, upland crop fields, and forests, whereas 30-fold greater concentrations were measured in roadside soil (NIER, 2005b). Residual PCDDs/DFs concentrations in soil decreased dramatically to concentrations less than 10 pg I-TEQ g^{-1} within 750 m of the incinerator (Fig. 2.23a-1). Gaussian modeling using ISC (Industrial Source Complex) and ISCLT (Industrial Source Complex Long Term), showed maximum concentrations occurred at a distance of approximately 250–500 m from the incinerator (NIER, 2005b). Meanwhile, absolute and relative concentrations of PCDF and PCDD congeners, particularly 1,2,3,4,7,8,9-HpCDF and 1,2,3,4,6,7,8,9-OCDF decreased while the concentration of 1,2,3,4,6,7,8,9-OCDD increased progressively from source to distant locations beyond 1 km (Fig. 2.23a-2–a-4). It is noteworthy that the trend of transition in the congener composition was clear, although the meta-analysis did not consider wind direction and land-use pattern, when the roadside samples that were collected within 500 m from an incinerator were excluded. Thus, incinerators have a significant impact only within a few kilometers.

The distance-dependent transition in relative congener composition was also observed in aged soils that had been affected by a forest fire (Fig. 2.23b-1) (Kim et al., 2003a). Five months after burning, concentrations decreased to be the same in unburned soil at a remote area. However, the weathering of congeners seems to progress more slowly (Fig. 2.23b-2–b-4). The predominance of OCDD composition in aged or remote soils results from: (1) its intrinsic fate property such as low vapor pressure, water solubility, biodegradability, and reaction with hydroxyl radicals; (2) release from use of pentachlorophenol (PCP); and (3) long environmental residence due to strong air-particle association and its deposition to underlying surface. The analysis of congener composition is found to be useful to identify the sources.

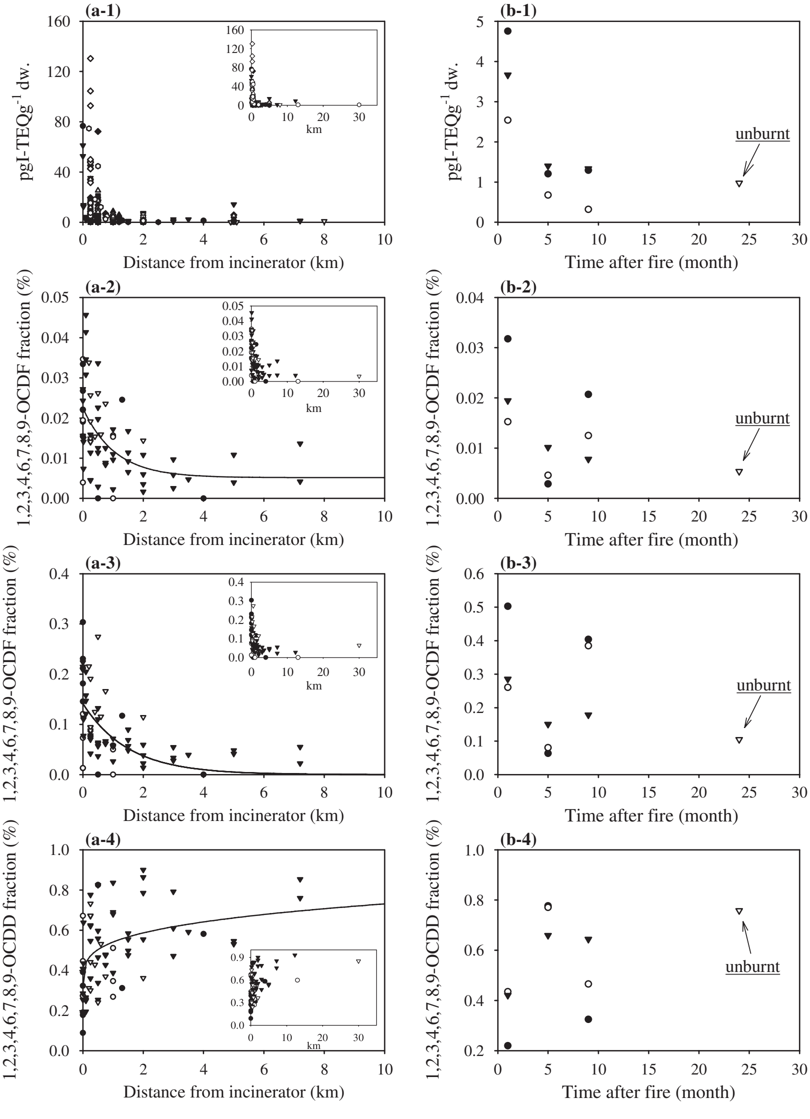


Fig. 2.23. Variation in total PCDDs/DFs concentration and congener fractions measured for soils with distance from a source (‘a’ group, Kim et al., 2002c; Park et al., 2004; Kim et al., 2005d; Oh et al., 2006; NIER, 2005b) and with time after forest fire (‘b’ group, Kim et al., 2003a). An unburned remote soil sample was assigned to 24th month after fire.

2.6.2. Case study of multi-media fate of POPs (PAHs vs. PCBs)

Classical organochlorine POPs are hydrophobic and semi-volatile. They distribute among environmental media via inter-media transfer, partitioning, volatilization, and dry/wet deposition. The direction and magnitude of movement across media are dependent on media and concentration at which they were emitted, chemical properties including volatility, solubility, hydrophobicity, and persistency, meteological/morphological/ecological conditions of the system. These factors vary with time and space. For determining the direction and magnitude of movement among media, it is inevitable to simultaneously measure chemical residues and environmental factors in each of the media. One can infer the transfer (or transport) among media through thermodynamic index such as fugacity ratio and environmental processes such as dry/wet or deposition flux.

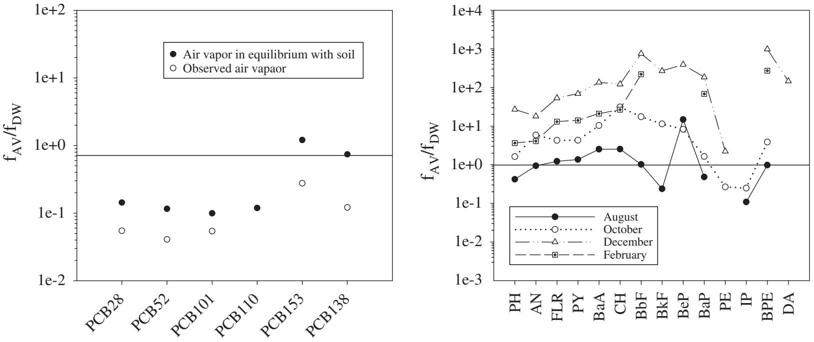
The multi-media fate of PAHs and PCBs in Seoul Metropolitan city with a population of over 10 million has been investigated by use of concurrent measurements in each season for multiple environmental media including air (gas and particle phases), water (dissolved and suspended solid phases), sediment, terrestrial soil and plant leaf, and aquatic plank tonic organisms (Kim, 2004). To our knowledge, this is the only study to describe multimedia fate and distribution of hydrophobic organic compounds (HOCs) in South Korea that has been conducted based on field-measured data. The study revealed that knowledge of the interrelationships among different media is critical to elucidating distribution and behavior of HOCs in each medium. In the study, the differences in overall fate such as distribution, behavior, and transport pathway were observed between PAHs and PCBs. We describe below some of the highlights of the study of multimedia fate and transport of POPs in South Korea.

2.6.2.1. Air–water exchange

'Fugacity', representing 'escaping tendency' of a chemical in a medium, has been widely applied in assessing the status of fate and transport of a chemical in and among environmental media (Mackay, 1991). If one knows chemical concentration and fugacity capacity in each medium, the fugacity difference can be calculated as in the Eq. (2)

$$\frac{f_i}{f_j} = \frac{C_i Z_i}{C_j Z_j} \tag{2}$$

(a) Fugacity ratio between air vapor and dissolved water



(b) Gaseous exchange flux between air and water

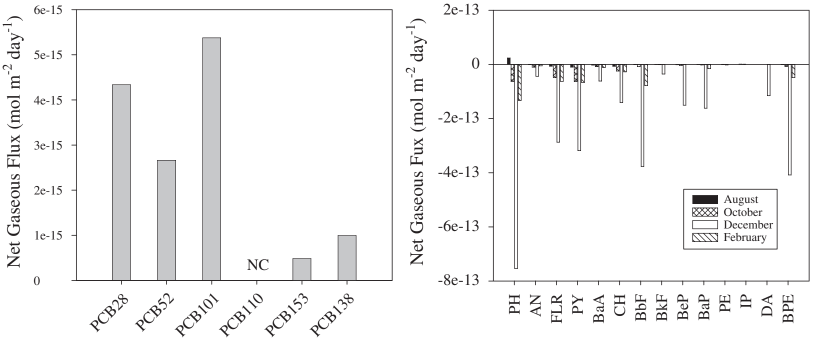


Fig. 2.24. Fugacity ratios (a) and gaseous exchange flux (b) between air and river water for PAHs and PCBs from Seoul Metropolitan city in 2001–2002 (quoted from Kim (2004)); fAV and fDW is fugacity in air vapor and dissolved water, respectively. Flux of PCBs was calculated on basis of observed vapor PCBs and 'NC' indicate 'not calculated'.

where, $C_{i,j}$, $Z_{i,j}$, and $f_{i,j}$, are chemical concentrations (mol m^{-3}), fugacity capacity (mol m^{-3} Pa^{-1}), and fugacity (Pa) in medium i and j, respectively. The ratio of i–j fugacity, f_i/f_j is a measure of departure from equilibrium. Values greater than unity indicate that there is net-diffusion from the medium i to medium j. Conversely, values less than unity indicate net diffusion to the medium i. For a system in equilibrium, f_i/f_j is approximately equal to 1. Based on these fugacity ratios among media, one can determine the moving direction of a chemical between two contacting media. For example, air–water fugacity ratios measured for PAHs in Seoul city area were over 1 in all seasons but summer, indicating the diffusive movement from air-to-water (Fig. 2.24a). Contrarily, the air–water fugacity ratios of PCBs were below unity, which suggests evaporation from water to air (Fig. 2.24a).

In addition to qualitative assessment of direction of movement of a chemical using fugacity ratio, quantitative assessment is determined by calculating net gaseous diffusion across air–water interface (Mackay et al. (1986); Baker and Eisenreich, 1990; Achman et al., 1993). The two-film theory as shown in Eq. (3) has been frequently used to determine the gaseous diffusion rate of chemicals (Whitman, 1923; Liss and Slater, 1974).

$$F = k_{\mathrm{ol}}\left(C_{\mathrm{DW}} - \frac{C_{\mathrm{AV}}}{\mathrm{H}'}\right) \tag{3}$$

where, F is the flux (mol m^2 day^{-1}), and k_{ol} (m day^{-1}) is the overall mass transfer coefficient for movement across air–water interface. C_{DW}, C_{AV}, and H' are dissolved concentrations in bulk water and the air vapor concentration in bulk air of HOCs, and the dimensionless Henry's law constant, respectively.

The air-to-water flux of PAHs and PCBs in the Han River was distinctive (Fig. 2.24b). The overall gaseous transfer of PCB congeners occurred from water to air with greater transfer rates for lower chlorinated congeners; for instance, 4.34×10^{-5} mol m^{-2} day^{-1} for PCB 28 and 4.84×10^{-6} mol m^{-2} day^{-1} for PCB 153. Obviously, the mass transfer coefficient is greater for lighter substances. The transfer of PAHs occurred from air to water with higher values in winter than in summer. This observation indicates that the burden and fate of PAHs in the Han River aquatic system can be strongly influenced by the variation in airborne concentration (i.e., atmospheric emission) whereas the distribution of PCBs could be controlled by the burden discharged into the water body (e.g., desorption from historically contaminated sediments or direct release into water) rather than atmospheric input.

The difference in environmental release of PAHs and PCBs is further supported by their differences in seasonality of atmospheric concentration. PAH concentrations in air increased gradually in winter. This seasonality was also observed in more extensive measurements in Seoul city's air (Panther et al., 1999). The seasonality in concentrations of PAHs in urban areas often results from greater combustion of fuel for heating in wintertime. To the contrary of PAHs, the potential emission sources of PCBs such as waste incinerators or metallurgical processes do not show significant seasonality. Atmospheric concentrations of PCBs were greater in summer than in winter (Yeo et al., 2003). In particular, a strong negative linear regression between partial pressure (i.e., ln p; concentration) of atmospheric PCBs and the reciprocal of temperature (i.e., 1 T^{-1}) was observed in urban air (Yeo et al., 2004a). Negative slopes of greater magnitude derived from the Clausius-Clapeyron equation (Eq. 4) indicate temperature-dependent distributions of PCBs in the air. PCBs in air may not originate from direct release but by secondary source such as volatilization from terrestrial surface.

$$\ln p = \frac{\mathrm{m}}{T} + \mathrm{b} \qquad (4)$$

where, p is partial pressure (Pa), T is ambient air temperature (K), and m and b are constant.

The major source of by-product PCB emission (~93%) was estimated to be ferrous metal industry (see Section 2.4.1.1). All metal production factories are located in coastal areas far from the Seoul metropolitan area. A possible emission source in Seoul is waste incinerators. However, the contribution from waste incinerators is generally small (see Fig. 2.6). Thus, direct atmospheric release is not likely to influence the distribution of PCBs in the air over South Korea. On the other hand, the leakage or spillage from capacitors and transformers may be a potential emission source of PCBs. This emission process is categorized as a major contributor of PCBs into the environment (EMEP/CORINAIR, 2000). Although regulation of the use of PCBs began in 1979, existing PCB-containing articles were in use for other purposes, except electric heater, until 1996. Therefore, PCBs are likely to have been introduced into aquatic system through leakage or spills from the use and/or storage of the articles. PCB concentrations were greater at the sites in the tributaries of the Han River flowing through the urban and industrial areas (Kim, 2004).

OCPs such as DDTs, HCHs, CHLs, and endosulfan showed a similar seasonal variation of atmospheric levels as PCBs with greatest levels in summer (Yeo et al., 2004a). This seasonal distribution is due to limited environmental release of OCPs following ban of OCPs in South Korea.

In contrast to PCBs and OCPs, the seasonal trend of atmospheric PCDDs/DFs in South Korea is not likely to be influenced by temperature, i.e., evaporation from surface. Oh et al. (2006) measured seasonal trend in ambient air around a large-scale municipal waste incinerator from August 1999 to November 2000. PCDDs/DFs concentrations ranged from 0.22 to 1.15 pg I-TEQ m^{-3} ($n = 10$, geomean = 0.64 pg I-TEQ m^{-3}). The great concentrations, including the greatest value, were detected in winter even though there was a weak relationship between temperature and concentration ($r^2 = 0.247$). This seasonal trend was also observed in monthly bulk atmospheric deposition samples at Busan and its surroundings (Moon et al., 2005). PCDDs/DFs bulk deposition flux was lowest in the summer season when temperature and precipitation

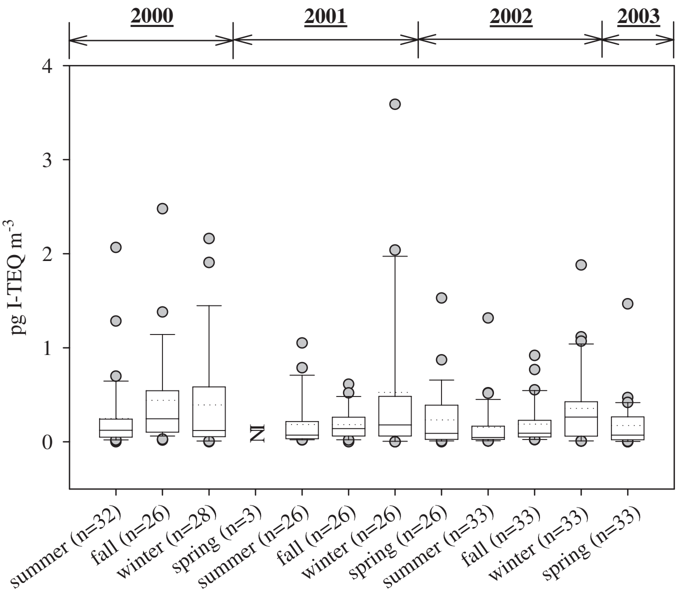


Fig. 2.25. Seasonal variation of atmospheric PCDDs/DFs concentration in Korea (from NIER, 2001, 2002, 2003). The boundary of the box indicates the 25th and 75th percentile, and a line within the box marks the median. Whiskers above and below the box indicate the 90th and 10th percentiles. Points and dotted lines are the arithmetic mean and outlying points. Values in the parenthesis are the number of samples. Three points from spring in 2001 ('NI') were not included.

were highest, whereas the flux was high in winter and moderate in spring and fall. Wet deposition by precipitation together with dry deposition is known to play a major role to scavenge PCDDs/DFs air to underlying surface. Thus, the lesser deposition flux that occurs in summer implies a minimum concentration would occur in air during the warm season. Extensive seasonal monitoring of ambient air was performed from 2000 to 2002 by NIER (2001, 2002, 2003). Atmospheric distribution of PCDDs/DFs was not expected to show any seasonality because waste incinerators and industrial facilities, two major emission sources of PCDDs/DFs, may emit PCDDs/DFs at a fairly constant rate throughout the year. However, as shown in Fig. 2.25, the concentrations in winter were significantly greater than those in other seasons in 2001 and 2002 (ANOVA test, $p < 0.05$). This might be a result of lower mixing heights and reduced photochemical degradation of PCDDs/DFs in winter. The little temperature dependency of atmospheric PCDDs/DFs concentration, is different from those of PCBs and OCPs, and indicates the ongoing release of

PCDDs/DFs into air. Thus, it is expected that the levels in other media, soil in particular, may also increase or only decrease slowly even though emission of PCDDs/DFs was dramatically reduced (Fig. 2.25). Therefore, further regulations on PCDDs/DFs emission is needed in South Korea.

The third piece of evidence for differences in the sources and fate of PAHs and PCBs is the fingerprint of isomers (or congeners) of each chemical group. Based on the differences in thermodynamic stability among PAH compounds, PAHs molecular indices have been widely used to identify potential PAH sources. For instances, PHE:ANT ratio <10 and FLT:PY ratio >1 tends to suggest that PAH contamination arises from pyrogenic origin (Yunker et al., 2002). Additionally, ratios such as BaA:CHR and I123cdP:BghiP have been also suggested as useful indices to identify various combustion processes (Dickhut et al., 2000; Yunker et al., 2002). Molecular indices from most sediment and suspended solid samples in the Han River suggested petroleum combustion as the major source of PAHs (Kim, 2004). Thus, it may be inferred that atmospheric release from petroleum combustion mainly contributed to contamination of the aquatic systems in Seoul. Alternatively, PCBs in sediment of the Han River appears to have originated from leakage of PCBs mixtures based on their congener pattern that is similar to that of Aroclor mixtures (ca., Aroclor $1242{:}1254{:}1260 = 2{:}1{:}1$) (Kim, 2004). This pattern from sediment was significantly different with those of terrestrial soils and settled air particles (Kim, 2004).

2.6.2.2. Control factors for multimedia fate

Many factors influence in complicated manners the magnitude and direction of transport and the distribution of chemicals in the environment. The factors include both the chemical properties and environmental variables such as emission, metrological and morphological conditions. Therefore, it is necessary to identify dominant factors to understand the fate and distribution of POPs in a system and to establish system-specific control strategies for POPs.

The difference in the emission histories of PAHs and PCBs was the predominant factor for their fate, transport, and distribution in Seoul. Besides transfer directions among media such as air–water partitioning, the relative residue levels in individual medium may be determined based on sources of release. PCB 52 and BaA have similar hydrophobicities (i.e., $\log K_{\mathrm{ow}} = 5.84$ vs. 5.55 for PCB 52 and BaA, respectively) but Henry's law constant for PCB 52 is 100-fold higher. Thus, if both the compounds are assumed to be released to the same media, BaA would show higher partitioning to aqueous media in an air–soil–water-sediment system as compared with PCB 52. However, the residual mass of PCB 52 in the aquatic system was 0.41% in the water column, 31% in sediment, and 68% in soil whereas almost all BaA of over 90% resided in soil, 0.01% was in the water column and 8.12% in sediment (Kim, 2004). This difference in relative residues in environmental media is associated with the difference in the main release media, i.e., into water via air for PAHs and into directly water for PCBs. The effect of release media on relative distribution of POPs among the media can be conveniently investigated by multi-media modeling simulation with different emission scenarios.

The size distribution of air particles not only influences the distribution and partitioning dynamics of POPs, but also determines dry and wet deposition flux of POPs. An interesting phenomenon was observed for relationship among atmospheric PAHs, particle size distribution, and the levels of PAHs in soil (Kim, 2004). For urban sites, the composition pattern and absolute concentrations of PAHs in soil were well correlated with those in air where the atmospheric particles' size was distributed evenly among seasons with predominant amount of fine particles $<3\,\mu m$. Dry deposition flux of PAHs followed seasonal variation in atmospheric concentration in urban site. However, at a suburban site with large seasonal variation in particle size distribution, dry deposition flux and soil residue did not reflect the seasonal variation of atmospheric PAHs. From this result, site-specificity in atmospheric particle distribution may also influence the distribution and residues in the underlying soil.

The behavior and phase distribution of POPs within an aquatic system is expected to be largely controlled by the affinity to particles according to their hydrophobicity and sorbent properties. In the Han River, which is frequently eutrophied, the partitioning between water and particles and distribution of PCBs were well explained by the conventional concept that their levels are determined by their hydrophobicity and the fractional organic carbon contents of particles. However, the K_{oc} values of PAHs obtained in the field were typically 10- to 100-fold greater than those predicted from the two-phase equilibrium partitioning model using the chemicals' hydrophobicity (i.e., K_{ow}) and the particles' fractional organic carbon (i.e., f_{oc}) (Fig. 2.26). In eutrophic seasons with algal blooms, the partition coefficients of PAHs were greater than those calculated by the combination of chemicals' hydrophobicity, K_{ow}, and organic carbon content, f_{oc}.

The same phenomenon was also observed in sediments (*not presented*). Gustafsson et al. (1997) explained the greater partition coefficients by using the expanded model, $K_d = f_{oc}K_{oc} + f_{sc}K_{sc}$, which accounts the role of soot-like particle with greater sorption capacity rather than organic carbon alone. Sorption capacities were extensively assessed in various

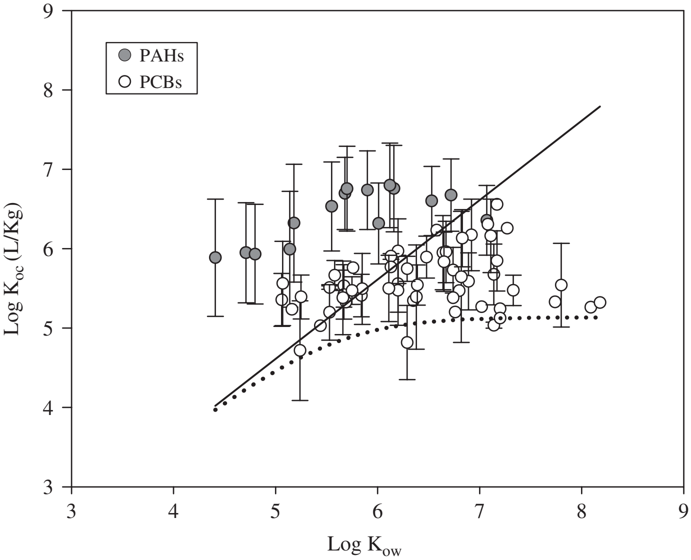


Fig. 2.26. Organic carbon-normalized partitioning coefficients (log K_{oc}) in the Han river water column for PAHs and PCBs (quoted from Kim (2004)); Linear solid line indicates the estimates from two-phase partitioning model (Karickhoff, 1981) and dotted line denotes those from three-phase partitioning model involving colloidal phase (Baker et al., 1986), where $K_{colloid} = K_{oc}$ was assumed and average DOC was used.

particles (Cornelissen et al., 2005) or other POPs (Persson et al., 2002). This observation supports that the fate and distribution of PAHs in locations with intensive combustion activity could be strongly influenced by external particles (e.g., soot-like particles) rather than organic carbon alone. Organic carbon-based chemical concentrations in sediment have been used to derive sediment quality guideline (SQG) to protect aquatic benthic organisms (DiToro et al., 1991; Swartz, 1999; Rogers, 2002). The equilibrium partitioning (EqP) method is currently supported by the US EPA for the development of sediment quality criteria for non-ionic organic chemicals. The EqP approach assumes that partitioning of sediment-bound chemicals between pore water and sediment organic carbon is governed by the organic carbon partition coefficient (K_{oc}) under steady-state conditions. These results indicates that further studies of sediment quality criteria needs to be conducted on soot carbon-bound concentration but not organic carbon-based concentration alone.

In contrast to PAHs, PCB congeners did not reach the equilibrium between suspended particles and dissolved water (Fig. 2.26). The more chlorinated congeners are, the greater is algal bloom, the greater was the deviation in partition coefficients from the equilibrium, based on the $K_{oc}-K_{ow}$ plot (Kim, 2004). This indicates that PCBs are still in the process of sorption from dissolved water to suspended particles.

2.6.3. Long-range transport (LRT)

One of issues of POPs is their Long Range Transport (LRT) passing the national boundaries. UNECE/EMEP (United Nations Economic Commission for Europe/Co-operative program for monitoring and evaluation of long range transmission of air pollutants in Europe) adopted 'CLRT protocol' in 1998 to control trans-boundary movement of 16 potential POPs (http://webdab.emep.int/). In 2004, Stockholm Convention for international cooperation against POPs entered into force. In addition, the project, funded by the GEF (Global Environment Facility) and implemented by the UNEP, was performed to make regional assessment of the damages and threats posed by Persistent Toxic Substances (PTS; www.chem.unep.ch/pts). As a result of GEF-UNEP project, countries involved in Region VII (i.e., Central and North East Asia) submitted the regional report in which dioxins and PCBs were assigned as priority PTS to manage in the region in 2002. In East Asia, there is another international effort to control trans-boundary movement of POPs such as 'Establishment of POPs Information Warehouse in East Asia', through which countries in the region share POPs monitoring data and cooperate for POPs control.

LRT of atmospheric pollutants has become a concern in South Korea partly because release of numbers of pollutants in eastern China may be a potential source of air pollution in South Korea (Kwon et al., 2002). Studies of LRT, however, have focused on suspended particulate matter such as PM_{10} or $PM_{2.5}$ (Lee et al., 2006b), particle-associated heavy metals (Han et al., 2002), or acidic air pollutants (Park and In, 2002). Since Gosan in Jeju Island is used as a reference site for ACE-Asia (Asian-Pacific Regional Aerosol Characterization Experiment) project in 2001, many studies are performed for LRT of pollutants from East Asia. Ghim et al. (2003) reported the variation in atmospheric concentrations of POPs including PCDDs/DFs, coPCBs, OCPs, and PAHs in Asian dust at the reference site, Gosan. Little increase in atmospheric concentrations of POPs was observed during the Yellow Sand season except for PAHs. Another study measured atmospheric bulk deposition of PCDDs/DFs in urban and suburban areas in South Korea during one year including periods of Asian dust. Elevated levels were not also observed in the presence of Asian dust (Moon et al., 2005). Instead, they illustrated the effect of Asian dust on South Korean air by using the specific congener patterns observed during the period, clearly differing from those of other seasons. These studies were, however, restricted to a short term. Thus, further long-term studies are needed on trans-boundary LRT of POPs in this region.

LRT dynamics of POPs can be predicted and evaluated by environmental multimedia modeling (MMM). The models with different spatial scale such as POPsME, EDCSeoul, and KoEFT-PBTs have been developed to predict the fate and transport of classical POPs or VOCs in multimedia environments (Lee et al., 2004; NIER, 2001, 2002, 2003; Lee, 2005). These models are considered to serve as a basis for the future development of LRT models of the north-east Asian region.

2.7. Conclusions

Due to their persistent, bioaccumulative, and toxic properties, POPs are worldwide categorized as priority pollutant group to be prohibited in their use and distribution, or removed from environments. Long-range transportation of POPs has result in relevant international efforts such as Stockholm Convention. South Korean government has followed actively the needs of the convention; 1) regulation in use, distribution, and treatment of POPs substances itself and/or POPs-containing facilities and wastes, 2) development and application of BAT and BEP to reduce POPs release, and 3) monitoring and investigation on POPs contamination nationwide. Nevertheless, the results of investigation and research efforts were not assessed through integrated overview and subsequently the POPs status in South Korean environments is not still evaluated until now.

The present study exhibits the meta-analysis results of data collected from total 228 references published since mid-1990s. Emission, contamination and exposure levels in environments and human for both classical and emerging POPs were firstly and thoroughly reviewed together with historical governmental management strategy and plans. Moreover, the environmental fate and transport natures of POPs in South Korean environments were analyzed, from which POPs behavior status were evaluated to suggest the efficient management strategy.

Most studies were focused on the classical POPs such as organochlorinated pollutants and little for emerging POPs such as PBDEs and PFAs. Preliminary emission inventory were estimated by use of the top-down approach for by-product POPs. Recently, an emission inventory, based on measurements, was established for dioxins. Over 80% of the total emission for all by-products was determined to be from two major sources, viz. waste incineration and metal production processes, among the sources, suggesting the necessity of control focused on corresponding sources.

Based on the seasonal atmospheric levels and their environmental fate, existing emissions are still influencing significantly the distribution of dioxins and PAHs but not for PCBs and OCPs. Due to governmental regulatory action, during the most recent five years, emissions of dioxins have been significantly reduced. However, the concentration levels in environments are likely to have decreased but the reduction extent was less clear, compared with that of emission. In particular, annual emission rate per unit area was still in great, relative to other countries. Consequently, environmental concentrations and human exposure levels in the source areas frequently exceeded criteria suggested to protect environments and human. Thus, to decrease human and ecological exposure, more reductions in emissions should be required. Besides dioxins, contaminations of other classical POPs (including PCBs and OCPs) were localized in hot spots, such as coastal industrial area and/or big harbors and waste incineration areas. In some of these areas, concentrations of residues exceeded corresponding quality criteria. If these hot spots are excluded from the analysis, general populations and ambient environments did not contain concentrations exceeding established criteria. In contrast to classical POPs, South Korean environments were observed to be relatively more contaminated with emerging POPs, than were other countries. This is likely due to the recent dramatic economic growth of South Korea. However, to evaluate emission rates status and trends of contamination of South Korea further monitoring efforts should be performed, especially for the emerging pollutants.

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Chapter 3

Organochlorine Pesticides in China

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Abstract

DDT, HCH, toxaphene, HCB, chlordane, heptachlor, and mirex were produced in China. Historically, there were about 60 POP pesticide-producing enterprises located in 18 provinces in China. The accumulated output of DDT, toxaphene, and HCB were 459,000, 20,660, and 79,278 MT, respectively, while the accumulated output of HCH was 141,366 MT during 1990-2003. In the 1980s, China set up the legal framework for controlling organochlorine pesticides, and the production and use of organochlorine pesticides for agriculture were banned. Presently, DDT and HCH can still be detected in air, water, sediment, field soil, grains, vegetables, fruits, meat, animals and human tissue in many areas, although their concentrations are lower than the relevant standards.

3.1. Institutional, policy, and legal framework for organic pesticides in China

3.1.1. Environmental policy, sustainable development policy, and general legislative framework

Environmental protection is one of the basic national strategies of China, as well as one of the basic functions of government at various levels. Since 1980, China has successively established agencies for environmental protection at central, provincial, municipal, and county levels. The environmental protection, supervision, and management system has gradually improved. According to environmental protection and other relevant laws and regulations, the environmental protection bureaus at various administrative levels shall be responsible for the overall supervision and management of the environmental protection within their jurisdiction, and other relevant agencies shall exercise supervision and management over pollution prevention within the scope of their responsibility. The local governments shall be responsible for the environmental

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quality within their jurisdictions. Chinese environmental policies mainly include:

(a) Prevention first and combining prevention with control. Environmental impact assessment and a "3-simultaneous" system should be carried out for new or expanded projects or regional development projects to reduce generation and discharge of pollutants. The existing polluters are required to declare, register, and apply for permits for pollution discharge and to pay pollution discharge fees. The government at the county level or above should take legal measures to make serious polluting enterprises treat pollution within a definite time limit.

(b) The principle of "polluters treat pollution". Chinese laws state that polluters shall bear the responsibilities of pollution treatment and ecological restoration. According to the Law on Prevention of Environmental Pollution Caused by Solid Waste, if the accountable units or individuals do not properly dispose of hazardous wastes, the department of environmental protection at the county level or above can designate other competent entities to make proper disposal, and the accountable units or individuals shall pay all associated costs.

(c) Strengthen environmental monitoring and management. Rules for environmental supervision and management should be established and improved. The public participation in environmental supervision and management should be encouraged and supported. Posters and information on national and local environmental status should be published periodically. Air quality and water quality in key basins should be published. Environmental hotlines and a system for complaint letters and visits should be established. According to Interim Measures for Public Participation in Environmental Impact Assessment, the environmental impact assessments of special programs involving public interests and construction projects having potentially significant environmental impacts should include hearings and other forms of communication to collect the views of stakeholders.

After the 1992 United Nations Conference on Environment and Development, the Chinese government developed its own strategy for sustainable development called China's Agenda 21. The strategy advocates sustainable development by industrial policies, including:

(a) Adjust the industrial structure by limiting or forbidding the production and use of equipment and industrial processes that are characterized by high consumption and pollution and are inconsistent with the industrial policies. The State Council Decision on Several

Environmental Protection Issues of 1996 required closure of 15 types of small-scale enterprises. The 2005 Guiding Catalog of Industrial Structure Adjustment issued by the State Development and Reform Commission classified more than 1,000 specific industries into categories of support, limitation, and phaseout. Persistent organic pollutants (POPs) were classified into the limitation or phase-out categories.

(b) Establish and implement policies for saving resources and improving the efficiency of resource and energy use. Related laws and regulations were enacted to require comprehensive use of resources and reduction of resource waste in the aspects of water, electricity, coal, minerals, land, forest, grassland, ocean, and climate and to support the enterprises and the society to recover and reuse waste resources. Related departments are drafting some special regulations such as Regulations on Comprehensive Use of Resources, Regulations on Recovery and Treatment of Waste Electric Appliances and Electronic Products, Regulations on Recovery and Reuse of Waste Tires, and Management Methods for Recovery and Reuse of Packaging Materials. In addition, some technical standards and codes for energy efficiency of energy-consuming equipment, a water drawing quota of water-consuming sectors, energy-saving design of energy-consuming sectors, and labeling of reusable products are being developed.

(c) Promote cleaner production and a recycling economy and accelerate the change of the economic growth manner. The Cleaner Production Promotion Law was enacted and came into effect in July 2003. The State Council issued Guidance on Acceleration of Development of Recycling Economy in July 2005. The State Development and Reform Commission, together with the State Environment Protection Administration, supervises, guides, and inspects the national implementation of the recycling economy. Metallurgy, nonferrous metal, electricity, coal, petrochemistry, chemical industry, building material, light industry, textile, and agriculture are determined as key sectors for development of the recycling economy, and specific targets have been established. The program for development of the recycling economy is under expedited preparation, and the recycling economy legislation has been initiated.

The Guideline of the 11th National Five-Year Program and the State Council Decision on Intensification of Environmental Protection emphasized socio-economic policies closely related to environmental protection, including boosting the optimization and upgrading of industrial structure, promoting regional harmonious development, and building a resource-economy and environment-friendly society. Optimized development should be conducted in regions that have limited environmental capacity and natural resources but a better-off economy. Environmental concerns should be treated as a priority. Technologies should be supported that optimize the industrial structure and accelerate the upgrading of the industries and products, as well as take the lead in reducing the total discharge of pollution and attaining growth with less pollution. Control of POPs, particularly the control of dioxin pollution, is consistent with the goals of these strategies and policies.

The Guideline of the 11th National Five-Year Program also put forward the strategic objective to build a new socialist countryside. It supports the development of modern agriculture and the application of advanced agricultural technologies, including scientific and proper application of chemical fertilizers and pesticides and extensive adoption of biological control of plant diseases and pests. These techniques are conducive to reducing, eliminating, and preventing pollution that results from intentional production and use of POPs.

China has established a policy and legal framework for environmental protection, which includes these levels: (1) the provisions related to environmental protection and resources in the Constitution; (2) the comprehensive law on environmental protection, viz. Law on Environmental Protection; (3) the thematic laws on environmental protection and pollution control (Table 3.1); (4) the administrative regulations on

Table 3.1. Existing laws on environmental pollution control and protection in China

Prevent and control environmental pollution	Protect the ecology	Protect natural resources
Law on air pollution prevention and control	Law on wild animal protection	Law on land management
Law on water pollution prevention and control	Law on water and soil conservation	Law on mineral resource
Law on the prevention and control of pollution from solid wastes	Law on prevention and control of desertification	Coal law
Law on noise pollution prevention and control		Water law
Law on the protection of the marine environment		Forest law
Law on environmental impact assessment		Prairie law
Law on the promotion of cleaner production		Fishery law
		Law on energy saving

environmental and resources protection; (5) the departmental regulations on environmental and resources protection; (6) the local regulations on environmental and resources protection; and (7) international treaties of resources and environmental protection China has approved of or acceded to. In addition, China has also set up comprehensive standards for resources and environmental protection.

3.1.2. Existing laws and regulations on pesticidal POPs

The Environmental Protection Law is a comprehensive law on environmental protection. Article 33, which is directly related to management of POPs, states, "The production, storage, transportation, sale and use of toxic chemicals and materials containing radioactive substances must comply with the relevant state provisions so as to prevent environmental pollution." In addition, the Law on the Prevention and Control of Water Pollution, the Law on the Prevention and Control of Air Pollution, the Marine Environment Protection Law, the Law on Environmental Impact Assessment, and the Law on the Prevention and Control of Environmental Pollution by Solid Wastes have all put forward pollution prevention requirements. Previous experience can also be used in the management of POP-like materials. Presently, China has no laws that specifically address management of POPs.

Currently, the Regulation on the Safety Management of Hazardous Chemicals issued in 2002 is closely related to POP management. It provides detailed regulations on the production, operation, use, import and export, and key hazardous source monitoring and management of hazardous chemicals. POP production falls under the management scope of these regulations:

Production of POPs: In accordance with the provisions of the Regulation on the Safety Manage ment of Hazardous Chemicals, a permit system is applied to the manufacturing and operation of POPs. In order to implement this management system, relevant government organizations issued the Measures for Permit Administration of Hazardous Chemicals in 2002, the Measures for Implementation of Work Safety Licenses of Hazardous Chemical Production Enterprises in 2004, and Measures on Safety Inspections of Construction Projects of Hazardous Chemicals in 2005.

Use of POPs (production sites): The management on the use (production sites) of hazardous chemicals shall observe the Regulations on Labor Protection in Workplaces Where Toxic Substances Are Used promulgated in 2002, the Provisions on the Safe Use of Chemicals in Workplaces promulgated in 1996, and the Occupational Exposure Limit for Hazardous Agents in the Workplace (GBZ2-2002).

Import and export of POPs: China follows the London Guidelines for the Exchange of Information on Chemicals in International Trade, the Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade, and other international conventions and trade regulations. The country has also implemented an import and export registration system. It mainly observes Environmental Management on the First Import of Chemicals and the Import and Export of Toxic Chemicals promulgated in 1994 and Detailed Rules on Implementing the Registration of the Environmental Management on the First Import of Chemicals and the Import and Export of Toxic Chemicals promulgated in 1995. In 2005, the State Environmental Protection Administration of China (SEPA) enacted Notice No. 65, the List of Toxic Chemicals Banned in Export and Import. Such substances include DDT, HCB, chlordane, and mirex. In December 2005, the Ministry of Commerce, General Administration of Customs, and SEPA jointly promulgated Notice No. 116, List of Goods Prohibited from Import (Sixth Group) and List of Goods Prohibited from Export (Third Group). Dieldrin and endrin were added on the List of Substances Prohibited from Import, and aldrin, dieldrin, endrin, heptachlor, and chlorinated camphene are on the List of Substances Prohibited from Export.

Packaging of POPs: China has adopted a designated manufacturer management system for POPs. It promulgated Hazardous Chemical Packing Material and Container's Labeling Manufacturing Management Means in 2002. Relevant standards include General Rules for Precautionary Labeling for Industrial Chemicals (GB6944-2005) and Labels for Packages of Hazardous Goods (GB190-1990).

Storage of POPs: Related enterprises shall establish storage facilities meeting relevant conditions and also that meet the requirements of Rule for Storage of Hazardous Chemicals (GB15603-1995). For new construction, renovation, or expansion projects of such facilities, the Chinese government shall impose a strict approval system. To this end, Measures on Safety Inspection of Construction Projects for Production and Storage of Hazardous Chemicals were issued in 2005.

Transportation of POPs: Relevant departments have formulated related provisions for railway, waterway, and highway transportation of POPs. These provisions include Rules Concerning the Railway Transport of Hazardous Goods, Rules Concerning the Waterway Transport of Hazardous Goods, and Provisions on the Administration of the Road

Transport of Hazardous Goods, as well as General Specifications For Transport Packages of Hazardous Goods (GB12463-1990).

Wastes containing POPs: China has listed wastes containing POPs in the Catalogue of Hypertoxic Chemicals as hazardous wastes, under the management of the Prevention and Control of Pollution of the Environment by Solid Wastes, the Measures on Prevention of Environmental Pollution Caused by Hazardous Waste, and the Technical Specifications for the Prevention and Control of Pollution Caused by Hazardous Waste. China implemented related provisions in the Measures for the Administration of Permits for Operation of Hazardous Wastes for business activities related to wastes containing POPs. Such provisions are in the List of Goods Prohibited from Import, Provisional Regulations on Environmental Protection. In cases of waste importation, Measures on the Management of Duplicated Forms for Transfer of Hazardous Wastes and the Basel Convention shall be observed for the import and export of wastes containing POPs. To prevent environmental pollution caused by wastes containing POPs, the Chinese government has formulated and implemented a series of standards, including Identification Standards for Hazardous Wastes, Standard for Pollution Control on Hazardous Waste Storage, Standard for Pollution Control on the Security Landfill Site for Hazardous Wastes, and Standard for Pollution Control on Hazardous Waste Incineration.

Sites contaminated by POPs: The Methods for the Prevention and Control of Environmental Pollution Caused by Abandoned Hazardous Chemicals promulgated and implemented in 2005 states that if hazardous chemical production, stockpiling, and consuming units want to change the line of production, stop production, close off, or dissolve, they should report the environmental restoration program to the environmental protection department above the county level. Upon obtaining the approval of the department, the contaminated sites shall be restored within a stipulated time period.

The Administrative Regulations of the People's Republic of China on Pesticides made specific regulations on pesticide production, import and export, operation and use, and established a corresponding management system, including a pesticide registration system and pesticide production permitting system. The regulations are also applicable to pesticide-related POPs management. As a responsible country, China has been very supportive of international environmental conventions. Since the 1980s, the Chinese government has joined more than 30 international treaties on environmental and resources protection, including the Stockholm

Convention on Persistent Organic Pollutants, the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal, and the Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade.

On May 23, 2001, the Chinese government signed the Stockholm Convention on Persistent Organic Pollutants. The 10th Standing Committee of the National People's Congress approved the decision to accede to this convention on June 25, 2004, and the convention came into effect in China on November 11, 2004.

The Chinese government signed the Basel Convention on March 22, 1990, which came into force in 1992. The Law on Prevention of Environmental Pollution Caused by Solid Waste, promulgated in 1995 and revised in 2004, prohibits other countries from dumping, stockpiling, or disposing of solid wastes in China's territory, and implements administrative and criminal punishment over illegal solid waste import. Industry and local government will also construct facilities for disposal of hazardous waste in line with the Basel Convention.

The Rotterdam Convention, which was signed by the Chinese government on August 24, 1999 came into effect in China on June 20, 2005. For implementation of the Rotterdam Convention, the Chinese government has taken a number of effective measures and actions, including accomplishing specific tasks of convention implementation, actively participating in international activities and work related with the convention, substituting severely hazardous pesticides, and strengthening capacity building in risk assessment of pesticides.

3.2. History of manufacturing, industrial applications, and emission sources

Organochlorine pesticides were predominantly used during the 1950s–1970s in China. DDT, HCH, toxaphene, HCB, chlordane, heptachlor, and mirex used to be produced in China. Historically, there have been $\sim$60 POP pesticide-producing enterprises, which were located in 18 provinces in China.

The production and use of most POP pesticides have been prohibited in China, but DDT, HCB, chlordane, and mirex were still in production and use in 2003. DDT is used as an intermediate for producing Dicofol, anti-fouling paint, as an ingredient in some mosquito-repellent incense, and for malaria prevention (including export). HCB is never used as a pesticide in China, but it is used as an intermediate to produce sodium pentachlorophenol (Na-PCP), which is used extensively to kill snails in those places where schistosomiasis prevails. Owing to their specific characteristics, chlordane and mirex are still used to prevent and kill termites, and small amounts are used in agriculture, sericulture, and to kill cockroaches. Tables 3.2 and 3.3 summarize the basic status of POP pesticides in China.

3.2.1. DDT

In China, the production of DDT started in the 1950s and there are 11 DDT producers in China. Until now the accumulated output of DDT

Table 3.2. Production and consumption of POP pesticides in 2003

Category	Output (MT yr^{-1})	Number of producers as of 2003	Total output (MT)	Consumption purpose
DDT	3236	2	459,000	Raw material for Dicofol, additives for paints and mosquito-repellent incense, and malaria prevention
HCB	3522	1	> 79,278[b]	Raw material for Na-PCP
HCH	1406	2	141,366[c]	Raw material for HCB, lindane for locust and wheat midge control
Chlordane	450	9	8673	Termite prevention
Mirex	9	5[a]	151	Termite and cockroach control

[a] All the enterprises that produce Mirex also produce chlordane.
[b] Total output during 1988–2003.
[c] Total output during 1993–2003.

Table 3.3. The basic status of other never-produced or already prohibited POP pesticides

Category	Status	The largest annual output (MT yr^{-1}, year)	Total output (MT)	Different consumption purposes
Toxaphene	Was produced, but production ceased in 1980s	3740 (1973)	20,660	Agriculture (foodstuff and cotton protection)
Heptachlor	Was produced, but production ceased in 1980s	11 (1968)	< 100	Crosstie (railway protection)
Aldrin		Researched but never produced		
Dieldrin		Researched but never produced		
Endrin		Never researched, never produced		

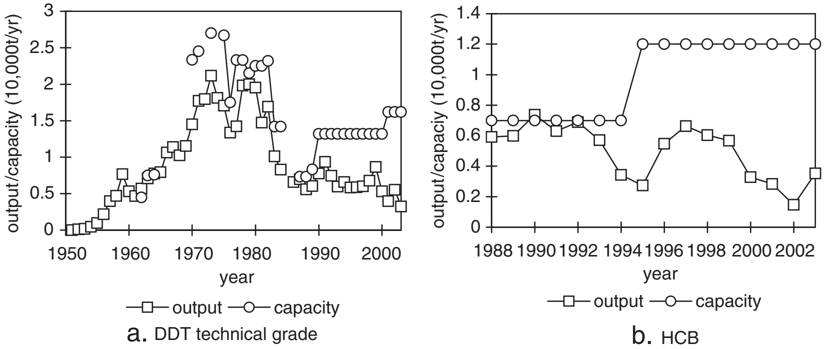

Figure 3.1. The output/capacity of technical grade DDT and HCB in China.

was ~459,000 MT (including 60,000 MT as raw material to produce Dicofol); the output of DDT in 2003 was 3236 MT. Figure 3.1 shows the annual output of DDT (Office for Stockholm Convention Implementation in China, 2004). The highest output of technical-grade DDT was 21,164 MT yr^{-1} in 1973. In March 1983, the State Council began to restrict the consumption of DDT in agriculture areas, and most plants subsequently stopped producing DDT. Since 1984, the annual output of DDT has never exceeded 10,000 MT. With the exception of an annual output of 8679 MT in 1999, the output of technical-grade DDT has been 5000–6000 MT since 1995, most of which is used to produce Dicofol. At present, only two plants are authorized to produce DDT: one is in Tianjin while the other is in Jiangsue Province where DDT is produced only as an intermediate for Dicofol production.

Before 1983, the Chinese government, under the planning economy policy, centrally controlled the production and marketing of pesticides. Individual plants had no right to sell or make other transactions regarding pesticides. After 1983, the Tianjin plant continued to produce DDT according to the quantity assigned by the former Ministry of Chemical Industry and sold DDT to appointed factories as a raw material to produce Dicofol, antifouling paint for ships, for mosquito-repellent incense, and for export. It is the only company that exports DDT. After the former ministry of Chemical Industry was repealed in 1998, the plant according to the relevant regulation issued by the State and the market demand determined the production and sale of DDT.

Before 1983, DDT was used as a pesticide in agriculture, forestry, and sanitation areas, part of which was used to produce Dicofol, and a small proportion of which was used to control termites. In agricultural areas, DDT was used to prevent migratory locusts, armyworms, acarids, aphids, phralidid caterpillars, and soil insects in orchards, paddy fields, and vegetable fields. For sanitation and epidemic prevention, DDT was used to kill mosquitoes, flies, cooties, fleas, bedbugs, cockroaches, etc.

After 1983, the Standing Committee of State Council decided to stop the application of DDT in agriculture. Thereafter, DDT was mainly used as a raw material to produce Dicofol, with a small portion consumed as raw material to produce paints, as additives to produce mosquito-repellent incense, and to prevent malaria. The Chinese Center for Disease Control and Prevention (CDC) has decided that DDT can be used in closed systems and indoor sites in small amounts to control disease vectors, but its outdoor use is forbidden to prevent pollution. Malaria control in China has been effective, and DDT has not been used by local CDCs since 2001. The sale and consumption of DDT in 2001 and 2002 are shown in Table 3.4. It is seen that 83.9% of DDT produced was used to produce Dicofol; 8.5% of that was exported for malaria prevention, 2.5% was used to produce mosquito-repellent incense, and 3.9% was used to produce paints. The investigation of consumption in 10 provinces and cities of China indicates that DDT is no longer used for agriculture or termite control, and a small portion of DDT is still used to prevent malaria. For example, 380 MT of DDT was used to control malaria between 1997 and 2000 in Yunnan province.

After 1983, most DDT produced was used to produce Dicofol. There were six Dicofol producers in China in 2003. The highest annual domestic output of Dicofol was 5613 MT in 1999, resulting in peak DDT consumption. The accumulative output of Dicofol was ~40,356 MT from 1988 to 2002, and the corresponding consumption of DDT was estimated as ~60,000 MT. The total output of Dicofol was 3345 MT in 2002.

Table 3.4. Domestic gross sales of DDT in 2001 and 2002 in China ($MT\,yr^{-1}$)[a]

Market	Purposes	2001		2002	
		Sales	Proportion (%)	Sales	Proportion (%)
Domestic	Dicofol	3341	78.5	3867	83.9
	Mosquito-repellent and others	208	4.9	113	2.5
	Anti-fouling paint for ships	152	3.6	180	3.9
Export	Malaria prevention	466	11.0	390	8.5
	Total	4254		4607	

[a] The data were provided by the producers. The final purpose has not been verified.

Table 3.5. Export volume of DDT from 1998 to 2003 (MT)

Content	Year					
	1998	1999	2000	2001	2002	2003
DDT	255.8	328.5	82.8	401.3	318.1	448.3

A certain amount of DDT is exported from China. In total, 1834.8 MT of DDT was exported during 1998–2002, as shown in Table 3.5. There is no DDT imported to China. DDT was mainly exported to Africa and Southeast Asia. The exported DDT was mainly used for malaria control, and a small portion was used to antisepticize woods.

There is a large volume of stockpiled or waste DDT in some DDT-producing sites, including those where DDT production has ceased for many years. Seven DDT producers have never cleaned their operating sites where DDT wastes still remain. These have become potential polluting sources.

3.2.2. HCB

China began to produce HCB in 1951, and there have been six HCB producers with a total output of 79,278 MT since 1988 (of which 78,323 MT was used to produce Na-PCP and PCP, accounting for 98.8% of the total output). The largest output volume of HCB of 7365 MT occurred in 1990. The HCB output was 3522 MT in 2003. Figure 3.1 illustrates the output of HCB from 1988 to 2002. After 1983, because the production of HCH was restricted, there remained only one HCB producer, which is located in Tianjin.

HCB is not used and has never been registered as a pesticide in China. As discussed above, it is used principally as an intermediate to produce pentachlorophenol (PCP) and Na-PCP in closed systems. After 1995, HCB was mainly used as an intermediate to produce Na-PCP. From 1988 to 2003, there was a cumulative output of 4840 MT of PCP (accounting for 5% of total output) and 104,323 MT of Na-PCP (accounting for 95% of total output) from the Tianjin plant. During this period, 793 MT of HCB (accounting for 1.2% of total output) was sold as raw material to produce fireworks and as reagents.

Na-PCP is highly effective in killing snails and is used extensively to kill them in places where schistosomiasis prevails. Na-PCP can kill mature snails, larva, eggs, the larva of a tapeworm, and the cercaria for disease vector control. Na-PCP is also registered as an herbicide and a timber preservative by some enterprises, and it is consumed for these purposes in some regions. Investigation shows that, after the largest output volume of 9049 MT in 1992, the output of Na-PCP decreased The Na-PCP output was 3,010 MT in 2003.

Without importing HCB, from 1998 to 2000, China exported 134.5, 112, and 9 MT of HCB, respectively, totaling 255.5 MT over these 3 years. However, HCB has not been exported since 2001.

3.2.3. HCHs

China began producing HCHs in 1951 in Shanghai. In 1983, HCHs were banned as pesticides for normal agricultural use, and only one producer in Tianjin continued producing HCHs as an intermediate of HCB. The production of lindane with a purity requirement of 99.5% began in 1982 in China. From 1986 until 1995, the former Ministry of Chemical Industry sanctioned another HCH plant in Shengyang to continue producing HCH only as the intermediate of trichlorobenzene; thereafter, the plant obtained permission to produce lindane for export. There were two plants producing HCH and lindane after 1986. The output of HCH and lindane decreased year after year, from 24,617 and 2260 MT, respectively, in 1996 to 1402 and 132 MT, respectively, in 2003.

In addition to the two lindane producers, there have been five plants that process lindane formulation in China. These plants were located in Henan Yuanyang, Anhui Woyang, Shenyang, Heilongjiang Pingshan, and Henan Anyang, but only one plant produces lindane products in 2003.

After the 1980s, γ-HCH was used to produce lindane; and other HCHs were mainly used as intermediates of HCB. There was no direct use of α- and β-HCH after the 1980s. Lindane was used for locust and wheat midge control. Three kinds of lindane formulation were registered in the pesticide registration information system of the Chinese Ministry of Agriculture for wheat midge and locust control: 1.5% powder, 6% powder, and 6% wettability powder.

Since 2000, sale of 1.5% lindane powder is approximately 700–800 MT yr^{-1}, whereas sale of 6% lindane powder is approximately 100–200 MT, much less than 1.5% lindane powder due to its higher price. The domestic use of raw lindane is estimated at approximately 16–24 MT in recent years. The main purchasers of lindane formulation from dealers in Shandong, Hebei, and Hennan province (the major areas that suffered wheat midge damage in China) and the end users are local farmers. The lindane is used for preventing wheat midge.China has exported lindane since the 1990s. The accumulated export amount is 1,861 MT (China Chemical Industry Yearbook).

3.2.4. Chlordane

Since the 1950s, China began to develop techniques to produce chlordane, and the production capacity and output steadily increased into the 1970s. The annual output of chlordane reached 465 MT in 1974, but chlordane production gradually stopped after 1975 due to faulty techniques and severe occupational harm to workers. However, the productive capacity of chlordane was rebuilt after 1988 because of a serious termite disaster in the south of China and the lack of effective and inexpensive termicides. There have been approximately 20 chlordane producers in China, but all of them were on pilot scale. In 2003, there were nine plants producing chlordane crude oil and emulsifiable solution in China, and six of them reported an output of 450 MT in total. Figure 3.2 shows the annual output of chlordane crude oil in China. It was shown that the output of chlordane was up to 834 MT in 1998, with a capacity of 1480 MT per year.

Before 1980, all the chlordane-producing enterprises were state-owned, and the central government managed sales. After 1988, most chlordane producers became privately owned, and their outputs were usually controlled by market demand. A statistical survey shows that usually 95% of Chlordane is used in houses and buildings to protect them from termite damage, 4% is used in clay embankment protection, and the rest (1%) is used to protect electric cables. Furthermore, there has also been a small amount of chlordane usage in sugarcane growing and sericulture operations.

The survey on the consumption of chlordane shows that there were differences in chlordane usage among different termite-affected provinces

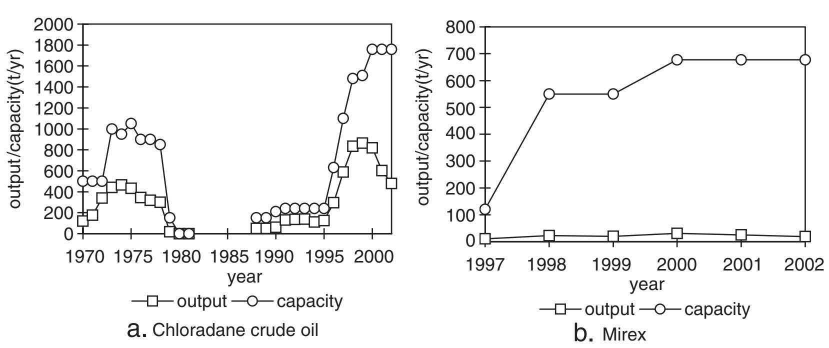

Figure 3.2. The output/capacity of crude oil chlordane and mirex in China.

from 1997 to 2001. Almost all of the 19 termite-affected provinces have used chlordane in termite control, except the City of Tianjin. Zhejiang province used the largest amount of chlordane, while Jiangsu, Guangdong, Sichuan, Jiangxi, Hunan, Guangxi, Anhui, Hubei, Fujian, Chongqing, Shanxi, Shanghai, and Shandong used moderate amounts. Hainan, Yunnan, and Liaoning used small amounts, and Beijing used the least amount. The amount of chlordane used peaked in 1999; thereafter, its consumption gradually declined due to the impact of the Stockholm Convention.

There has been no import or export of chlordane in China.

3.2.5. Mirex

Since the 1960s, China began to develop the techniques to produce mirex, but the output was kept at a low level for a long time. After 1975, due to faulty techniques and severe harm to artisans, mirex production gradually stopped. However, as was the case with chlordane, the production of mirex resumed after 1997 because of a serious termite disaster in the south of China. There had been seven mirex producers in China, five remained until 2003, and three of them reported a total output of 9 MT. Figure 3.2 shows the annual output and productive capacity of mirex by year. It can be seen that the productive capacity of mirex was much larger than the output. The output of technical-grade mirex reached its peak value of 31 MT in 2000, and the accumulative output of technical-grade mirex is 151 MT.

The existing mirex-producing enterprises are privately owned, and outputs are controlled by market demand. Most mirex is used to control and kill termites, ants, and cockroaches. It is estimated that ~20–30% of the total annual consumption of mirex is used for termite control, 10–20% for ant control, and the rest is used for control of other pests. In China, mirex is not used as a pesticide for agriculture, and the Chinese Ministry of Agriculture has never registered it. Mirex is the major termicide in termite control, and there is no viable alternative product yet. Fifteen termite-affected provinces have used mirex. Mirex was used mostly in Jiangxi, Guangxi, Fujian, Guangdong, Zhejiang and Jiangsu—all located in Southeast China, where termite damage is severe.

In addition, in the sanitation field, Shanghai, Jiangsu, Yunnan, Shanxi, and Guangxi once used mirex to kill domestic ants. There are no records of import and export of mirex after 1998.

3.2.6. Other POP pesticides

3.2.6.1. Toxaphene

In the early 1970s, toxaphene-producing facilities with a capacity of 1200 MT per year were built in China. This capacity reached 5930 MT per year in 1973, with 16 toxaphene producers and a maximal output up to 3740 MT. By 1985, the accumulative output of toxaphene was 20,660 MT.

Toxaphene was used to protect cotton and foodstuffs from damage by bollworms, red spiders, and aphids. Before 1980, toxaphene was uniformly purchased and sold by the government.

Since 1979, the output of toxaphene constantly reduced. In 1985, toxaphene production ceased due to its low efficiency in pest control, high toxicity to fish, and inconsistent quality.

According to the Memorandum of Registration of Pesticides, during the period from May 1990 to May 1995, toxaphene was approved by the Ministry of Agriculture to be registered as an agricultural pesticide. It was regulated to protect cotton, forests, and maize from pests and soil insect damage by spraying and soaking of seeds. In 1996, the ministry repealed the registration of toxaphene as an agricultural pesticide and stopped its production and use.

3.2.6.2. Heptachlor, aldrin, and dieldrin

In China, heptachlor was produced mainly between 1967 and 1969. The accumulative output was 17 MT. Thereafter, small-scale heptachlor production continued until 1978, when it was stopped due to high toxicity and poor environmental condition at the production sites. In 1978, the heptachlor-producing equipment was disassembled, and the sites were cleaned up. Currently, heptachlor is generated as a by-product of chlordane production.

Historically, heptachlor was mainly used to prevent termite damage to railroad crossties. However, it has never been registered or used as a pesticide in agriculture in China.

Aldrin and dieldrin have never been produced industrially in China but were produced on a pilot scale for termite control. Endrin has never been produced in China. Both aldrin and dieldrin are agricultural pesticides, which can prevent the damage caused by soil insects, such as termites, locusts, moths in wood, etc. However, the Ministry of Agriculture has never approved the registration and use of aldrin and dieldrin as agricultural pesticides. The application of dieldrin was concentrated in

Zhejiang, Shanghai, and Guangdong, and the use of aldrin was concentrated in Shanghai, Guangdong, Chongqing, and Shanxi.

According to data from the Customs General Administration, China did not import and export any toxaphene, heptachlor, aldrin, or dieldrin.

3.2.7. Summary

(1) China had produced many kinds of POP pesticides, i.e., DDT, HCB, HCH, chlordane, mirex, toxaphene, heptachlor, aldrin, and dieldrin, although some were produced only tentatively and on a very small pilot scale. While endrin has never been produced in China, DDT, HCH, HCB, toxaphene, and chlordane have been produced in relatively large amounts.

(2) There were ~60 enterprises, which have produced POP pesticides in the past. There are still two enterprises producing technical-grade DDT, and a few are producing chlordane and/or mirex.

(3) The pollution in pesticide production is serious due to faulty technology and a lack of pollution prevention technology. These problems include: DDT powder dust pollution from the production of soluble DDT powder; polluted mud in sink pools and other dangerous wastes containing obsolete acids and wastewater generated during DDT production; leakage of DDT during the production of Dicofol when the sacks containing DDT are torn open and fed into equipment; and remnants of DDT in Dicofol. It is necessary to improve the environmental regulations and standards and to adopt clean production and technology for preventing pollution.

(4) Most former manufacturers in China have dismantled their equipment and roughly cleaned the stockpiles and wastes of POP pesticides. However, there was no regulation on clean-up and remediation of the former operating fields during that time.

(5) Before the 1980s in China, DDT and toxaphene were extensively used as agricultural pesticides. After 1983, DDT was banned as an agricultural pesticide, but it is still allowed for disease vector control. The production and use of toxaphene stopped in 1985. Chlordane was registered as an agricultural pesticide prior to 1992. Chlordane is still used in termite control, and a small fraction is consumed for seed soaking and sericulture. Mirex is widely used to control termites and cockroaches. China has never used or has stopped using toxaphene, heptachlor, aldrin, dieldrin, and endrin.

3.3. Research on POP pesticides

3.3.1. Atmosphere

3.3.1.1. General description

Besides the spray drift during the application of pesticides, the organochlorine pesticides in air could also come from the exchange between air and polluted water or soil. Due to their persistence and semi-volatility, organochlorine pesticides could be transported over long distances after entering the atmosphere and thus contribute to the organochlorine pesticide pollution in areas far from the emission sites, such as in the Arctic and the Mt. Everest (Li et al., 2006). The long-distance transport of POPs plays an important role in their global distribution. However, studies on airborne POP pesticides in China are very limited. As a result, available data are scarce. Due to the diffusivity of air, spatial differences in the air concentration of POP pesticides are very small compared to other media.

3.3.1.2. Atmospheric pollution of POP pesticides in China

The POP pesticides in the atmosphere can exist in gaseous or particulate phases. In China, studies on persistent pesticides in the atmosphere mainly focus on particles. For example, from 1994 to 1995, Cheng et al. (2000) analyzed the compositions and concentrations of organochlorine pesticides from aerosol samples collected in industrial, chemical industrial, commercial, traffic, and "clean" (i.e., considered non-polluted) districts in Guangdong, Shenzhen, Zhuhai, and Hong Kong, as well as smoke samples from a restaurant in Guangzhou. Twelve organochlorine pesticides, including six DDTs and metabolites, three HCHs, dieldrin, and heptachlor were detected in the aerosol and smoke samples from the study areas. The concentration of DDT and its metabolites in aerosols collected in Hong Kong and Shenzhen was relatively low ($3.97–7.01\,\mathrm{pg\,m^{-3}}$), compared to $65.07–112.70\,\mathrm{pg\,m^{-3}}$ in aerosol samples collected in Zhuhai and Guangzhou and smoke samples from a Guangzhou restaurant (Cheng et al., 2000).

Tong et al. (2000) used a five-stage sampler and collected and measured organochlorine pesticides in airborne particles with different sizes ($>7.0\,\mu\mathrm{m}$–7.0–$3.3\,\mu\mathrm{m}$, 3.3–$2.0\,\mu\mathrm{m}$–2.0–$1.1\,\mu\mathrm{m}$, and $<1.1\,\mu\mathrm{m}$). Samples collected in residential and traffic areas in Huhehaote during the winter and summer of 1996 were compared. The results showed that organochlorine pesticides (HCH and p,p'-DDE) were found on airborne particles of all sizes. The mean concentration of HCH was $0.502\,\mathrm{ng\,m^{-3}}$ in winter and 1.070 ng m^{-3} in summer, and the *p,p′*-DDE concentration was 0.085 ng m^{-3} in winter and 0.108 ng m^{-3} in summer. The air concentrations of organochlorine pesticides in Huhehaote were higher in summer than in winter. Distribution of organochlorine pesticides on particles of different diameters showed that ~30.6–70.5% of the organochlorine pesticides were associated with fine particles ($<1.1\,\mu m$) in winter, while in summer the organochlorine pesticides were distributed on five sizes of particles. The total HCH concentrations were close to that found in samples collected in Stockholm of Sweden in 1986 (Bidleman et al., 1987) but lower than those measured in Paris in 1992–1993 (Cheveruil et al., 1996). The *p,p′*-DDE concentrations were also close to those measured in Mexico Bay in 1977 (Glam et al., 1980) and were higher than those measured more recently in Stockholm and Paris (Tong et al., 2000).

In China, measurements of gas-phase POP pesticides are very limited. Qiu et al. (2004) analyzed organochlorine pesticides in air samples collected in the Taihu Lake region in July-August 2002. α-HCH, β-HCH, γ-HCH, HCB, Heptachlor, α-endosulfan, *p,p′*-DDT, *p,p′*-DDE, *p,p′*-DDD, and *o,p′*-DDT were detected in the samples, with average concentrations of 74, 47, 46, 47, 53, 307, 124, 212, 36, and 767 pg m^{-3}, respectively. While the concentrations of HCH and HCB in the Taihu Lake region were lower than those measured in the Great Lakes (McConnell et al., 1993, 1998) and Lake Baikal (McConnell et al., 1996), concentrations of DDTs were much higher. It is worth mentioning that not only were DDT concentrations high in the Taihu Lake region, but also the average ratio of *o,p′*-DDT/*p,p′*-DDT was as high as 6.3, and the average ratio of *p,p′*-DDE/*p,p′*-DDT was as high as 1.8. This indicates that there could be new sources for *o,p′*-DDT and *p,p′*-DDE. Dicofol has been proposed as a new source of DDTs and its contribution to current DDT pollution in China has been estimated. (Qiu et al., 2005).

While studying the global fate and transport of POPs, Iwata et al. (1993) measured POPs in the atmosphere over the South China Sea and the East Sea and detected HCH, chlordane, DDTs, and PCBs. The concentrations of ΣDDTs in the East and South China Sea were 2.9–43 and 7.8–140 pg m^{-3}, higher than the concentrations measured in the Bering Strait, North Atlantic, and the East Indian Ocean, while close to those measured in the Mediterranean Sea, Red Sea, and Mexico Bay andlower than those measured in the Strait of Malacca and Bengal Bay (Iwata et al., 1993).

Besides gas and particulate phases, samples of precipitation collected in the 1980s in a number of cities in China were analyzed for organochlorine pesticides. For example, Zhao et al (1985) and Yang and Zhang (1987) detected HCH and DDT in rain samples collected in Shijiazhuang and

Wuhan. The concentrations of ΣDDT were in the range of ND-30 $\mathrm{ng\,l^{-1}}$ (Zhao et al., 1985; Yang and Zhang, 1987).

In addition to direct measurement of POPs in air, particles, and rainwater, there is an indirect measurement method using concentrations of POPs in pine needles to describe the POP pollution in the air. Recently, pine needles have been used as a bio-indicator in air pollution research. Xu and Zhong (2002) measured concentrations of HCH and DDT in pine needles from the north, east, south, and southwest of China. The results showed that the concentrations of HCH in pine needles ranged from 24.7 to 35.5 $\mathrm{ng\,g^{-1}}$ dry weight, 14 and 10 time higher than those measured in Sweden and France. Among the four HCH isomers, β-HCH had the highest concentrations and accounted for 38–46% of total HCH. The concentrations of ΣDDT in pine needles were in the range of 6.0–12.6 $\mathrm{ng\,g^{-1}}$ dry weight, 34 and 8 times higher than those reported in Sweden and France. The ratio of DDE/DDT was 1.1 in North China, but was <1 in South and Southwest China, which indicated new inputs of DDT to the air in these regions. However, compared to concentrations of organochlorine pesticides in pine needles in the north of China in the 1980s, concentrations of HCHs and DDTs decreased to 99% and 90%, respectively, which could reflect the effectiveness of the 1980s ban on agricultural use of organochlorine pesticides (Xu and Zhong, 2002).

Currently, there are no air quality standards for pesticide POPs in China. Measurement results can only be evaluated by comparing them with results from other countries and regions. Using DDT as an example, Table 3.6 summarizes measurement results of air concentrations of pesticide POPs in recent years in China.

3.3.1.3. *Summary*

The research on persistent pesticides in the atmosphere has focused on the gas phase, particulate phase, rainfall, and pine needles. In China, there are only a limited number of studies on POP pesticides in the atmosphere, and these focus mainly on airborne particles. The spatial difference in concentration of persistent pesticides in air is small due to diffusion and transport. Since the agricultural ban on use in 1983, the concentration of POP pesticides in the atmosphere has decreased dramatically in China. In some regions, however, the concentrations of pesticide POPs in the atmosphere are unusually high, particularly for DDTs, which indicates that there might be new sources of POPs in these regions, such as Dicofol. In China, no environmental quality standards about pesticide POPs in the atmosphere have been established.

Table 3.6. Pesticide POPs concentrations in the atmosphere of China (exemplified by DDTs)

Regions	Type	Monitoring time	POPs measured	ΣDDTs (pg m^{-3})	References
Guangzhou plant	Aerosol	1994–1995	α,β,γ-HCH, *o,p′*-DDT/DDD/DDE, *p,p′*-DDT/DDD/DDE, heptachlor, dieldrin	109.38	Cheng et al. (2000)
Shenzhen plant	Aerosol	1994–1995		7.01	Cheng et al. (2000)
Shenzhen downtown	Aerosol	1994–1995		3.97	Cheng et al. (2000)
Zhuhai school	Aerosol	1994–1995		65.07	Cheng et al. (2000)
Hong Kong shore	Aerosol	1994–1995		6.56	Cheng et al. (2000)
Guangzhou restaurant	Cooking smoke	1996		122.07	Cheng et al. (2000)
Huhehaote winter	Particle	1996	α,β,γ-HCH, *p,p′*-DDE	85 (41–134)	Tong et al. (2000)
Huhehaote summer	Particle	1996		108 (72–138)	
Tianjin downtown	Particle	2002	α,β,γ,δ-HCH, *p,p′*-DDT/DDD/DDE	1874	Wu et al. (2003)
Taihu region	Air	2002	α,β,γ-HCH, *o,p′*-DDT, *p,p′*-DDT/DDD/DDEHCB, heptachlor, α-endosulfan	1139	Qiu et al. (2004)
East China Sea	Air	1989–1990	α,γ-HCH, *o,p′*-DDT, *p,p′*-DDT/DDE, chlordane, PCBs	19 (2.9–43)	Iwata et al. (1993)
South China Sea	Air	1989–1990		54 (7.8–140)	
North China, South China, Southwest China	Pine needle	2001	α,β,γ,δ-HCH, *p,p′*-DDT/DDD/DDE, chlordane, heptachlor, aldrin	1.5–12.1 ng g^{-1}DW	Xu and Zhong (2002)
Beidaihe		1982	HCH		Mo et al. (1984)
Shijiazhuang	Rainfall	1981–1983	α,β,γ,δ-HCH		Zhao et al. (1985)
Wuhan	Rainfall	1984	α,β,γ,δ-HCH, *o,p′*-DDT	ND–30 ng l^{-1}	Yang and Zhang (1987)

3.3.2. Water

3.3.2.1. General description

The POP pesticides are hydrophobic compounds with low water solubility. However, natural waters play an important role in the transport and transformation of POPs, because similar to air, water is capable of transporting POPs through convection to areas far from application sites, such as β-HCH found in the Arctic. More importantly, water is essential for humans and all living species and is closely related to their activities. Aquatic mammals are the species most seriously endangered by POP pollution of natural waters. Fish and shellfish are important pathways for POPs to enter the human body through diet. Aquatic ecosystems are very influential on human beings. Therefore, water pollution by pesticides has generated wide concern.

The main pathways of the POP pesticides that enter water include drift during field application, air-water diffusion, dry and wet deposition from the atmosphere, discharges of polluted wastewater, and exchange between groundwater and sediments. Water, suspended particles, living species, and sediments are often monitored separately. In this section, pollutants in the water phase and pore water are summarized. Suspended particles and sediments will be described in Section 3.3.4.

3.3.2.2. Water pollution by POP pesticides in China

Studies on water pollution by POPs can be categorized according to the water bodies studied, such as rivers, seas, and oceans; harbors, lakes, and reservoirs; and groundwater. They can also be categorized according to sample types, e.g., surface water, deepwater, surface micro-layer, and pore water in sediments. In China, extensive monitoring of pesticide POPs has been carried out in rivers, bays and harbors, and lakes. The results show that the spatial differences of pesticide concentrations in water are larger than that in air, but smaller than that in soil.

Rivers: Monitoring of organochlorine pesticides in rivers of China began relatively early. In 1976, Li (1985) measured concentrations of HCH and DDT in the water of the Hangu section of the Ji Canal. The discharge of wastewater from the Tianjin Chemicals Factory was responsible for ΣDDT concentrations in the upstream water of the canal that were as high as 21,900 ng l^{-1}. In 1977, the wastewater flow was diverted from the unpolluted stream. Consequently, the HCH and DDT concentrations in the river decreased significantly. In 1980, the ΣDDT concentration was as low as 69 ng l^{-1} (Li, 1985). Li et al. (1989) studied the Second Songhaujiang River in 1982, and Lang et al. (1993) studied the mid-section of the Songhuajiang River in 1984. The ΣDDT concentrations were typically ~10–100 ng l^{-1} (Li et al., 1989). In recent years, with the development of more sensitive monitoring techniques, other persistent pesticides, such as heptachlor and eldrin, have also been detected. Information about isomers and metabolites of HCH and DDTs has been obtained from detailed analyses. In May and December of 1998, Zhang et al. (2000a) detected eight pesticides, including DDTs, HCHs, dieldrin, endrin, and heptachlor in the downstream water of the Liao River. The ΣDDT concentrations were in the range of nd–4.16 ng l^{-1} (December) and 17.5–63.2 ng l^{-1} (May), which were much lower than the concentrations measured in the Ji Canal and the Songhuajiang River during the 1970s and 1980s. However, these levels were much higher than those measured in the St. Lawrence River of Canada in 1993, the Guadalquivir River in Spain in 1992, and the Swiss Ebro River in 1999 (Zhang et al., 2000a; Zhang and Dong, 2002).

From 1999 to 2001, with the support of the European Union, the Nanjing University and the Dalian Technology University collaborated with German and Australian institutions to carry out systematic monitoring of organochlorine pesticides in the Liao and Yangtze rivers. Various methods were used simultaneously to monitor DDTs, HCHs, dieldrin, aldrin, endrin, and heptachlor in the river water. The ΣDDT concentrations in the Liao and Yangtze rivers were 7.04 and 1.68 ng l^{-1}, respectively, with low spatial differences (China-EU Project Report, 2002). Studies on other rivers include Zhang et al. (1998) on the Hai River and the New Port River, Zhang et al. (1982) on the Xiangjiang River, Wang et al. (1986) on waste emissions in rivers in Beijing, and Zhang et al. (1982) and Wen (1990) on the Huaihe River.

Bays and Harbors: Due to close ties with human activities, the pollution by POP pesticides in bays and harbors is of great concern. In November 1994, Cai et al. (1997) studied concentrations and distributions of HCH and DDT during the dry season in the seawater of the Pearl River estuarine. The results showed the ΣDDT concentrations in surface and deep-sea water were 80 and 506 ng l^{-1}, respectively, slightly lower than that reported by Liao in 1983 (Cai et al., 1997). In 1999, Zhang et al. (2002) measured 18 organochlorine pesticides in surface waters at 15 stations and in pore water at 13 stations of the Jiulongjiang River estuarine. The results showed that the total concentrations of organochlorine pesticides in the surface water were in the range of 51.3–2479 ng l^{-1} and ΣDDT concentrations were in the range of 0.16–63.2 ng l^{-1}. ΣDDT concentrations in the pore water were in the range of 1.00–193 ng l^{-1}.

DDE was the main DDT, and its concentration accounted for more than 50% of the total DDTs. This indicates that DDT in the environment has mainly degraded to DDE. Besides DDT and HCH, methoxychlor/endosulfan sulfate, endrin, endosulfan, and dieldrin were found in relatively high concentrations. The pollution level was comparable with other harbors in China, while at a number of stations the water quality exceeded the first level of the National Water Quality Standard for organochlorine pesticides (HCHs and DDTs) (Zhang et al., 2001c). In July 1998, Zhang et al. (2000b) analyzed 18 organochlorine pesticides in surface water from nine stations of the West Harbor of Xiamen. The concentrations of organochlorine pesticides were in the range of 60–32.6 ng l^{-1}. The DDT concentrations were in the range of 0.95–2.25 ng–l^{-1}, with a mean of 1.45 ng l^{-1}. Aldrin, dieldrin, and heptachlor epoxide were also found in small amounts. The pollution level was relatively low compared to other harbors. The DDTs were ranked as DDT $>$ DDE $>$ DDD by decreasing concentration, indicating new emission of DDT in recent years (Zhang et al., 2000b, 2001c). In August 1999, Qiu et al. (2002) collected subsurface water in the Daya Bay and analyzed 18 organochlorine pesticides. The concentrations of total organochlorine pesticides were in the range of 143–5105 ng l^{-1}, with a mean value of 927 ng l^{-1}. The ΣDDT concentrations were in the range of 26.8–976 ng l^{-1}, with a mean value of 188 ng l^{-1}. The DDT/DDE + DDD ratio was relatively high, indicating that there were still emissions of DDT into the Daya Bay. Aldrin, dieldrin, endrin, endosulfan, heptachlor epoxide, and methoxychlor were also detected (Qiu et al., 2002). In July 1999, Lv et al. (2002) measured concentrations of 16 organochlorine pesticides in surface and micro-surface water of the Dalian Bay and the Liaodong Bay. The results showed that the average concentration of organochlorine pesticides in the surface water of the Liaodong Bay was 41.9 ng l^{-1}, much higher than that of the Dalian Bay (4.52 ng l^{-1}). However, the organochlorine pesticide concentrations of the two bays did not exceed the National Sea Water Quality Standard (GB3097-1997, State Ocean Administration, P. R. China). The organochlorine pesticide concentrations in micro-surface water of the stations in the Dalian Bay were significantly higher than those of the surface water, indicating micro-surface water could strongly concentrate organochlorine pesticides, with average concentration factors of 5.1–15.4 (Lv et al., 2002). Other estuarine studies include those on isomers of HCH and α-HCH enantiomer in the New Harbor (Zhang et al., 1998); HCH, DDT, and PCBs in the Yangtze River estuarine (Ye et al., 1991); some pesticides in the Minjiang River estuarine (Zhang et al., 1999); and others (Zhang, 1998; Ye et al., 1991; Zhang, et al., 2001c).

Other water bodies: During 1994–1995, Dou and Zhao (1996) measured HCH and DDT in the Beiyangdian Lake. The results showed that the concentrations of DDT and its degradation products were in the range of 0–900 ng l^{-1}, with a mean value of 250 ng l^{-1}, which are lower than the Chinese National Fishery Water Quality Standard. Compared to the measurement results of 1975–1977, the concentrations of organochlorine pesticides in water increased slightly, possibly due to the emission of wastewater from pulp and dye industry, as well as irrigation using wastewater (Dou and Zhao, 1998). Other water bodies investigated for organochlorine pesticides include the Guanting Reservoir-Yongding River in Beijing in 2000 (Kang et al., 2003), Taihu Lake in 1999 (Feng et al., 2003), Jingtang Reservoir in Liaoling province in 1997 (Yu et al., 2001), Fuxian Lake in Yunnan province in 1998 (Lin and Duan, 1999), and the Jiulongjiang River in Fujian province in 1989 (Lin and Huang, 1994). Table 3.7 summarizes monitoring results of pesticide POPs in water bodies in China (DDT concentrations are used as the example).

3.3.2.3. Summary

The number of studies on pesticide POPs in China is relatively large, and the studies covered different regions and water bodies. Since the ban on agricultural use in 1983, the concentrations of persistent pesticides in water gradually decreased. However, in some regions, the concentrations of POP pesticides in water still exceed the national water quality standards. Similar to the air, high concentrations of pesticide POPs were observed in some waters, such as Baiyangdian, Xiamen Harbor, and Daya Bay, indicating recent emission of pesticide POPs. Some POP pesticides such as DDT are included in the Chinese National Water Quality Standards for seawater, groundwater, fishery water, and drinking water, which could be used as the criteria when assessing the pollution level of POP pesticides in water.

3.3.3. Soil

3.3.3.1. General description

Soil is the main media for POP pesticide residues in the environment. Approximately 40–50% of pesticides deposited on soil during application, and 10–20% of the pesticides on the surface of plants will enter air and soil through volatilization and rainfall, respectively. Most of the

Table 3.7. Pesticide POP concentrations in water bodies of China (exemplified by DDTs)

Water area	Monitoring time	Depth	POPs	DDTs ($ng\,l^{-1}$)	References
Ji Canal (Hangu segment)	1976		DDTs, HCHs	21,900	Li (1985)
2nd Songhua River	1982		DDTs, HCHs, PCBs	71	Li et al. (1989)
Huai River	1986		DDTs, HCHs	ND	Wen (1990)
Hai River	1997	3 m	DDTs, HCHs, α-HCH enantiomer		Zhang et al. (1998)
Liao River	1998		DDTs, HCHs	ND–4.16	Zhang and Dong (2002)
Liao River	1998		DDTs, HCHs, dieldrin, aldrin, endrin, heptachlor	17.5–63.2	Zhang and Dong (2002)
Yangtse River (Nanjing segment)	1998		HCB, DDTs, HCHs, PCB	67 (1.57–1.79)	Jiang et al. (2000)
Liao River	1998–2000		DDTs, HCHs, dieldrin, endrin, heptachlor	7.04	China-EU Project report (2002)
Yangtse River	1998–2000		DDTs, HCHs, HCB, endosulfan, methoxychlor	1.68	China-EU Project report (2002)
Xiangjiang			HCHs		Zhang et al. (1982)
Pearl River Estuary	1994	Deep surface	α,β,γ,δ-HCH, *o,p*′-DDT, *p,p*′-DDT/DDD/DDE	87 (ND–236) 506 (ND–1220)	Cai et al. (1997)
Minjiang Estuary	1999		DDTs, HCHs, heptachlor, endosulfan	159 (89.1–234)	Zhang et al. (2003)
Xiamen harbor	1998	Surface	α,β,γ,δ-HCH, *o,p*′-DDT, *p,p*′-DDT/DDD/DDE, heptachlor, aldrin, dieldrin, endrin, endosulfan	1.45 (0.95–2.2)	Zhang et al. (2000)
Jiulongjiang Estuary	1999	Surface Pore water	DDTs, HCHs, methoxychlor, endosulfan, dieldrin.	12.8 (0.2–63) 31.1 (1.00–193)	Zhang et al. (2001c)
Jiulongjiang Estuary	2000	Surface	18 OCPs	19.24–96.64	Zhang et al. (2002)
Daya Bay	1999	0.5 m	DDTs, HCHs endosulfan, heptachlor, aldrin, dieldrin, endrin	188.4 (26.8–975.9)	Qiu et al. (2002)

Dalian Bay	1999	Surface	16 OCPs DDTs, HCHs, HCB, heptachlor, aldrin	1.01 (0.53–2.02)	Lv et al. (2002)
Dalian Bay		Micro-surface		3.16 (0.80–7.77)	Lv et al. (2002)
Liaodong Bay		Surface		8.19 (ND–36.16)	Lv et al. (2002)
Changjiang Estuary	1986		DDT, HCH, PCBs	0.18–1.58	Ye et al. (1991)
	1986			0.11–6.80	Ye et al. (1991)
Baiyangdian	1995		α,β,γ,δ-HCH, *o,p*′-DDD, *p,p*′-DDT/DDD/DDE	100	Dou et al. (1997)
Baiyangdian	1994–1995		α,β,γ,δ-HCH, *o,p*′-DDD, *p,p*′-DDT/DDD/DDE	250 (0–900)	Dou and Zhao (1998)
Taihu Lake	1999–2000		HCH, DDT	0.2–9.3	Feng et al. (2003)
Guanting reservoir–Yongding River	2000		DDTs, heptachlor, aldrin, dieldrin, endrin, etc.	ND–46.8	Kang et al. (2003)
Fuxian Lake	1998	Deep surface	DDTs, γ-666, etc.	ND	Lin and Duan (1999)
Jiulongjiang tidewater	1989	Tidewater	DDTs, HCHs	210–670	Lin and Huang (1994)
Beijing drainage river	1984		DDT, HCH	ND	Wang et al. (1986)
East China Sea	1989–1990	Surface	α,γ-HCH, *o,p*′-DDT, *p,p*′-DDT/DDE, chlordane, PCBs	16 (1.5–41)	Iwata et al. (1993)
South China Sea	1989–1990	Surface		6.9 (3.5–12)	Iwata et al. (1993)
Sea water quality standard	1997			DDTs < 50, HCHs < 1000	GB3097-1997
Drinking water quality standard	1985			DDTs < 1000, HCHs < 5000	GB5749-1985
Fishery water quality standard	1989			DDTs < 1000, γ-HCH < 2000	GB11607-1989
Groundwater quality standard	2002			DDT ⩽ 1000	GB3838-2002

Notes: Sea water quality standard (GB3097-1997), 1997, State Oceanic Administration, P. R. China. Drinking water quality standard (GB5749-85), 1985, Ministry of Health, P. R. China; fishery water quality standard (GB11607-89), 1989, State Environmental Protection Administration, P. R. China; surface water quality standard (GB3838-2002), 2002, State Environmental Protection Administration, P. R. China.

pesticides will enter soil when they are applied directly into the soil or in the form of soaked seeds. Combined with the fact of slow pesticide degradation in soil, soil becomes the most important reservoir for pesticide POPs and impacts on humans through agricultural crops.

Besides drift of pesticides during application, air-surface exchange, dry and wet deposition from the atmosphere, and groundwater are all pathways for POPs to enter soil. The sinks of pesticide POPs in soil include biochemical degradation, evaporation, and erosion. Because soil is a nonfluid media, the spatial distribution of pesticide POPs has large differences and is closely related to the application of pesticides, irrigation, and plant coverage.

3.3.3.2. Soil pollution of POP pesticides in China

Based on literature reports, in 1985, the average concentration of DDT in soil in China was at the level of 0.2–0.3 mg kg^{-1}. Since the 1983 ban on agriculture use of HCH and DDT, the concentration of DDT in soil has gradually decreased.

From 1999 to 2000, Feng et al. (2003) studied POP pesticides in soil at different depths in the Taihu Lake region. The DDT concentrations were in the range of 0.3–5.3 $\mu g kg^{-1}$ in the upper layer of soil (0–15 cm), 0.5–4.0 $\mu g\,kg^{-1}$ in the middle layer (16–30 cm), and 0–2.7 $\mu g\,kg^{-1}$ in the deep layer (31–50 cm). HCH had a similar vertical distribution pattern. The soil concentrations of POP pesticides were significantly less than the concentrations measured by Lin et al (2000) in the Yangtze River Delta (Feng et al., 2003). From 1993 to 1999, Zhao and Ma (2001a) measured DDT and HCH in soil from seven counties of the Ninbo district, the agricultural production base of Zhejiang province. The results showed that due to the wide application of DDT during a 5-year period in the 1980s, (600 tons of DDT were used from 1980 to 1984), DDT was detected in all types of soil for different crops in the Ninbo district. The average concentrations of DDT in different areas ranged from 0.002 to 0.764 mg kg^{-1}, and the average concentrations of HCH ranged from 0.0003 to 0.0152 mg kg^{-1}. The pollution level in some areas still exceeded the second level of the Chinese National Soil Environmental Quality Standards (GB15618-95) (Table 3.8). The study also indicated differences in POP pesticide concentrations exist for different types of soil and different types of cultivation (Zhao and Ma, 2001a). In 1989–1999, Zhang et al. (2001a) collected 186 soil samples from the green food production base in the Liaolin provinces of Shenyang, Yingkou, Dalian, Panjing, and Benxi and analyzed HCH and DDT. The results showed that the

Table 3.8. Pesticide POP concentrations in soil of China (exemplified by DDTs)

Regions	Monitoring time	Soil type	POPs	DDTs ($mg\,kg^{-1}$)	References
Ningbo	1993–1999	Vegetable, tea garden, dry and paddy fields	DDT, HCH	0.002–0.7644	Zhao and Ma (2001a)
Liaoming	1998–1999	Meadow soil, paddy soil	α,β,γ,δ-HCH, *o,p′*-DDT, *p,p′*-DDT/DDE/DDD	0.022–0.030	Zhang et al. (2001a, b, c)
Cixi	2001	Vegetable land	DDTs, HCHs	0.032	Wang et al. (2003)
Tianjin	2001	Wastewater irrigated area	α,β,γ,δ-HCH, *o,p′*-DDT, *p,p′*-DDT/DDE/DDD	0.628–2.840	Gong et al. (2002a)
Jiashan, Zhejiang	2001	Paddy soil	HCHs, DDTs, PCP-Na	0.049–0.1905	Zhao et al. (2002b)
Anhui	1988	Cropland	α,β,γ,δ-HCH, *o,p′*-DDT, *p,p′*-DDT/DDE/DDD	0.361 (0.018–4.43)	Yue and Hua (1990)
Inner Mongolia Grassland	1985	Grassland	DDT, HCH	ND	Wu et al. (1995)
Huhehaote	1986–1988	Garden	DDT, HCH	0.0046–0.852	Liu et al. (1991)
Shenyang	1987	Garden	DDTs, HCHs	0.53 (ND-2.92)	Niu et al. (1991)
Wu county Jiangsu	1982–1983	Cropland, woodland, grassland	DDTs, HCHs	0.147 (0.013–5.747)	Ma et al. (1986)
Suzhou	1980–1981	Paddy soil	HCHs		Liu and Ji (1983)
Heilongjiang	1978	Cropland	DDTs, HCHs	0.014–0.09	Dou et al. (1982)
Tianjin	1976	Cropland	DDTs, HCHs	0.037	Li (1985)
Shenyang	1979–1980	Garden, dry and paddy field	DDTs, HCHs	0.02–0.06	
South China	1980	Tea garden	DDTs, HCHs	0.05–0.361	Chen et al. (1986)
Soil quality standard	1995			Level 1: $\leqslant$0.05; Level 2: $\leqslant$0.5; Level 3: $\leqslant$1.0	GB15618-95

Note: Soil environment quality standard (GB15618-95), 1995, State Environmental Protection Administration, P. R. China.

concentrations of DDT and HCH were quite low, with DDT concentrations in the range of 0.022–0.030 mg kg^{-1}, while HCH concentrations ranged from 0.007 to 0.025 mg kg^{-1}. In addition, the pollution index was smaller than 1, indicating the soil was relatively unpolluted and met the national standard (Zhang et al., 2001a).

In 1985, Wu et al. (1995) collected soil samples in 15 villages in the Hulunbeier grassland of Inner Mongolia, and analyzed DDT and HCH. The results showed that the pollution level of pesticides in the Hulunbeier Grassland was low. HCH concentrations ranged from 0.0140 to 0.0574 mg kg^{-1}, and those of DDT were close to the detection limit (Wu et al., 1995). In contrast, in 2001 Gong et al. (2002a) studied soil from three agricultural fields in a wastewater irrigation area in Tianjin. DDT and HCH were detected, with average concentrations in the range of 0.628–2.84 mg kg^{-1} for DDT and 0.386–4.69 mg kg^{-1} for HCH. β-HCH and *p,p′*-DDE had concentrations of 4.67 and 1.42 mg kg^{-1}, respectively, which are the highest among the HCHs and DDTs. By comparison, the concentration of *p,p′*-DDE in an agricultural field in Alabama (U.S.) was only 0.052 mg kg^{-1}, and the average concentrations of β-HCH and *p,p′*-DDE in a paddy field in Korea were only 0.0008 and 0.00034 mg kg^{-1}. This indicated that in Tianjin the soil in the wastewater irrigation area, especially the soil on which vegetables were grown, was seriously polluted by organochlorine pesticides.

In 1988, Qiu et al. (2002) conducted research on DDT and HCH in agricultural soil of 16 counties in Anhui province. The average concentration of HCH in soil was 0.150 mg kg^{-1}, and the main compounds were α- and γ-HCH. At the provincial level, the average concentration of DDT in agricultural soil was 0.36 mg kg^{-1}, and the main compounds were *p,p′*-DDT and *p,p′*-DDD. The high concentrations of HCH and DDT in some areas indicated new pollution sources.

Other studies on pesticide POPs in soils include Wang et al. (2003) on soil used for vegetable production in Chixi; the Nankai University (1976) on soil used for grain production in the Han-Gu district in Tianjin; Zhao and Ma (2001) on paddy soil in the Jiashan County of Zhejiang province; Liu et al. (1991) on soil for vegetable production in rural areas of Huhehaote; Niu et al. (1991) on soil for vegetable production in Shenyang; Ma et al. (1986) on soil from Wuxian County of Jiangshu province; Liu et al. (1983) on paddy soil in Suzhou; and Dou et al. (1982) on soil of Heilongjiang Province. Table 3.8 summarizes recent monitoring results on pesticide POPs in soil in China (concentrations of DDT were used as the example).

3.3.3.3. Summary

There is a relatively small number of studies on persistent pesticides pollution in soil in China. The reported studies only cover a few regions and most of them were conducted 10–20 years ago. Since the 1983 ban on agricultural use, recent reported studies are even less and the concentrations of pesticide POPs in soil gradually decreased However, in some areas, such as wastewater irrigated fields and vegetable fields, the soil pollution caused by pesticide POPs was serious. This indicates the large spatial differences in concentration of pesticide POPs in soil. Until now, the reported studies are about agricultural fields, and no studies on pesticide POPs pollution of production and storage sites are reported. More attention should be paid to POP pesticides at polluted sites at local level. In addition, monitoring activities need to be strengthened in future implementation of the Stockholm Convention in China, to reduce risk to humans and the environment from pesticide POPs and for soil remediation.

3.3.4. Sediment

3.3.4.1. General description

Sediment is an important media for the transformation of POPs in the environment. Many years after production has ceased and the ban on the use of POP pesticides globally, research in other countries indicates that sediment has the highest concentrations of POP pesticides, as compared to soil, water, and air. Without emission sources of POP pesticides on land, sediment in some water bodies, especially inland lakes, became the source of POP pesticides in air and water. The recent research in China on sediments of inland lakes and costal areas has corroborated this finding.

Sediment can be divided into solid and liquid phases. The liquid phase is the pore water, which is discussed above in Section 3.3.2. In the following section, suspended particles and the solid phase of sediment will be described. Usually, studies on sediments and water bodies were carried out at the same time.

3.3.4.2. Studies on sediment pollution of POP pesticides in China

There are many studies on monitoring POP pesticides in sediments in China. In 1976, Li (1985) measured DDT and HCH in the sediment of the Han-Gu section of the Jiyun Canal. Because of the emission of wastewater from the Tianjin Chemicals Factory, the ΣDDT concentrations in the sediment of the Jiyun Canal were as high as 14,720 (150–179,000) ng g^{-1} (Li, 1985). Studies in the early 1980s on the mid-section of the Songhuajiang River and the Second Songhuajiang River found that the ΣDDT concentrations in sediment were in the range of 0.5–1 and 7.5–56.1 ng g^{-1} (Lang et al., 1993; Li et al., 1989). In recent years, with the further development of monitoring techniques, other pesticide POPs, such as heptachlor and eldrin, have also been detected. Information about isomers and metabolites of HCH and DDTs has also been obtained from detailed analyses. From 1999 to 2001, with the support of the European Union, the Nanjing University and the Dalian Technology University collaborated with German and Australian institutes to carry out systematic monitoring of organochlorine pesticides in the Liao and Yangtze rivers. Various methods were simultaneously used to monitor DDTs, HCHs, dieldrin, aldrin, endrin, and heptachlor in river sediment. The results showed that the main pollutants in the upper layer of the sediment were HCB and its metabolites, pentachlor, and metabolites of DDT. The concentrations of other persistent pesticides were low. The ΣDDT concentrations in sediment of the Liao and the Yangtze rivers were 0.84–6.93 and 3.24 ng g^{-1}, respectively, much lower than those of the Jiyun Canal and the Second Songhuajiang River, and comparable to those of Simbrirzzi Lake in Italy (1998) and the Ebro River in Switzerland (1999). Compared to the relatively homogeneous distribution in water, the organochlorine pesticide pollution in sediment is quite different for different water bodies, indicating differences in deposition of suspended particles (China-EU Project Report, 2002). Organochlorine pesticides in river sediments were also investigated for the Pearl River (Mai et al., 2001), the Guanting Reservoir, the Yongding River (Ma and Wang, 2001), and the Yellow River (Zhang et al., 2001b).

Because of close ties with human activities, the POP pesticide pollution in estuaries, harbors, and bays has generated wide concern, and many studies on pesticide POPs in sediments of these waters have been carried out. Usually, concentrations of pesticide POPs in the sediment of estuaries and bays are generally higher than that in rivers, but lower than that in oceans and straits. From 1981 to 1993, Wu et al. (1999) studied DDT, HCH, and PCBs in estuarine sediments from the Daliaohe, Lun, Hai, Yellow, Yangtze, Huangpu, Qiantang, Min, Jiulong, and Pearl rivers. Except for the Pearl River, the HCH concentrations in sediments were low. The DDT concentrations have followed the trend of being lower in the north of China and higher in the south, and the sediments of the Pearl River, Min River, and Haihe River have relative high sediment concentrations of DDT. Based on the DDE/DDT ratio, it was suggested that a new emission source could exist in the estuaries of the Jiulongjiang and the Pearl rivers (Wu et al., 1999).

Organochlorines in the sediment of the estuarine beach of the Yangtze River were measured in 2001 (Yang et al., 2002), and the results showed that the total concentration of organochlorine pesticides ranged from 1.25 to 36.0 ng $^{-1}$g. Aldrin, dieldrin, and endosulfan were also detected. The closer to the emission sources of wastewater, the higher the concentrations, and the concentrations in the estuarine areas were much higher than those in coastal areas. In the estuarine beach of the Yangtze River, the co-relations between the organochlorines, total organic carbon, and particle size of the sediment were low, which indicated the unique and complicated characteristics of the research area (Yang et al., 2002).

In 1989, Liu et al. (2001) measured OCPs in the surface sediment of the Dalian Bay, and detected 10 organochlorine pestices, including DDT, HCH, aldrin, dieldrin, and endrin. Concentrations of HCHs and DDTs accounted for 54.5 and 38.1% of the total organochlorine pesticides, respectively, and β-HCH was the most abundant of the HCHs. Compared to 1996 data, concentrations of organochlorine pesticides in the sediment decreased significantly (Liu et al., 2001). In 1992, the surface sediment of the Victoria Bay in Hong Kong was found to contain DDTs in the same concentration range as the sediment in costal areas (Zhang et al., 1994). In 1997, Mai et al (2001) studied organochlorine pesticide pollution in the sediment of the Guangzhou, Xijiang, and Lingdingyang estuaries of the Pearl River. DDT concentrations were between 10 and 100 ng g^{-1} and significantly higher than the range of surface sediment in global coastal areas reported by Fowler ($<$0.1–44 ng g^{-1}) and also higher than the DDT concentrations in river sediment reported in other agricultural areas in the world (e.g., San Joaquin California, U.S.) (Mai et al., 2001). DDT and HCH in the sediment of the Yangtze estuarine area and the Hangzhou Bay were measured using laminated sediment cores to reflect the pollution history of the area (Chen et al., 1999). Other studies on the sediment of estuarine areas include Kang et al. (2001) on the Macao estuarine of the Pearl River; Doong and Liao (2001) on the Wushi River in Taiwan; Chen et al. (1996) on Xiamen Island and Minjiang Bay; Lv et al. (2002) on the Dalian Bay and the Liaodong Bay; Zhao et al. (2002a) on areas of fishery cultivation in Dalian; Qiu et al. (2002) on the Daya Bay; Ma and Wang (2001) on the Guanting Reservoir and the Yongding River; and Zhang and Chen (1996a) on the West Harbor of Xiamen.

Sediments in other water bodies, such as inland lakes, have also been studied. From 1994 to 1995, Dou and Zhao (1998) measured HCH and DDT in surface sediment of the Baiyangdian Lake of the Hebei Province.

The results showed concentrations of DDT and its degradation products that were in the range of 0.56–2.61 ng g^{-1}, which is lower than that of the Lagoon River and the Jamuna River of India, the Ovens Lake of Australia, and the Vojvodina Lake of Yugoslavia. The main degradation product of DDT was *p,p′*-DDE. In some areas, *o,p′*-DDT and *p,p′*-DDT were also found, which indicated recent pollution by DDT (Dou and Zhao, 1998). In 2000, Yuan et al. (2003) analyzed organochlorine pesticides in the sediment of the Taihu Lake and found DDT and its metabolites, isomers of HCH, eldrin, aldrin, HCB, and heptachlor. β-HCH, *p,p′*-DDT, and HCB were found in the highest concentrations. The average concentrations were as high as 6.57, 1.43, and 2.16 ng g^{-1} (dry weight), respectively. The HCH concentrations were significantly higher than DDT concentrations. The results showed that concentrations of HCHs and DDT in the sediment of the Taihu Lake were higher than those measured in rivers but lower than that of bays in Xiamen, Hong Kong, and Macao. Compared to lake sediment of remote areas of Canada and the Arctic, the DDT concentrations in the sediment of the Taihu Lake were slightly higher, and the HCH concentrations were a magnitude higher, indicating relatively high usage and emissions of organochlorine pesticides in the Taihu Lake catchments (Yuan et al., 2003). Table 3.9 summarizes recent results of the measurement of pesticide POPs in sediment in China (concentrations of DDT were used as an example).

3.3.4.3. Summary

Since the 1983 ban of the agriculture use of POP pesticides in China, the concentrations of the POP pesticides have gradually decreased. However, the POP pesticides tended to concentrate in sediment, and resulted in relatively high concentrations of POP pesticides in this environmental media. Many measurements of POP pesticides in sediment have been conducted in China, covering different regions and different types of water bodies. Sediments of harbors and estuaries have the highest concentration of POP pesticides, compared to concentrations measured in other water bodies. The concentration of POP pesticides was highest in the sediments of estuaries of the Pearl River, Minjiang River, Jilongjiang River, and the Macao Harbor. Although the concentration of POP pesticides in sediments has fallen dramatically since the 1980s, in some regions the ecological risk standards for oceans and estuaries established by other countries are still exceeded. Serious ecological impact might have been caused by the high concentrations of POP pesticides in sediment, and these regions should be classified as high environmental risk areas.

Table 3.9. Pesticide POPs concentrations in sediment of China (DDTs as example)

Regions	Monitoring time	Types	POPs	DDTs (ng g^{-1})	References
Yangtze River (Nanjing segment)	1998	Suspended particles	DDT, HCH, aldrin, dieldrin, heptachlor	14.63–20.72	Jiang et al. (2000)
Yangtse River (Nanjing segment)	1998			0.21–4.50	Xu et al. (2000)
Liao River	1998		HCH, DDT, endrin, HCB, aldrin, heptachlor, etc.	1.0–2.7	Zhang et al. (2002)
Jiyun River (Hangu)	1976			356	Li (1985)
Second Songhua River	1997		DDT, HCH, PCBs, aldrin, heptachlor	2.0–56.1	Liu et al. (1998)
Guanting Reservoir–Yongding River	1999		HCH, DDT	2.5–26.7	Mai et al. (2001)
Several estuaries, China					
LiaoHe	1989		HCH, DDT, PCBs	0.2	Wu et al. (1999)
LianHe	1991	Downriver country		ND	
Hai	1984–1985			9.5–11.5	
HuangHe	1984–1986	City in estuary		ND	
Yangtse	1986–1988			0.1–0.2	
Huangpu	1988	City downriver		1.3	
Qiantang	1984			0.1	
Minjiang	1986	City in estuary		6.9–13.1	
Jiuling	1993			4.1–6.1	
Zhujiang	1984			6.5–14.5	
Dalian Bay	1996		HCH, DDT, aldrin, dieldrin, endrin, HCB, heptachlor, endosulfan, etc.	21.746 (2.118–72.299)	Liu et al. (2001)
Dalian Bay	1999			2.208 (0.727–5.723)	
Liaodong Bay	1999			2.95 (0.98–7.51) specific site 155	Lv et al. (2002)
Daya Bay	1999			0.14–20.27	Qiu et al. (2002)
Minjiang Estuary	1996	Offshore launch	DDT	6.17–63.88	Yuan et al. (2001)

Table 3.9. (*Continued*)

Regions	Monitoring time	Types	POPs	DDTs (ng g^{-1})	References
Zhujiang Estuary	1996		DDT	28.57	
Jiulongjiang Estuary	1999		DDT	8.61–73.70	
Minjiang River	1999		DDT, HCH, heptachlor, endosulfan	1.57–13.6	Zhang et al. (2003)
Xiamen Harbor	1993		HCH, DDT, PCB, endrin, aldrin, heptachlor	9.27 (4.45–17.4) specific site 311	Zhang et al. (1996)
Xiamen Harbor	1998			0.025 (0.01–0.06)	Hong et al. (1999)
Xiamen-inmen Sea Area	1995		DDT, HCH	4.71 (2.97–9.16)	Chen et al. (1996)
Victoria Harbor	1992		HCH, DDT, PCBs	10.2 (1.38–25.4) specific site 69	Zhang et al. (1994)
Pearl River Delta	1997	Guangzhou	HCH, DDT, PCBs, PAHs	35.1–90.9	Mai et al. (2001)
		Shiziyang		22.9–40.4	
		Xijiang		4.94–16.6	
		Lingdingyang		2.6–115.6	
		Macao Harbor		1628.8	
Zhujiang Estuary	1994		HCH, DDT	33.46 (17.79–51.71)	Cai et al. (1997)
Yangtse Estuary Hangzhou Bay	1981	Sediment core	DDT, HCH	6.93–12.6	Chen et al. (1999)
	1988			1.04–3.46	
	1992			0.56–1.85	
	1997			0.05–0.31	
Yangtse Estuary	1981		HCH, DDT	10.9 (6.9–16.0)	
Macao Estuary	1999	Sediment core	DDT, HCH, aldrin, endrin	1.92–39.13	Kang et al. (2001)
				10.53	
Baiyangdian	1994		DDT, HCH	0.56–2.61	Dou and Zhao (1998)
	1995				
Taihu Lake	1999–2000		DDT, HCH	0.1–8.8	Feng et al. (2003)
Taihu Lake	2000		DDT, HCH	3.27	Yuan et al. (2003)
Boyang Lake	1983		DDT, HCH	ND	Qian et al. (1986)
Yangtse Beach	2001	Sediment	HCH, DDT, PCB, dieldrin, aldrin, heptachlor, endosulfan	ND–0.565	Yang et al. (2002)

Monitoring and remediation of polluted sediment should be an important task in the implementation of the Stockholm Convention in China.

3.3.5. Food

3.3.5.1. General description

The POP pesticides have three pathways to enter the human body: inhalation, ingestion (food intake), and dermal contact. The intake of food through the digestive system accounts for 90% of the pesticide POPs that enter the human body (Campoy et al., 2001). HCH and DDT can enter plants through soil and water, and enter animal bodies through water and food. These compounds remain in fat tissues for a long time. Although most of the recent monitoring reports indicate that the pollution level of pesticide POPs such as DDT in food have been reduced to low levels, it should not be ignored because it is closely related to adverse health effects in humans and animals.

3.3.5.2. The pollution level of POP pesticides in foodstuff in China

Two investigations of organochlorine pesticides in food were carried out in China, one in 1992 and one in 2000. The investigation in 1992 was to implement the Global Food Pollutants Monitoring Program constituted in 1976 by the UNEP, FAO and WHO. China joined the program in 1981. During the 1992 investigation, organochlorine pesticides and heavy metals in food were measured. Helongjiang Province, Beijing, Sichuan Province, Zhejiang Province, and Guangdong Province were selected as monitoring sites to represent the northeast, north, southwest, and south of China (Zhang et al., 1996b).

The investigation in 2000 was carried out by the food pollution monitoring network of the Ministry of Health of China in Beijing, Chongqing and provinces of Jilin, Henan, Shanxi, Zhejiang, Fujian, Guangdong, Hubei, and Shandong. Compounds monitored included organochlorine pesticides and other pollutants. The results indicated that after nearly a 20-year ban on agricultural use, the pollution level of organochlorine pesticides in the environment was significantly reduced through degradation. Currently, concentrations of HCHs and DDTs in food are below the national standards. Table 3.10 shows the concentrations of HCH and DDT in several foods in China in 2000 (Wang et al., 2002).

Among various foods, grains, vegetables, fruits, meat, fish, eggs, milk, vegetable oil, and tea are often monitored for pesticide POPs. Currently, only HCH (including α-HCH, β-HCH, and γ-HCH) and DDT (including

Table 3.10. Residue of DDT and HCH in several types of food in China, 2000

Types	Number of samples	Average concentration ($ng\,g^{-1}$)			National standard
		p,p'-DDE	o,p'-DDT	p,p'-DDT	
Grain	80	4.1	7	14.1	200
Vegetables	88	0.8	1.3	0.8	100
Fruits	40	0.8	2.3	2.7	100
Meat	41	5.6	1.3	1.8	200
Fish	30	3.6	0.9	2.5	500
Eggs	51	2.5	0.5	1.5	1000
Milk powder	15	0.6	0.6	2.0	Convert to milk
Milk	5	5.7	25.5	1.3	100
Vegetable oil	10	0.2	0.5	1.0	500
Tea	44	10.8	13.8	31.1	200
		α-HCH	β-HCH	γ-HCH	
Grain	80	1.0	3.8	0.5	300
Vegetables	88	0.9	0.8	3.1	200
Fruits	40	0.4	1.1	0.2	200
Meat	41	5.3	7.1	7.0	400
Fish	30	1.8	1.4	1.8	500
Eggs	51	0.6	13.3	0.4	1000
Milk powder	15	2.1	10.2	1.1	Convert to milk
Milk	5	0.4	0.2	0.1	100
Vegetable oil	10	2.6	20.2	5.1	500

p,p'-DDT, p,p'-DDE, and o,p'-DDT) are measured. Besides the investigations of foods in 1992 and 2000 at the national scale, for public health purposes comprehensive investigations in Zhejiang and Sichuan Provinces and a large number of local investigations on certain foods have been conducted.

Grain: Compared to the early 1980s, during the 1990s the concentrations of organochlorine pesticides in food in China have significantly decreased and many meet the national standards. Among the DDTs, p,p'-DDT has the highest concentration in grain. For example, concentrations of DDT in commercial grains from the north and southwest of China significantly exceed the national average value. Because more HCHs are used than DDT during grain production in China, the concentrations of HCH in grain in China are relatively high among the organochlorine pesticides. Table 3.11 lists concentrations of organochlorine pesticides in grain in China.

Fruits and vegetables: Table 3.12 shows that the concentrations of organochlorine pesticides in fruits and vegetables in China decreased year after year. The concentration values obtained in 2000 are significantly

Table 3.11. Residues of organochlorine pesticides in grain in China

Regions	Types	Monitoring time	Number of samples	DDT (ng g^{-1})	HCH (ng g^{-1})	References
Yixing	Rice	2000	1	<0.04	0.05	Nakata et al. (2002)
Yixing	Wheat	2000	1	0.46	0.10	Nakata et al. (2002)
Weihai	Wheat	1998	30	6.4–17.9	<5.0–50.7	Su et al. (2001)
	Maize		30	<5.0–7.2		Su et al. (2001)
	Earthpea		30	5.8–41.7	<5.0–38.9	Su et al. (2001)
Xinjiang	Wheat	1989	200		13 (5.5–221)	Ma et al. (1996)
	Maize		90		6.2 (3.6–98.4)	Ma et al. (1996)
	Rice		14		5.1	Ma et al. (1996)
Hangzhou	Rice	1992–1999	16	7.4 (6–14)	4.2 (3–7.3)	Lu et al. (2000)
Hangzhou	Flour	1992–1999	14	6.3	4.3	Lu et al. (2000)
Gansu	Wheat	1991	127	2.2	46.2	Zhou et al. (1995)
	Maize		86	1.7	44.6	
	Rice		5	3.1	6.7	
	Millet		2	1.6	12.6	
Jiashan, ZJ	Rice		143	0–137	0–220	Zhao et al. (2002b)
Chengdu	Corn	1996		4.6	309	
Heilongjiang	Food grain	1992	16	6.5	5.3	Xiao et al. (1999)
China (average)	Food grain	1992	65	27	13	Xiao et al. (1999)
China (average)	Food grain	2000	80	25.2	5.3	Wang et al. (2002)
National standard	Level 1	1981		<20	<10	GB2763-81
	Level 2			20–200	10–300	
	Level 3			200	300	

Note: Residual standard of HCH and DDT in grain, vegetables, and other food (GB2763-81), Ministry of Health, P. R. China, 1981

Table 3.12. Residue of DDT pesticides in fruits and vegetables in China

Regions	Types	Time	Number of samples	DDT ($ng\,g^{-1}$)	References
Shanghai fruits	Apple	2000	1	0.40	Nakata et al. (2002)
	Grape	2000	1	0.83	
Shanghai vegetables	Celery	2000	1	2.49	
	Soybean	2000	1	3.9	
	Cucumber	2000	1	0.09	
	Taro	2000	1	0.07	
	Pea	2001	1	0.33	
	Mushroom	2001	1	ND	
	Asparagus	2001	1	ND	
	Eggplant	2001	1	0.09	
	Spinach	2001	1	0.12	
	Onion	2001	1	0.15	
	Green pepper	2001	1	ND	
Sichuan	Vegetable	1992	11	0.9–10.1	Lin et al. (1995)
Zhejiang	Vegetable	1975–1979		70	Zhao and Ma (2001a,b)
Zhejiang	Vegetable	1994–1996	76	3.2 (0–24.7)	Zhao and Ma (2001a,b)
Zhejiang	Fruit	1975–1979		30–210	Zhao and Ma (2001a,b)
Zhejiang	Fruit	1994–1996	31	0.5 (0–1.4)	Zhao and Ma (2001b)
Hangzhou	Vegetable, fruit	1992–1999	40	4.5	Lu et al. (2000)
Hainan	Vegetable			ND–48	Zhuo et al. (1998)
Huhehaote	Potato	1986–1988	51	7.5	Liu et al. (1991)
	Cabbage		39	6.6	
	Carrot		31	8.2	
	Beans		21	11.9	
	Pepper		46	11.9	
	Tomato		34	10	
Gansu	Vegetable	1991	182	1–27.5	Zhou et al. (1995)
Gansu	Fruit	1991	77	0.8–14.5	Zhou et al. (1995)
Chengdu	Vegetable	1996		13.7	Hou et al. (1999)
Chengdu	Fruit	1996		13.3	Hou et al. (1999)
Heilongjiang	Vegetable	1992	11	6.1	Xiao et al. (1999)
Heilongjiang	Fruit	1992	9	12	Xiao et al. (1999)

Table 3.12. (*Continued*)

Regions	Types	Time	Number of samples	DDT (ng g^{-1})	References
China (average)	Vegetable	1992	68	24	Xiao et al. (1999)
China (average)	Vegetable	2000	88	2.9	Wang et al. (2002)
China (average)	Fruit	1992	33	35	Xiao et al. (1999)
China (average)	Fruit	2000	40	5.8	Wang et al. (2002)
National standard	Vegetable			100	GB2763-81
National standard	Fruit			100	GB2763-81

Note: Residual standard of HCH and DDT in grain, vegetable and other food (GB2763-81), 1981 Ministry of Health, P. R. China.

lower than those measured in 1992. During the national-scale investigation in 2000, the major DDT compounds in fruits and vegetables were *p,p′*-DDT and *o,p′*-DDT, respectively.

Fish and mussels: Organochlorine pesticides have serious impacts on aquatic species. Because of bioaccumulation effects, concentrations of POPs in fish are a few orders higher than those in water. Fish and mussels are important sources of human exposure to POPs due to consumption (i.e., ingestion route). From 1994 to 2001, Monirith et al. (2003) investigated DDTs, HCHs, HCB, and PCBs in sea waters of a number of Asian-Pacific countries and found concentrations of DDTs in fishes and mussels of certain sea waters close to Xiamen, Shenzen, Shanghai, Zhejiang, and Fujian (1999–2001) were much higher than those in India (1998), Indonesia (1998), Korea (1998), and Japan (1994). Table 3.13 summarized the concentrations of DDTs in fish and mussels during investigations in China in recent years.

Meat, eggs, and milk: The POPs are hydrophobic and lipophilic substances, and can easily transfer into materials with high organic contents, leading to bioaccumulation. Due to the high fat content of meat, eggs, and milk, these foods are important potential sources of human exposure to pesticide POPs. Table 3.14 shows the residue of pesticide DDT in meat, eggs, and milk in China.

Others: Investigations on POP residues in edible materials, such as tea, breast milk, and herbs, have also been carried out in China. Tables 3.15

Table 3.13. Residue of DDT pesticides in fish and mussels in China

Regions	Types	Monitoring time	Number of samples	DDTs (ng g^{-1})	Remark (Lipid %)	References
Xiamen	Green mussel	1999	24	23,000	0.56	Monirith et al. (2003)
Shenzhen	Green mussel	1999	18	30,000	1.1	
Fuzhou	Green mussel	1999	20	2400	2.4	
Liaoning	Blue mussel	2001	34	830	1.7	
Jiaozhouwan	Blue mussel	2001	17	6200	2.4	
Chongmingdao	Blue mussel	2001	33	29,000	2.2	
Zhejiang	Blue mussel	2001	12	8600	2.9	
Zhejiang	Blue mussel	2001	8	2200	3.5	Monirith et al. (2003)
Fujian	Green mussel	2001	20	7800	1.9	
Fujian	Green mussel	2001	9	54,000	1.2	
Shanghai	Mussel	2000	10	34,000	1.3	Nakata et al. (2002)
	Shrimp		37	200	1.2	
	Crab		4	830	1.1	
	Squid		12	220	1.2	
	Fish		1	1000	0.91	
	Horse-mackerel		4	710	5.9	
	Tongue sole		6	560	2.3	
Hong Kong	15 fishes	1997		3.3–76	WW	Chan et al. (1999)
Hong Kong	Fish liver	1997	2	27 ± 11 71 ± 34	WW	Chan et al. (1999)
Xiamen Island	Shellfish	1995–1996	12	75.2–2143	DW	Chen et al. (2002)
Minjiang Bay	Shellfish	1995–1996	9	21.5–2396	DW	Chen et al. (2002)
Xiamen	Fish liver	1998–1999		150–2200	WW	Klumpp et al. (2002)
	Fish meat			<0.5–220	WW	Klumpp et al. (2002)
	Mussel			50–200	WW	Klumpp et al. (2002)

Coastal area in North China						
Yalujiang	Many kinds of mussels	1990	5	1.9	WW	Liu et al. (1996)
Dalian Bay			5	4.5	WW	
Jinzhou Bay			5	3.1	WW	
Bohai Bay			4	1.03	WW	
Jiaozhou Bay			4	11.9	WW	
Liaohe			2	0.5	WW	
Lvsi			4	3.9	WW	
Yangtse			2	13.5	WW	
Sichuan	Fish	1992–1999	10	12.5	WW	Lu et al. (2000)
Hangzhou	Marine product	1992–1999	8	11.5	WW	Lu et al. (2000)
Pearl River Estuary	Jade mussel	1996	13	9.5–191	WW	Fang et al. (2001)
Pearl River Estuary	19 Animals	1985–1993		1–133	WW	Luo et al. (2001)
Yangtse Estuary	Fish	<1991		410	WW	Luo et al. (2001)
Hangzhou Bay	Fish	<1991		270	WW	
Baiyangdian fish	Herbivorous	1995		29.6	WW	Dou and Zhao (1998)
	Polyphagia			108.5		
	Carnivorous			124.4		
Baiyangdian	Crucian	1994–1995		14.1	WW	Dou and Zhao (1996)
Coastal area in Guangdong	Oyster	1989	10	8.3	WW	Jia et al. (1996)
		1991	10	3.1		
		1992	10	1.5		
		1993	10	0.6		
Heilongjiang	Aquatic product	1992	6	33		Xiao et al. (1999)
Chengdu	Aquatic product	1996		81.2		Hou et al. (1999)
China (average)	Aquatic product	1992	35	46		Xiao et al. (1999)
China (average)	Fish	2000		7		Wang et al. (2002)
National standard	Fish			500		GB2763-81

Note: Residual standard of HCH and DDT in grain, vegetable, and other food (GB2763-81), 1981, Ministry of Health, P. R. China.

Table 3.14. The residue of DDT pesticides in meat, eggs, and milk in China

Regions	Types	Monitoring time	Sample number	DDT (ng g^{-1})	References
Shanghai	Pork fat	2000	1	3.32	Nakata (2002)
Shanghai	Pork muscle	2000	1	0.15	Nakata et al. (2002)
Shanghai	Ham	2000	1	0.55	Nakata et al. (2002)
Shanghai	Sausage (pork)	2000	1	6.67	Nakata et al. (2002)
Yixing	Chicken	2000	1	0.64	Nakata et al. (2002)
Yixing	Chicken (liver)	2000	1	3.92	Nakata et al. (2002)
Shanghai	Eggs	2000	1	1	Nakata et al. (2002)
Yixing	Milk	2000	1	1.91	Nakata et al. (2002)
Sichuan	Milk	1992	10	0.9–2.8	Lin et al. (1995)
Sichuan	Meat	1992	10	4.4–113.6	Lin et al. (1995)
Sichuan	Eggs	1992	10	2.1–48.9	Lin et al. (1995)
Hangzhou	Vegetable oil	1992–1999	12	21.2	Lu et al. (2000)
	Eggs		12	10	
	Pork		10	10.6	
Hangzhou	Duck	1992–1999	10	6	Lu et al. (2000)
	Beef		11	6	
	Chicken		12	4	
	Milk		12	10	
Chengdu	Meat	1996		5.9	Hou et al. (1999)
	Eggs	1996		40.4	Hou et al. (1999)
Heilongjiang	Vegetable oil	1992	6	65	Xiao et al. (1999)
	Fowl		10	13	
	Eggs		6	32	
	Milk		16	50	
China (average)	Vegetable oil	1992	34	35	Xiao et al. (1999)
	Fowl		58	32	
	Eggs		28	30	
China (average)	Vegetable oil	2000	10	1.7	Wang et al. (2002)
	Meat		41	8.7	
	Eggs		51	4.5	
	Milk		5	32.5	
National standard	Vegetable oil			500	GB2763-81
	Meat			500	
	Eggs			1000	
	Milk			100	

Note: Residual standard of HCH and DDT in grain, vegetable and other food (GB2763-81), 1981, Ministry of Health, P. R. China.

Table 3.15. Residues of organochlorine pesticides in tea in China

Regions	Monitoring time	Sample number	DDT ($ng\,g^{-1}$)	HCHs ($ng\,g^{-1}$)	References
Shanghai	2000	1	4.58	0.53	Nakata et al. (2002)
	2000	1	0.50	0.34	
	2000	1	1.98	0.57	
Weihai	2000	40	5–3630	5–80	Cong et al. (2001)
Zhejiang	1975–1979		6–750	30–1300	Zhao and Ma (2001b)
Zhejiang	1994–1996	22	1.8 (0–5.6)	3.5 (0.2–22.9)	Zhao and Ma (2001b)
China (average)	2000	44	55.7		Wang et al. (2002)
National standard			200		GB2763-81

Table 3.16. Residue of DDT pesticide in breast milk in China

Regions	Time	Number of samples	p,p'-DDT ($\mu g\,g^{-1}$ fat)	p,p'-DDE ($\mu g\,g^{-1}$ fat)	References
Beijing	1983		1.6	5.9	Yu et al. (2001)
Beijing	1998	15	0.24	1.72	Yu et al. (2001)
Changchun	1987		0.260	7.91	Li et al. (2000)
Changchun	1998	52	0.230	0.488	Li et al. (2000)
Nanchang	1988	60	4.23	10.4	He et al. (2001)
Nanchang	1998	60	0.21	1.46	He et al. (2001)
Weihai	1985	50	3.78	7.00	Cong et al. (2001)
Weihai	1998	89	0.005	2.03	Cong et al. (2001)
Guangzhou	2000	54	0.70	2.85	Wong et al. (2002)
Hong Kong	1985	25	2.17	11.67	Wong et al. (2002)
Hong Kong	1999	132	0.39	2.48	Wong et al. (2002)
Hangzhou	1983	80	4.96	20.40	Lu et al. (2000)
	1985	59	2.82	13.95	Lu et al. (2000)
	1987	60	1.59	12.20	Lu et al. (2000)
Nanjing	1985	60	3.4	12.0	Jiang (1989)
Nanjing	1987	60	1.5	10.5	Jiang (1989)
China (average)	1984	861	2.64	8.08	Cong et al. (2001)

and 3.16 summarize concentrations of organochlorine pesticides in tea and breast milk in China. The DDT concentrations in breast milk directly reflect the impact of DDT on the Chinese population. Large amount of HCHs and DDT have been used in China as pesticides; therefore, the concentrations of HCHs and DDT in breast milk in China are apparently

higher than those in some other countries. Compared to the early 1980s, the concentrations of DDT and DDE in breast milk in major cities in China have decreased significantly but are still higher than those measured in Sweden and Canada. Cities with relatively high DDT concentrations in breast milk include Hangzhou and Hong Kong.

3.3.5.3. Summary

The large amount of application of DDT and HCH in 1950–1970 in China has caused serious and large-scale food contamination. However, with the ban on agricultural use and the degradation in environment, the concentrations of DDT and HCH in food have significantly decreased. According to the follow-up investigation and monitoring in Zhejiang Province from 1972 to 1999, using the 1985 concentrations for comparison, the concentrations of HCH in rice, vegetables, pork, freshwater fish, and eggs measured in the 1990s decreased by almost 100%, and concentrations of DDT decreased by 20–90%. Recent monitoring of drinking water, tea, and breast milk indicates a large reduction in the DDT pollution level since the 1980s, and the DDT concentrations now meet the national standards.

However, the pollution of pesticide POPs in food or the food web in China is still a serious concern. The concentrations of DDT in breast milk in China are still higher than those often observed in developed countries and also higher than levels specified in the guidelines of international organizations. Emission sources of pesticide POPs still exist in some areas in China, and the concentrations of DDT in tea, fish, and mussels are still high in some regions. Even after a 20-year ban on the use of organochlorine pesticides in China, monitoring in the Taihu Lake, an inland lake located in the economically developed part of China, has found isomers of HCHs, DDT and its metabolites, endrin, and heptachlor epoxide in bird eggs. The concentrations and detection rate of HCH and DDT are very high. Therefore, the potentially high impact of pesticide POPs on human health still exists.

3.3.6. Others

Above, the pollution situation associated with persistent pesticides in China has been summarized for environmental media including air, water, soil, and sediment. The residues of pesticide POPs in food have also been summarized. Other studies on POP residues, such as residues measured in Hubei, in snails in Yixin, and in fat tissues of whales in the South China Sea are not summarized here (Lu et al., 2000).

While the residues in the environment could reflect the current pollution level of pesticide POPs in China, the residues in fat, blood, and tissues of the human body reflect the impact of pesticide POPs on humans. Currently, the research on residues of pesticide POPs in the human body is being done mainly for medical purposes. Although a detailed description is outside the scope of this paper, a brief description is provided below.

An investigation in the 1970s and 1980s showed that the residues of DDT in the body fat of residents in a number of cities in China were in the range of 2.59–23.6 $\mu g\, g^{-1}$. The concentrations were higher in Zhejiang and Shanghai, at levels close to 20 $\mu g\, g^{-1}$. These values are comparable to the levels measured in the 1960s and 1970s in the U.S. Canada, and Japan (Wang et al., 1981). However, a study in 2001 in Shanghai showed DDT concentrations in women's breast milk were still as high as 7.6 $\mu g\, g^{-1}$, while the figures for the U.S. (1998) and Japan (1997) were 0.072 and 0.78 $\mu g\, g^{-1}$ respectively. The concentrations of HCHs in breast milk in China were also much higher than those measured in many other countries (Nakata et al., 2002). This can be explained by the relatively high concentrations of POPs in food and subsequently high human exposure to pesticides in China.

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Chapter 4

Polychlorinated Dibenzo-*p*-Dioxins, Dibenzofurans, and Biphenyls, and Polybrominated Diphenyl Ethers in China☆

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Abstract

China was one of the first proponents of the Stockholm Convention, but only recently have we started to prepare the national inventory of PCDD/Fs and PCBs, which are among POPs specified by the convention. PBDEs have been extensively used as flame retardants in various products, and recently, the environmental problems associated with these compounds have become great concern. Data about the pollution status of these pollutants were extremely scarce in China due to the lack of regulations and monitoring capacity. In this chapter, sources of PCDD/Fs, PCBs, and PBDEs and their levels in the environmental media in China are summarized, based mainly on available scientific literature. The challenges for management of these compounds are also discussed.

4.1. Introduction

As polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) are compounds with similar structures and monitoring methods, they are discussed together in this chapter. The structures of PCDDs, PCDFs, PCBs, and PBDEs are shown in Fig. 4.1.

PCDDs and PCDFs (PCDD/Fs) are often just called "dioxins". The number of chlorine atoms in each molecule can vary from 1 to 8, and there are 75 and 135 congeners for PCDDs and PCDFs, respectively. The congeners with chlorine substitutions in the 2, 3, 7, and 8 positions are thought to have dioxin-like toxicity. PCDD/Fs are formed as unwanted

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☆Taiwan, Hong Kong and Pearl River Delta are not included this chapter.

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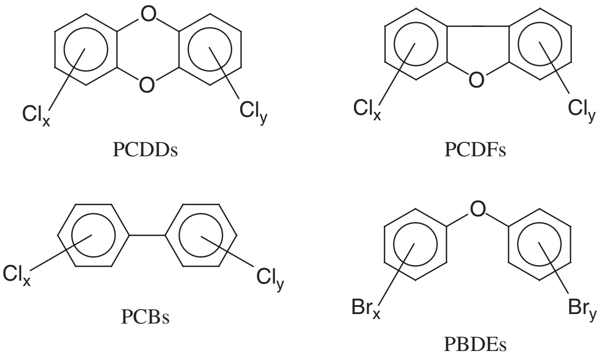


Figure 4.1. Chemical structures of PCDD/Fs, PCBs, and PBDEs.

by-products in many combustion and industrial processes. They have also been formed from natural processes, such as forest fires and volcanoes, but these formations are in general of less importance compared to the anthropogenic emissions. The major sources of environmental contamination with PCDD/Fs can be cataloged as: waste incineration, chemical industry, and pulp and paper industry.

There are 209 PCB congeners, differentiated by the numbers and positions of the substituted chlorine atoms. The 12 PCB congeners with 4 or more chlorines with just 1 or no substitution in the ortho position are thought to have dioxin-like toxicity and are often called "dioxin-like PCBs". PCBs have been used commercially since 1929 as dielectric and heat exchange fluids, as well as in a variety of other applications. The total amount of PCBs produced worldwide has been estimated to be 1.5 million metric tons (t). The majority of the PCBs in the environment are thought to be the result of leaks from PCB-containing electrical capacitors and transformers. Waste incineration is also a potential air emission source of PCBs.

PBDEs have been called one of the "emerging pollutants". They are extensively used as flame retardants (FRs) in various polymers and especially in electronic equipment such as computers and television sets. Similar to PCBs, there are 209 congeners of PBDEs, and the nomenclature system is also based on the same IUPAC scheme used for PCBs. But unlike PCBs, for which large-scale production has been banned for many years, PBDEs are still widely used and their transport and transformation in the environment are still poorly understood. The global demand for PBDEs has increased rapidly since the 1970s. In 1992, the global production of PBDEs was ~40,000 t, but in 1999 this had increased to approximately 70,000 t (Renner, 2000).

PCDD/Fs, PCBs, and PBDEs are usually classified as groups of persistent organic pollutants (POPs). They have been found in almost all compartments of the global ecosystem in at least trace amounts. They can be transported over long distances in the atmosphere, resulting in widespread distribution across the Earth, including regions where they have never been used. PCDD/Fs and PCBs were specified as POPs in the Stockholm Convention. China was one of the first proponents of the convention and ratified it on June 25, 2004. However, due to a lack of monitoring capacity and regulation, these pollutants have not yet been regularly monitored in China. Although PBDEs are categorized as emerging POPs, few scientific papers have reported their occurrence in China. Therefore, only very limited knowledge on the pollution of PCDD/Fs, PCBs, and PBDEs in China is available.

4.2. Sources of PCDD/Fs in China

According to a number of pilot surveys of dioxins carried out by some Chinese institutions, dioxins have a broad distribution in China. Based on the available data, the major sources of PCDD/Fs in China are discussed below.

4.2.1. Solid waste incineration

With the explosive development of the economy and urbanization in China, more and more municipal solid wastes (MSWs) are generated. In 2000, 150 million tons of MSW were generated in China, and the total MSW dumped was 6 billion tons (Zhao, 2004). The MSW is mainly disposed of by three processes in China: landfill, MSW incineration (MSWI), and compost. Whereas solid waste incinerators (SWI), especially MSW incinerators, have proven to be the most significant PCDD/F generators in industrialized countries, SWI are presently not considered as the biggest source in China because only a small portion of MSW are currently being disposed of by incineration. However, numerous MSW incinerators are under construction in various cities to save limited land space. The emission of dioxins will increase rapidly from the boom of MSWI in China.

The MSWI furnaces in China can be divided into four major types: stack furnaces, fluid-bed furnaces, rotary kiln furnaces, and gasification. Incinerators with the largest capacity are mostly stack furnaces. Monitoring data on dioxins emitted from MSWI in China are extremely scarce because there is no regular monitoring requirement. A project funded by

United Nation Environmental Program (UNEP) to investigate PCDD/Fs in some Chinese industries and processes is presently being carried out, but the results are not yet available.

A preliminary investigation on dioxin emission from MSWI in China has been campaigned by Tian and Ouyang (2003). Flue gas of 15 different types of MSW incinerators was monitored. About half of the data exceeded the national standard for dioxin emissions limit (1 ng TEQ m^{-3}; National Standard of the People's Republic of China, 2001) and the highest was at 100 ng TEQ m^{-3} level. However, this report did not provide precise concentrations. Total dioxin emissions to air from MSWI was estimated to be 72 ng TEQ annually in China based on the monitoring data of Tian and Ouyang (2003). Stack furnaces (with bag filters for dust removal) are the major type of MSW incinerators in China but not the major contributor to dioxin emissions. Fluid-bed furnaces accounted for ~60% of the dioxin emissions from MSWI.

Dioxins in fly ash of stack MSW incinerators from three cities were investigated by Jin et al. (2003b) and the concentrations were 7.53, 1.52, and 0.44 ng TEQ g^{-1}, respectively. The concentration of dioxins in flue gas will decrease if active carbon powder is used before the bag house equipment, but the concentration of dioxins in the fly ash will increase accordingly.

4.2.2. Chemical industry

PCDD/Fs can be formed during the manufacture of chlorophenols, chlorobenzenes, and chlorobiphenyls, and the production and use of them could be important sources. Some researchers believe that the manufacture of halogenated organic chemicals is the largest contributor of PCDD/Fs in China (Huang et al., 2001). While some specified sources have been closed in developed countries, the release of PCDD/Fs from chemical manufacturing is still a problem in China due to the use of dated processes or technologies, despite their limited use. These chemical manufactures are described below.

4.2.2.1. Chloralkali industry

Rapp et al. (1991) found that the total concentration of PCDD/Fs in a Swedish graphite electrolytical sludge was 650 ng g^{-1}. The use of graphite electrodes has been banned in developed countries because of the associated high pollution levels. The chloralkali industry is the fundamental raw material industry in China. Among the 500 chloralkali manufactures all over the world, China has 230 of them and ranks second in the world behind America. In these plants, it is common to use graphite electrode as the anode and ferric net covered with asbestos as the cathode. This production technique may be a significant source of PCDD/Fs in China. Graphite electrode sludge collected from a huge chloralkali plant in central China was analyzed, and the concentrations of total PCDD/Fs and I-TEQ were 379 ng g^{-1} and 21.7 ng g^{-1}, respectively (Xu et al., 2000). The congener pattern in the electrode sludge corresponded very well to the typical "chloralkali pattern", and it indicated the same formation mechanism in the manufacturing process. The annual dioxin emissions from graphite electrode sludge in China were estimated to be 5.4 kg I-TEQ based on the 254,000 t sludge generated annually. Some of the sludge can enter the environment through effluent or runoff and seriously pollute the surroundings.

4.2.2.2. Chlorophenols

Chlorophenols have been widely used for a variety of pesticidal applications. Chlorophenols and their sodium salts have been primarily used for wood preservation and as chemical intermediates in the manufacture of other pesticides or chemicals. In China, sodium pentachlorophenate (Na-PCP) was especially used to eradicate snails, *Oncomelania hupensis*, in the schistosomiasis area in China. Chinese commercial PCP or Na-PCP contained appreciable amounts of PCDD/Fs, and their concentrations in PCP and Na-PCP were 142 and 92 ng I-TEQ g^{-1}, respectively (Bao et al., 1995).

4.2.2.3. Hexachlorocyclohexanes (HCHs)

γ-HCH or lindane is used as an insecticide on fruit and vegetable crops. Global technical HCH and lindane usage was estimated to be as high as 6,000,000 t in 1998 (Willett et al., 1998). Because of the environmental and biological persistence of HCHs, their use has been regulated. China banned technical HCH in 1983, but the use of lindane is not completely prohibited in China because there are exemptions that HCH can still be used as pesticides for forests and to control plagues of pests. The annual production of HCH was ~4000 t before 1983, and the amount decreased to ~500 t in recent years. In China, the most common method to produce trichlorobenzene (TCB) is pyrolysis of HCH wastes. Solid wastes from the production of TCB contained extremely high level of PCDD/Fs (Bao et al., 1994). The average concentrations of total PCDD/Fs and TEQ were 129 mg g^{-1} and 768 μg g^{-1}, respectively. The TEQ generated from this source were estimated to be 90 kg annually based on the quantity of HCH production. Although HCH has been banned for many years, large quantities exist in the environment and pose potential threats to human and environmental health.

4.2.2.4. PCBs

PCDD/Fs can be found as contaminants in commercial PCB products and may contribute more to the toxicity of the mixture due to their much higher TEFs than PCBs. PCBs were once produced in China until they were banned in 1974. TEQs of PCDD/Fs in two Chinese commercial PCBs were 217 and 417 ng g^{-1}, respectively (Li and Jiang, 1995). Many transformers containing PCBs as dielectric fluids were discarded, but they were not registered properly. In some metal recovery sites, leaks and spills from illegal disposal of PCBs in the 1980s during the dismantling of transformers have seriously polluted the environment.

4.2.2.5. Chloranil and dye

While chloranil is an important raw material in the dye industry, it is considered to be a source of PCDD/Fs (Christmann et al., 1989). Levels of OCDD/F between 1 μg g^{-1} and 100 μg g^{-1} were detected in chloranils and C. I. Violet 23 dye, which was synthesized from chloranil (Zhang et al., 2000a). Chlorophenol proved to be the real source of PCDD/Fs in the chloranils because technical PCP or trichlorophenol (TCP) was used as raw material. After substituting PCP and TCP with hydroquinone as an intermediate, the PCDD/Fs in chloranils were dramatically reduced (Zhang et al., 2002a).

4.2.3. Chlorine bleaching pulp

Traces of PCDD/Fs can be generated as by-products during the bleaching of pulp with chlorine. Emission from the pulp-bleaching process was characterized by US EPA as the third largest source of dioxins in the United States. Non-wood plant fibers such as cereal, rice, and reed are extensively used as raw material for paper production in China. Much higher concentrations of PCDD/Fs than from wood pulping in European or American pulp mills were reported from Chinese pulp and paper mills that bleach non-wood fibers. The typical bleaching sequence in China includes three stages: C (chlorine), E (alkaline extraction), and H (hypochlorite). Stage C has been identified as the major PCDD/F formation process. The PCDD/Fs in different stages were investigated in a paper mill using non-wood plant fibers as raw material in southern China (Zhang et al., 2000b). The concentration of PCDD/Fs in discharge water from stage C was 253 pg L^{-1}, which is much higher than that from other stages. The level of PCDD/Fs in the bleaching pulps ranged from 34 to 44 pg TEQ g^{-1} dw (Zheng et al., 1997a). The PCDD/F concentration in the wastewaters from a pulp mill in China using a bleaching sequence C-E-H was 316 pg I-TEQ L^{-1} whereas 2,3,7,8-TCDD was 230 pg L^{-1} and 2,3,7,8-TCDF was 122 pg L^{-1} (Zheng et al. 2001).

4.2.4. Iron and steel industry

Several operations for the production of iron and steel, including sinter production, coke production, and electric arc furnaces, have been identified as potential emission sources of PCDD/Fs. China is the largest producer of steel in the world. According to 2005 statistical data, the iron and steel production of China was 349 million tons. It is reasonable to assume that the iron and steel industry could be a major source of PCDD/F emission to air in China, but data are not available for an assessment of the emissions from this source.

4.2.5. Other sources

In addition to those sources discussed above, there are various other sources that could release considerable amount of dioxins. For instance, power/energy generation, non-ferrous metal processes, medical waste incineration, transportation, and cement kilns are all potentially significant dioxin sources, according to the experiences of other countries. However, there are no related data reported in China.

4.3. Sources of PCBs in China

PCBs were manufactured in China between 1965 and 1974, and the production was estimated to be 10,000 t. This is a minor fraction of the 1.5 million tons of total production worldwide. The major components in the Chinese PCB technical mixtures were tri- to penta-chlorinated congeners (named as PCB3 and PCB5, respectively). PCB3 was mainly used as an additive in paint, and PCB5 was mainly used as dielectric fluid in transformers. Some transformers containing PCBs as dielectric fluids were imported mainly for the steel industry and power plants, but the exact quantity is not known. Leaks and spills of PCBs could be a major source of releases.

In the 1980s, the activity of dismantling electric equipment to reclaim copper and other metals occurred in some places in China. Many of the transformers containing PCBs had been dismantled manually, and the environment was seriously polluted by PCBs because of illegal disposal.

According to the Chinese disposal regulations, wastes that contain PCBs are categorized as dangerous wastes and must be incinerated to destroy the PCBs. Jiang et al. (1999) analyzed fly ash collected from a PCB incinerator and found that the residual PCBs in fly ash were 0.022 ng TEQ g^{-1}. Compared to the 2–3 μg TEQ g^{-1} in technical PCBs, PCBs were destroyed effectively. The destruction and removal efficiency (DRE) for PCB incineration of the incinerator had achieved the requirements of design ($>99.9999\%$) (Jin et al., 1997), although considerable levels of PCDD/Fs could still be detected. Most of the existing PCB wastes are sealed up in chemical waste landfills or caves for safekeeping. Many of these were not registered because of a lack of management. Leakage of some stockpiled PCBs has been found (Shao, 2001).

MSWI has been identified as an important existing potential PCBs emission source, but currently no information on stack gas concentrations of PCBs in MSWI has been reported in China. Dioxin-like PCBs are not categorized as dioxins in China so there are no regulations for PCBs in stack gas from MSWI and other combustion processes.

4.4. Sources of PBDEs in China

The release of PBDEs to the environment can occur during initial synthesis, incorporation into products, and the use of such products. In China and mainly in the eastern part of the country, large quantities of deca-BDE have been produced. In 2001, the production of deca-BDE was ~13,500 t per annum and the consumption has increased rapidly in recent years (Xia et al., 2005). In addition, three of the largest brominated FR manufacturers in the world (i.e., Great Lakes Chemical, Indianapolis, IN; Albemarle Chemical, Richmond, VA; and Dead Sea Chemical, Beer-Sheva, Israel) all have distributors in China.

The recycling of electronic items is another important source of PBDEs released into the environment. PBDEs make up from 5 to 30% of the weight of plastics and ~6 to 12×108 kg of PBDEs were released into environment via electronic wastes (E-wastes) from 1997 to 2004 (Martin et al., 2004). In China, much E-waste has long been imported for recycling, such as the world's obsolete computers and electronic components.

The current volume of E-waste disposed of in China is unknown. Martin et al. (2004) estimated that up to 261,000 t of PBDEs were imported into Guangdong province in 2002 in scrap electronic devices. The Chinese government is unable to provide details of the E-waste disposal practices but now has its own ban on such imports of E-waste.

In February 2006, China passed the Law on Pollution Control of Electronic and Information Products, which among other things, forbids producing, selling and importing of electronic and information products containing PBDEs. The legislation will come into force on July 31, 2007. Like PCBs, the levels of PBDEs in the environment will decline in China and around the world due to our awareness and the regulations.

4.5. Levels of PCDD/Fs, PCBs, and PBDEs in China

This section briefly reviews the existing status of PCDD/Fs, PCBs, and PBDEs in China. The amount of available data is inadequate to precisely evaluate the pollution situation. PCDD/Fs, PCBs, and PBDEs are not regular monitoring targets because the regulation limits for them in water, air, and soil are not yet established in China. Most of the data are collected from public scientific works and are not systematic. Some seriously polluted areas where investigation has been extensively campaigned are described separately in the next section.

4.5.1. Contamination levels of PCDD/Fs, PCBs, and PBDEs inenvironmental media in China

4.5.1.1. Aquatic environment

Aquatic media, including sediment and water, were more extensively investigated than other environmental media for PCDD/Fs, PCBs, and PBDEs in China. But the data are difficult to compare because of the inconsistency in the analytical procedures. In many cases, the data were reported without providing the results of quality control, making it impossible to evaluate the data quality. Most of the results reported were performed with GC-ECD and congener-specific data were rarely reported. Table 4.1 summarizes the level of PCDD/Fs, PCBs, and PBDEs in water and sediment collected around China from both freshwater and marine environments. Most of the investigations were carried out in eastern China. The research focused on sediments, and the targets were mostly PCBs. Chen et al. (1999) investigated PCBs in sediments of 11 rivers in eastern China and reported that the total concentration of PCBs (14 congeners) ranged

Table 4.1. The PCDD/Fs, PCBs, or PBDEs levels in aquatic environmental media in some locations of China (unit: ng g^{-1} dw for sediment samples and ng L^{-1} for water samples if not specified)

Location	Media	Time	Pollutants	Level	Reference
Huanghe River	Sediment	2004	PCBs^{-}	n.d.–5.98	Sun et al., 2005
Huaihe River	Sediment	–	PCBs^{57}	6.34, 8.24	Wang et al., 2001
Jiulongjiang River	Water	1999	PCBs^{12}	0.36–150	Zhang et al., 2000c
	Porewater	1999	PCBs^{12}	209–3869	
Liaohe River	Sediment	1998	PCBs^{4}	0.9–42.9[b]	Zhang et al., 2000d
	Water	1998	PCBs^{4}	n.d.	
Minjiang River	Sediment	1999	PCBs^{12}	15.13–57.93	Zhang et al., 2002b
	Water	1999	PCBs^{12}	0.20–2.47 μg L^{-1}	
	Porewater	1999	PCBs^{12}	3.19–10.86 μg L^{-1}	
Second Songhuajiang River	Sediment	–	PCBs^{-}	0.6–337	Liu et al., 1998
Yangtze River	Sediment	2000	PCBs^{-}	18.12	Chen et al., 2003
Yongding River	Sediment	1999	PCBs^{26}	0.81, 9.72	Ma et al., 2001
Guanting Reservoir	Sediment	1999	PCBs^{26}	4.23, 5.63	Ma et al., 2001
Baiyangdian Lake	Sediment	1992	PCBs^{-}	31.1–510.9	Zhu et al., 1995
Taihu Lake	Sediment	2004	PCDD/Fs	0.12–1.32	Zhang and Jiang, 2005
			PCBs^{209}	0.89–29.75	
Dalian Bay	Sediment	1999	PCBs^{9}[a]	0.040–3.230 (2.141)	Liu et al., 2001
Qingdao Bay	Sediment	1996	PCBs^{-}	1.021–153.132 (19.104)	Li et al., 1998
		1997/1999	PCBs^{50}	0.65–32.9	Yang et al., 2003b
		1997/1999	PBDEs^{21}	0.12–5.5	Yang et al., 2003c
Jinzhou Bay	Sediment	1996	PCBs^{-}	0.598–32.563 (5.863)	Li et al., 1998
Xiamen Bay	Sediment	1998	PCBs^{12}	n.d.–0.32	Zhang et al., 2000e
	Water	1998	PCBs^{12}	0.08–1.69	Zhang et al., 2000f
Xiamen coastal area	Sediment	–	PBDEs^{12}	0.10–2.06	Ou, 2006
	Sediment	2001	PCBs^{7}	0.19–18.95 (2.70)	Yang et al., 2003a
Yangtze River Delta	Sediment	2002	PBDEs^{12}	n.d.–0.55	Chen et al., 2006b
	Sediment	2002	BDE 209	0.16–94.6	Chen et al., 2006b

[a] Number of congeners of PCBs or PBDEs determined; "–" means unknown.

[b] Expressed as min-max (mean) (if available).

from 10.5 to 25.5 ng g^{-1}. In general, the level of PCBs in the sediments of Chinese waters was relatively low compared with those reported in industrialized countries. Considering that the levels in eastern China tend to be higher than those in western China, we can conclude that the pollution of PCBs in the Chinese aquatic environment is generally low.

4.5.1.2. Soil

Although soil is believed to act as a significant repository for POPs, we have almost no idea about the pollution situation of PCDD/Fs, PCBs, and PBDEs in soils of China, because only a few surveys have been conducted in some specified areas. A preliminary study showed that the level of PCDD/Fs in soils in the Beijing area ranged from 12 to 260 pg g^{-1} (Li et al., 2004). PCB concentrations in soils of industrial plants and rural areas of Shanghai were reported to be 0.05–587 ng g^{-1} (Xie et al., 2005). A chloralkali plant was suspected to be an emission source of PCBs. Soil in the former Cheoy Lee Shipyard at Penny's Bay, Hong Kong was contaminated with dioxins, petroleum hydrocarbons, and metals. Approximately 100,000 m^3 of soil were decontaminated before the land was used for infrastructure development.

4.5.1.3. Air

Several atmospheric aerosol samples were collected in Shanghai and Dalian and PCDD/Fs in total suspended particles were reported (Yang et al., 2004). The mean concentrations of total PCDD/Fs were 55.5 and 19.2 pg m^{-3}, and the mean I-TEQs were 0.928 and 0.334 pg m^{-3}, respectively. The predominant congeners were the lower chlorinated congeners. The pollution level is comparable to the general trend of urban industrial sites (0.1–0.4 pg TEQ m^{-3}, Lohmann and Jones, 2000).

Jaward et al. (2005) conducted a large-scale passive air sampling survey for PCBs, OCPs, and PBDEs across Asia in 2004. Thirty-two samplers were successfully deployed in 13 rural and 19 urban sites. Air concentrations in China ranged from 7.0 to 117 pg m^{-3} for PCBs (sum of seven congeners) and from ND to 340 pg m^{-3} for PBDEs (sum of eight PBDEs). They concluded that the levels of PCBs were elevated in some Chinese locations, and PBDE level were generally low in the region.

4.5.1.4. Sewage sludge

In addition to PBDE manufacturing and specific industries, wastewater treatment including storm water runoff and sewage sludge is considered to be a major source of environmental PBDEs. The concentrations of PBDEs in sewage sludge from wastewater treatment plants give an indication of the general exposure to and uses of these compounds. In the early 1990s, European researchers identified high levels of PBDEs (i.e., for BDE-47 and -99, at concentrations between 100 and 190 ng g^{-1} dw) in sludge samples (Darnerud et al., 2001). In the United States, a survey of sewage sludge biosolids from 26 publicly owned treatment works (POTWs) in 9 states revealed that the PBDE concentrations exceeded those found in Europe 10–100 times (Hale et al., 2001, 2003). In China, data on PBDEs in sewage sludge are scare. PBDEs were recently detected in sewage sludge collected from three different provinces of China (Wang et al., 2005). The total PBDE (19 congeners) concentrations were 27.2, 8.0, and 5.2 ng g^{-1} dw, respectively. The results showed that PBDE levels in the sewage sludge in China were substantially lower than those in the sludge from Europe and North America. Furthermore, data analysis indicated that the concentration of PBDE congeners was not correlated with facility location, size of the population served, or processing capacity.

4.5.1.5. Biota

Most of the available data on PCDD/Fs, PCBs, or PBDEs in biota were obtained using fish or mussel samples. Table 4.2 summarizes the results reported in China. PCBs in marine biota were found to be substantially higher than that from freshwater, and compared with that in biota from north or east, the levels of PCBs from the south of China were significantly higher. In addition to fish and mussels, pine needles have been used as passive samplers to determine regional contamination of POPs in China (Zhu et al., 1999; Chen et al., 2006a). The PCDD/F and PCB levels in these pine needles are low or comparable with other regions that were not impacted by evident sources (Chen et al., 2006a).

4.5.2. Food

An investigation about PCDD/Fs and PCBs in Chinese food is being conducted by the Chinese Center for Disease Control and Prevention to evaluate the dietary exposure to dioxins of Chinese people, but no data are available at this time.

4.5.3. Human blood and milk

Jin et al. (2003a) investigated the dioxin concentrations in the breast milk of 79 first-time mothers in Shengyang and Dalian, Liaoning Province, by

Table 4.2. The PCDD/Fs, PCBs, and PBDEs levels in biota samples in some locations of China

Location	Biota	Time	Pollutants	Level	Reference
Huaihe River	Silver carp	–	PCBs^{57}	4.65 ng g^{-1} ww	Wang et al., 2001
Minjiang River		1995/1996		n.d.–6.78 ng g^{-1} dw	Chen et al., 2001
Fujian	Pine needle	1998	PCBs	16–32 (19) ng g^{-1} ww	Zhu et al., 1999
Shanghai	Pine needle	1997	PCBs	54–62 (61) ng g^{-1} ww	Zhu et al., 1999
Zhejiang	Crucian carp	–	PCBs^{6}	150–1757 (528.2) pg g^{-1} ww	Tie et al., 2005
	Silver carp	–	PCBs^{6}	48–524 (176.0) pg g^{-1} ww	
	Pine needle	1998	PCBs	48–63 (55) ng g^{-1} ww	Zhu et al., 1999
Dalian	Pine needle	1997	PCDD/Fs	127 ± 40 ng kg^{-1} dw	Chen et al., 2006a
Dalian	Pine needle	1997	PCBs	4389 ± 1575 ng kg^{-1} dw	Chen et al., 2006a
Bohai Sea	Mollusks	–	PCDD/Fs	0.9–15, 317 pg g^{-1} lipid	Zhao et al., 2005
			PCBs^{209}	66.1–583.6 pg g^{-1} lipid	
East China Sea	Skipjack tuna	1996–2001	PBDEs^{11}	21 ng g^{-1} lipid	Uneo et al., 2004
Fujian coastal area	Shellfish	2002	PCBs	n.d. ($<$0.8 ng g^{-1} ww)	Xue et al., 2004
North of Yangtze River mouth	Shellfish	1990	PCBs	n.d.–22.9 ng g^{-1} ww	Liu et al., 1996
Qingdao Bay	Mussel	1997–1999	PCBs^{50}	8.4, 4.4 ng g^{-1} ww	Yang et al., 2003b
South China Sea	Finless porpoise	1990, 2000/2001	PCBs^{62}	1400–28,000 ng g^{-1} lipid	Ramu et al., 2006
			PBDEs^{10}	84–980 ng g^{-1} lipid	
	Skipjack tuna	1996–2001	PBDEs^{11}	23, 34 ng g^{-1} lipid	Uneo et al., 2004
Xiamen Island	Shellfish	1995	PCBs	n.d.–234 ng g^{-1} dw	Chen et al., 2001
Yangtze River estuary	Mussel/crab/fish	2002	PCBs^{36}	43.7–1260.4 (342.5) ng g^{-1} ww	Liu et al., 2004
		1997	PCBs	104–128 (115) ng g^{-1} ww	

CALUX bioassay. The mean concentrations of 15.84 and 7.21 pg TEQ g^{-1} fat were obtained for the two cities, respectively. They concluded that the dioxin level in Chinese breast milk was at the global average level, although it was higher than the lowest limit of the Tolerable Daily Intake (TDI) proposed by WHO. Pollution levels of dioxins and related compounds in pooled samples of human breast milk collected from primiparae in Dalian and Shenyang have been determined (Kunisue et al., 2004). The levels of PCDD/Fs and coplanar PCBs were in the range of 3.5–5.7 and 2.5–3.2 pg TEQ g^{-1} lipid wt., respectively. Concentrations of dioxins and PCBs in humans in China are in general lower than those in many other countries.

Bi and Xu (2000) reported the residue levels of PBDEs in human serum and breast milk samples from southern China. The concentrations of seven congeners ranged from 1.5 to 17 ng g^{-1} lipid. The levels were within the range reported in European samples but lower than that reported in North American samples.

4.5.4. Some severely polluted areas in China

4.5.4.1. The Ya-Er Lake

Ya-Er Lake is located in the east part of Wuhan, Hubei province, China. It is a shallow, eutrophic lake along the middle-lower reach of the Yangtze River. The water covers 20 km^2, and there are 270 km^2 of farmland with a population of 300,000 people around the lake. Ya-Er Lake was once famous for fishing before a large chemical factory was built on the bank in 1962. From 1962 to 1987, the lake was seriously polluted with PCDD/Fs and other pollutants, such as hexachlorocyclohexane (HCH), chlorinated benzenes (CBs), chlorinated phenols (CPs) and its sodium salts, and mercury, by direct discharge of effluent from the factory. The macrophytes vanished completely and the fishing was ruined. Nowadays, the wastewater is discharged by other means, which has resulted in the reappearance of the lake biota. In view of the historical input to lake sediments, PCDD/Fs were found to originate from the production of chlorinated chemicals in the 1980s, but more recently these compound mainly originate from graphite electrode sludge (Xu, et al., 1999). In the highest polluted sublake, the concentration of total PCDD/Fs in the surface sediment was 13.8 ng g^{-1} and I-TEQ was 0.42 ng g^{-1}. To investigate the transfer and bioaccumulation of PCDD/Fs in the foodweb, samples from different aquatic animals, aquatic plants, duck eggs, bird eggs, mother's milk, and human hair from the Ya-Er Lake area were collected and analyzed. The results showed that the aquatic organisms were seriously contaminated by PCDD/Fs. These compounds have bioaccumulated in biota of various trophic levels and biomagnified along the food chain. The concentrations of PCDD/Fs in fish muscle tissue ranged from 34.4 to 134 ng I-TEQ kg^{-1} lipid. Fish was the primary protein intake source in the diet of residents in the area. The high accumulation of PCDD/Fs in the foodweb has been seriously threatening the health of local residents in the Ya-Er Lake area.

4.5.4.2. The Dongting Lake

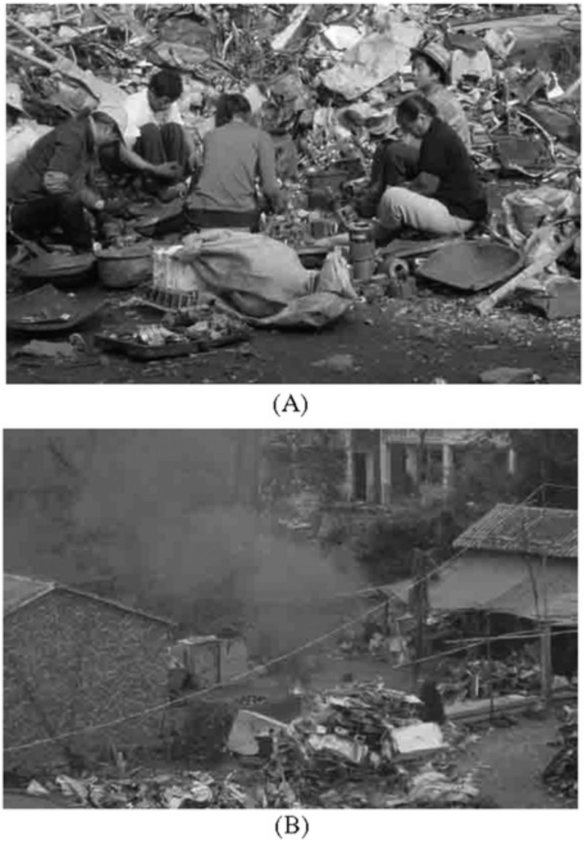
Dongting Lake, located in southern China, is the second largest freshwater lake in China. The total area of the lake is ~3,000 km^2, and it is regarded as very important due to its multiple functions: flood prevention, water supply, fishing, sightseeing, and shipping. However, a severe blood parasite, *Schistosomiasis japonica*, prevailed in this region for a long time. Technical Na-PCP has been sprayed since the 1960s to kill *O. hupensis* the snail hosts of the parasite, and Na-PCP has polluted most of the area (Zhang et al., 2001). The region was also seriously polluted by PCDD/Fs, which are contaminants in Na-PCP technical products (Zheng, et al., 1997b). The highest concentration of PCDD/Fs in sediments was 891 pg TEQ g^{-1}, and OCDD was the major contributor with a concentration of 151 ng g^{-1}. Now the molluscacide has been mostly replaced because of the awareness of the harm it causes (Liu et al., 2005). Fortunately, PCDD/Fs in human breast milk samples collected from the region were low, with the exception of several samples (Zheng et al., 2003).

4.5.4.3. Tianjin

Tianjin, located in northen China, is adjacent to the Bohai Sea and is one of the largest industrial cities in China. The Haihe River, the largest water system in north China, flows through Tianjin city and empties into the Bohai Sea. With the rapid economic growth, industrialization, and urbanization, accompanied by inadequate infrastructure investment and management capacity, water shortage has become a bottleneck to the further development of the economy and agriculture production in this region. Meanwhile, water pollution is becoming extremely serious. The Dagu Drainage River, situated in the south of the Haihe River, is a very important channel for the discharge of various domestic and industrial wastewater to reduce water pollution in the Haihe River. Along the Dagu Drainage River, there are several large-scale chemical factories including the largest DDT and PCP producer in China. Endemic chloracne among the workers in a plant here had been noted since 1974. The prevalence of chloracne was 73.4% in total and 95.2% in a TCB tank area where PCDD/Fs levels were thousands of ppm (Cheng et al., 1993). In addition, there are hundreds of small-scale chemical factories in this area, including pulp and paper, printing and dyeing, leather, medicine, etc. Hu et al. (2005) reported the occurrence of trace organic contaminants in Bohai Bay and its adjacent Nanpaiwu River (another name for the Dagu Drainage River). The maximum concentration of PCDD/Fs in sediment samples from the river was 8714 ng g^{-1} dw and 22 ng TEQ g^{-1} dw and the maximum concentration of co-PCBs of the sediment samples was 315 ng g^{-1} dw and 0.88 ng TEQ g^{-1} dw. Another investigation (Zhang, 2004) of this area showed that the maximum levels of dioxins in the sediment of Dagu Drainage River were 557 ng g^{-1} dw and 893 pg TEQ g^{-1} dw, and the concentrations of PCBs were 154 ng g^{-1} dw and 21 pg TEQ g^{-1} dw. The pollution level increased significantly after the river passed through a big chemical industry area. The congener profile of dioxins of both investigations indicated that the most significant source was the production of pentachlorophenol (PCP) and PCP-Na in this area. However, the source of PCBs in this area is still not clearly understood.

4.5.4.4. Taizhou

Taizhou, situated in the coastal central section of Zhejiang Province, is one of the most active cities in the Yangtze River Delta. The main industries of Taizhou include plastic moulds, automobile, chemical medicine, and electric appliances. In the 1980s, dismantling operations of scrap electric equipment to reclaim metals emerged and boomed in some villages of Taizhou. At present, Taizhou is one of the largest dismantling centers in China (Fig. 4.2). In 1989, serious pollution of PCBs in soil and sediment was found because of the scrap transformer dismantling operation in this region (Chu et al., 1995). The concentrations of PCBs in a farmland soil and a sediment sample were 788 and 691 ng g^{-1}, respectively. PCDD/Fs were detected in two farmland soils in this area in 2005, and the mean total PCDD/Fs and TEQs were 2.6 ng g^{-1} and 21 pg g^{-1}, respectively (Luo et al., 2005). Because the scrap transformers containing PCBs as dielectric fluids are rarely available, open burning of wires and other parts with PVC insulation to recover metals such as copper and steel has been considered the major source of PCDD/Fs in the region in recent years.



(A)

(B)

Figure 4.2. (A) Workers are dismantling electric appliances in Taizhou. In 1980s, dismantling the scrap transformers containing PCBs as dielectric fluids has severely polluted the environment. (B) Open backyard burning of wires and other parts to recycle copper or other metals is very typical although it is illegal. The activity has been considered the major source of PCDD/Fs in the region in recent years.

4.5.4.5. Guiyu

The town of Guiyu is located in Guangdong province, China, and very famous for its E-waste recycling. Before the 1990s, it was only a cluster of small villages. It became a booming recycling center for E-waste arriving from various regions of the world since 1995 (Fig. 4.3). Today, millions of tones of E-waste are imported to this area for recycling metals, plastics, and other useful materials. The potentially hazardous recycling practices included the manual and unprotected removal of printer cartridge toner,

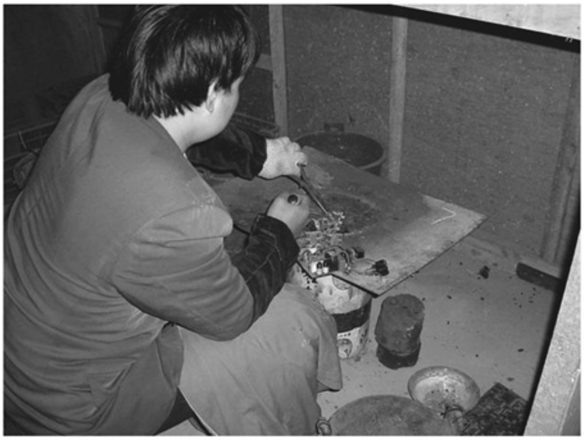


Figure 4.3. A worker is de-soldering circuit boards over a grill. The E-waste recycling practice causes severe environmental pollution of PBDEs and other contaminants in Guiyu.

the open incineration of wires to recover copper, etc. Aside from contributing to the prospering the local economy and improving the living standards of the inhabitants, these operations have also brought serious environmental problems to this area. Nowadays, the government has realized the severity and is preparing legislation on electronic waste to limit the import of E-waste. However, it might need a long time and large amounts of economic investments to remediate the severe environmental impacts caused by the pollution. More and more research has also been focused on this area. Information on pollution status in this area is being collected, such as PBDE congener profiles. The reported data of PBDEs from one recent published paper (Wang et al., 2006) showed that the concentrations are in the range of 0.26–824 ng g^{-1} dw. The isomer profiles of PBDEs were similar to various technical formulations of FR products.

4.6. Challenges of PCDD/Fs, PCBs, and PBDEs management in China

Implementation of the Stockholm Convention will be pivotal in the fight against POPs. Implementing the Convention involves a number of important departments and covers economic, ecological, and social fields. It is thus a very difficult and challenging task. Compared to other specified POPs, PCDD/Fs, and PCBs are more difficult to control because they can be formed and released unintentionally. The main challenges for China are summarized below.

1. Analysis and monitoring capacity is still low, particularly for dioxins. The current number of laboratories qualified for PCDD/Fs, dioxin-like PCBs and PBDEs analyses are not sufficient for the implementation of the Stockholm Convention. There are 13 laboratories equipped with HRGC/HRMS, and more are under construction for dioxin analysis in China. However, these laboratories belong to different blocks of the political infrastructure and were built for different purposes. Effective coordination among existing laboratories capable of dioxin analysis will help with building and strengthening the monitoring network in order to meet the need to implement the Stockholm Convention. In addition, currently available equipment in many laboratories and the proficiency of the personnel are also in need of updating.
2. Regulatory standards are urgently needed for waste discharges, food safety, etc. For example, there are no regulations for dioxins in food and numerous products or processes. There is a regulatory limit for dioxins in stack gas from MSWI, but there is no regulated monitoring. The heavy industry and chemical industry with possible dioxin emission have grown rapidly in recent decades. Some processes differ from those used in other countries, thus the standards for emissions from other countries should not be directly applied.
3. Relevant policy and financial support plans need to be improved to meet the requirement of the implementation of the Stockholm Convention. Public awareness plays a very important role in the fight against POPs, but in China it suffers from a lack of sufficient funding for public environmental education, and for research results dissemination and technology transfer.
4. There is a lack of effective reduction technologies. Fundamental research on dioxins emission control needs to be effectively promoted. The best available techniques (BAT) and best environmental practices (BEP) for the destruction of the existing PCB wastes need to be implemented. More environmentally benign alternatives to PBDEs are to be sought to meet the demand for FRs.

Solutions to problems caused by POPs are closely linked to China's environmental protection, social and economic development. Updating management policy and monitoring capability is likely the first step that needs to be taken at the present stage.

4.7. Conclusions

This chapter reviews the sources, environmental levels, and current situation of PCDD/Fs, PCBs, and PBDEs in China. Although there are diverse sources and serious contamination in some places, the current status of pollution throughout the country is still not clear. China has not been able to conduct nationwide inventory surveys on these chemical pollutants of high concern. A national or regional inventory has proven to be a crucial step toward the reduction and elimination of dioxins and PCBs. As one of the components of the Stockholm Convention, updating management policy and monitoring capability, and applying BAT and BEP are urgent tasks for the Chinese government and research institutions.

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Chapter 5

Pollution of Polycyclic Aromatic Hydrocarbons in China

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Abstract

With its rapid economic growth, China is encountering serious environmental problems. As the result of a sharp increase in energy consumption in the past 20 years, large quantities of polycyclic aromatic hydrocarbons (PAHs) were released into the environment. PAH concentrations in the atmosphere, water, and soil were increasing year by year. Because the Chinese government had financed many research programmes on the investigation of environmental pollution with PAHs, basic understanding of the pollution patterns and pollution sources of PAHs in China was achieved. In this paper, PAH pollution in the atmosphere, water and sediment, and soil and plants was reviewed. Comparisons of literature values of PAHs in China and those of western countries show that PAH pollution in China is more serious than in other countries. PAHs concentrations in atmosphere, water, sediment and soil in China were in the range of $60–2900\,\mathrm{ng\,m^{-3}}$, $1–98\,\mu\mathrm{g\,l^{-1}}$, and $0.005–182\,\mu\mathrm{g\,g^{-1}}$, respectively. The identification of sources of PAHs in different environmental media revealed that atmospheric PAHs come from primarily coal combustion and petrogenic sources; and water and soil PAH pollution from atmospheric deposition, industrial wastewater discharge, and wastewater irrigation. The environmental pollution of PAHs in water and soil also caused the bioaccumulation of PAHs in fish, bivalves, vegetables and agriculture plants. The human health risks of PAH pollution in China need to be more extensively investigated in the future.

5.1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of persistent organic pollutants (POPs) and widespread environmental contaminants, some of which may exhibit toxic, carcinogenic and mutagenic effects Because of their low water solubility and hydrophobic nature, PAHs are partitioned

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strongly into nonaquatic phases. They tend to be associated with particulates and are widely transported through atmospheric routes. PAHs have been detected throughout the environment (i.e., aerosol, soil, water, sludge and sediment). There has been a worldwide increase in interest in PAHs. Sixteen individual PAHs have been identified as priority pollutants by the United States Environmental Protection Agency (USEPA).

PAH contamination not only reduces the quantity and quality of natural resources, but may also have a deleterious impact on wildlife. Low molecular weight PAHs that have 2 or 3 rings, such as naphthalene, methylnaphthalene, and acenaphthene, are acutely toxic but noncarcinogenic to a broad spectrum of organisms. On the other hand, high molecular weight (HMW) PAHs that have 4, 5, or 6 rings, such as flouranthene, pyrene, benzo[*a*]pyrene, chrysene, and benzo[*g*,*h*,*i*]perylene, are less acutely toxic but have greater carcinogenic potential (Kennish, 1996). Once they enter the atmosphere, PAHs are distributed between gas and particle phases and subject to removal mechanisms, such as oxidative and photolytic reactions and wet and dry deposition (Garban et al., 2002). Low molecular weight PAHs are found mostly in the gas phase, whereas high molecular weight PAHs are typically associated with airborne particles (Gundel et al., 1995; Lighty et al., 2000).

PAHs enter the environment from both natural and man-made sources, and the anthropogenic point and nonpoint sources are the major sources. The nonpoint sources are diffuse sources disseminated through the air and waterways. In aquatic systems, PAH-enriched particles or flocs may settle to the lake's bottom under calm conditions and accumulate in the sediments. Once the PAH-enriched particles have accumulated in the lake's floor, they may undergo a number of changes that are mediated by chemical or microbial activities. As a result, the bound PAHs can be released from the sediment into the water phase. Once they enter the water column, they may also enter phytoplankton. The PAHs in phytoplankton may then bioaccumulate in the food web. This can cause both acute and chronic effects in fish, birds and other mammals that feed on aquatic organisms (Zhang, 1998).

5.2. PAHs in the atmosphere

5.2.1. Distribution and transportation of PAHs in the atmosphere

PAHs are semi-volatile organic compounds that are persistent in atmosphere, both in gas phase and particles. Much work has been done about the seasonal variation, vertical distribution and particle size distribution of PAHs in the atmosphere. In China, research on PAHs has been conducted since the 1980s. The concentrations of PAHs in the air have been investigated in several cities, especially those in northern China. Table 5.1 shows the total PAH and benzo[*a*]pyrene concentrations reported in literature, comparing the levels of PAHs in several Chinese cities. Most of these studies focused on aerosol PAHs at ground level in different seasons or in different function zones. Other studies involved PAHs in the gas phase, at higher altitude, or in indoor airborne particles. Though the sampling conditions and analytical procedures (e.g., sampling height, number of PAHs, etc.) of these studies were different, this comparison reveals meaningful basic information about PAH distribution in cities of China.

The data shown in Table 5.1 indicate that the atmospheric concentrations of PAHs vary largely in cities despite the different sampling conditions. In cities north of the Changjiang (Yangtze) River, coal-fueled space-heating systems are usually utilized, accounting for a large contribution of particles and PAHs in the atmosphere. The ΣPAHs in the winter in Taiyuan, Tianjin, and Lanzhou were 1703 (ΣPAHs9, sum of 9 PAHs, Peng & Zhang, 2000), 465 (ΣPAHs10, Zhu et al., 1998) and 1077 ng m^{-3} (ΣPAHs16, Peng et al., 2000), respectively. In the southern cities, the ΣPAHs16 in the winter was 146 (Liuzhou) (He et al., 2005) and the ΣPAHs10 in Hengyang was 127 ng m^{-3} (winter) (Li et al., 2004). In the summer, the differences of total PAH concentrations were smaller than those in winter, as 596 ng m^{-3} in Lanzhou (ΣPAHs16, Peng et al., 2000) and 141 ng m^{-3} in Hengyang (ΣPAHs10, Li et al., 2004). Although these values involve different numbers of PAHs, the most abundant ones, such as phenanthrene and benzo[*a*]pyrene were included in all the investigations. Thus, the total PAH concentrations summarized in Table 5.1 can be ranked. Benzeno[*a*]pyrene (BaP) was monitored in all the studies due to its strong carcinogencity and severe public health concerns. Average BaP concentrations shown in Table 5.1, except the concentrations in Hengyang and Liuzhou (spring), are all higher than 10 ng m^{-3}, the China National Atmospheric Environmental Standard. Several data were even higher than 30 ng m^{-3}. The observations suggest considerable differences in the levels of PAH pollution among Chinese cities.

In the same city, the distribution patterns of PAHs were examined in four interactive main aspects: PAHs composition, spatial distribution, seasonal variation, gas phase and particle size distribution and vertical distribution.

Table 5.1. Some PAH concentrations in airborne particles in cities of China (the data were obtained from aerosol samples at ground level if without specific explanation)

City	Region function	Concentrations (ng m^{-3})			Sampling time	Literature
		ΣPAHs	No. of PAHs	BaP		
Taiyuan	Industry	2020.4	9	91.0	February 1998 (heating)	Peng and Zhang (2000)
	Chemical industry	2898.0		119.3		
	Downtown	1052.1		56.4		
	Residential region	843.6		32.0		
	Average	1703.5		74.7		
Tianjin	Downtown	465.4	10	465.4	November 1994 (heating)	Zhu et al. (1998)
	Petrochemical industry	173.1		13.6		
Liuzhou	Average	145.7	16	19.19	December 2002 (no heating) January 2003 (no heating)	He et al. (2005)
		59.9		4.72	February 2003 (no heating) March 2002 (no heating)	
Lanzhou	Chemical industry	1604.4	16	64.4	March 1996 (heating)	Peng et al. (2000)
	Residential area	1640.6		113.9		
	Traffic area	653.3		59.5		
	Rural area	411.2		22.6		
	Average	1077.4		65.1		
	Chemical industry	1501.7		87.0	July 1996 (no heating)	
	Residential area	376.8		25.8		
	Traffic area	233.2		9.4		
	Rural area	270.3		–		
	Average	595.5		30.6		
Hengyang	Average	140.7	10	6.29	July 2002 (no heating)	Li et al. (2004)
	Average	127.0		7.27	February 2003 (no heating)	
Beijing		107.49		5.85	Four seasons, 2003	Zhou et al. (2005)

5.2.1.1. Composition

The composition of PAHs is mainly influenced by the source as well as degradation. Different sources contain PAHs with distinct composition. Because PAHs with low degradability usually exist longer than those with high degradability, the composition of PAHs in samples can reveal source and aging information.

Zhou et al. (2005) have reported the composition of atmospheric PAHs in Beijing. Lower molecular weight (2–3 rings) PAHs were less than 15% of the total mass (except in urban summer sample), while heavier PAHs (4 rings and more) showed three distribution patterns: spring type, summer type, and autumn and winter type.

Spring type: the normalized concentration of PAHs increased with molecular size. 6-ring benzo[*g*,*h*,*i*]perylene, indeno[1,2,3-*cd*]pyrene, and 5-ring benzo[$b+k$] fluoranthene accounted for the majority of the total PAH concentrations, indicating that traffic emission was clearly a significant source of PAHs in spring.

Summer type: the distribution characteristic of PAHs varied greatly in two sites. Four-ring fluoranthene, pyrene, and 3-ring phenanthrene dominated the total PAHs in urban sampling site, and BeP/BaP ratio was 2.17, resembling the PAH source fingerprints for diesel engines (Rogge, 1993). These distribution characteristics were presumably related to emission of diesel-fueled, heavy-duty trucks in the nighttime. Meanwhile, 6-ring benzo[*g*,*h*,*i*]perylene, 5-ring benzo[$b+k$]fluoranthene and benzo[*e*]pyrene were the most abundant in suburban samples.

Autumn + winter type: 4-ring PAHs were found to be the most abundant; floranthene, pyrene, benzo[*a*]anthracene, and chrysene accounted for more than 50% of the total PAHs. The likely sources are coal combustion and vehicle exhaust.

5.2.1.2. Spatial distribution

Spatial distribution is mainly attributed to the differences in emission patterns, meteorological conditions and local topography of distinct city functional areas. Many studies have examined the effects of these differences.

Zheng et al. (1997) have reported the total concentration of PAHs in Hong Kong in the winter months of 1993. These concentrations ranged from 2.4 to 54 ng m^{-3}. In this study, the highest value of BaP (1.07 ng m^{-3}) was found in Mong Kok site (commercial, residential and traffic environment) and the lowest (0.03 ng m^{-3}) in Hok Tsui (rural and marine environment), suggesting that the Mong Kok site, located near streets in one of the busiest districts of Hong Kong, was heavily influenced by traffic.

Guo et al. (2003a) also studied PAH spatial distribution in 2000–2001 in Hong Kong. The two sampling sites were Hung Hom (PU) and Kwun Tong (KT). The former is adjacent to a road with very high traffic volumes and the latter lays in a commercial, industrial and residential area. The mean concentrations of individual PAHs in the aerosols at the PU site were much higher than those at the KT site, especially in winter. The total PAH concentrations in $PM_{2.5}$ and in PM_{10} at PU site were ~1.25 and 1.45 times that at KT site, respectively. The major cause of the difference was the distinct characteristics of sampling sites. It is well known that PAHs are major components of vehicle exhaust, especially gasoline and diesel-powered vehicles (Miguel et al., 1998). Traffic influenced the PU site severely. The major sources of PAHs at KT site were household cooking activities, industrial sources and vehicle emissions. However, the source strength of PAHs at this site was much lower than that at PU site, because the traffic volume was much lower and the sampling site was far from the ground level. PAHs, whether released by anthropogenic or biogenic processes, have their primary sources near the surface and are lost as they are transported from the surface to the boundary layer (Goldan et al., 2000).

A similar pattern was obtained from the PAH concentrations at four functional zones in Liuzhou (He et al., 2005). The highest total PAH concentrations were observed at the sampling site south of an industrial zone during winter and spring, when the north wind dominates in Liuzhou. The main source of PAHs in Liuzhou was industrial fuel combustion, suggesting that the meteorological conditions affect the distribution and transportation of PAHs greatly.

Studies conducted in Macao (Qi et al., 2000) showed that the PAH concentrations of commercial and traffic zones were higher than that of relatively cleaner function zones.

In the northern cities, the results may be quite different from those in the south such as Hong Kong and Liuzhou. In the north, coal- and petrol-fueled space-heating systems are widely used in winter in residential areas, and coal and petrol are also the energy source and materials of several important industries. Thus, coal and petrol combustion, as opposed to traffic emission, contributes most of the PAHs in the atmosphere, as demonstrated in some studies.

Zhu et al. (1998) have investigated the PAH concentrations in airborne particles in Tianjin. Four sampling sites were set at Dagang, a petrochemical industry zone. A sampling site in downtown was used as a control. Results showed that the sum of 10 PAHs in the Dagang petrochemical industry zone ($168.8\,ng\,m^{-3}$) was lower than that in Tianjin downtown ($465.4\,ng\,m^{-3}$). The concentration of BaP was lower in Dagang as well ($13.6\,ng\,m^{-3}$ in Dagang and $41.4\,ng\,m^{-3}$ in downtown).

However, an opposite result was obtained by Peng et al. (2000). This study investigated the distribution and sources of PAHs in airborne particles in Taiyuan. The results showed that the mean concentration of the sum of nine PAHs was 189.2 ng m^{-3}, and the mean concentration of BaP was 74.7 ng m^{-3}. The concentration changed with function zones: chemical industrial zone > industrial zone > commercial and dwelling zone > cultural zone. The concentrations of 16 PAHs in airborne particles in the different function zones of the city of Lanzhou showed a different pattern: chemical industry zone > commercial zone > traffic zone > suburban zone (Peng et al., 2000) The difference in the spatial distribution was possibly due to the local emission patterns and meteorological conditions.

Zhou et al. (2005) have reported the spatial distribution of PAHs in atmospheric PM_{10} in Beijing. 17 PAHs were quantified in samples collected at 15 m high in urban and suburban areas. Individual concentrations between 0.01 and 55.2 ng m^{-3} were found and the total PAH concentrations varied from 8.6 to 297 ng m^{-3} with an average of 107 ng m^{-3}. PAH concentrations in the urban site were 1.02~1.58 times higher than those measured in the suburban site.

5.2.1.3. *Seasonal variation*

The seasonal distribution of particle-associated PAHs is controlled by a combination of emission factors (EFs), dispersion conditions and chemical mechanisms (Caricchia et al., 1999; Menichini et al., 1999). This balance depends on the relative importance of degradation processes and emission sources (Guo et al., 2003b). The highest PAH concentrations of a sampling site were usually obtained from winter samples, and the differences were far higher in northern cities than southern ones, suggesting that coal combustion for space heating contributes the most PAHs in winter in Northern China.

PAHs in total suspended particle samples collected in Qingdao during June 2001–May 2002 were analyzed by Guo et al. (2003b). The total concentrations ranged from 2.2 (summer) to 240.5 ng m^{-3} (winter). The annual average was 87.5 ng m^{-3} and the seasonal averages were 12.3, 28.0, 177.2 and 13.1 ng m^{-3}, respectively for summer, fall, winter and spring. The lowest concentration of total PAHs was found in the summer samples followed by the spring and fall samples while the highest was observed in the winter samples. The concentration of PAHs was 14.4 times higher in winter than in summer. The seasonal variations were mainly due to seasonal energy profiles. Other studies showed that the changes in emission patterns (stationary and vehicular) and meteorological conditions (including fewer daylight hours, reduced ambient temperatures, and lower volatilization and photochemical activity) contributed to the higher PAH levels during the winter (Bjorseth & Ramdahl, 1985; Freeman & Cattlel, 1990; Baek et al., 1991).

Guo et al. (2003a) has observed higher PAH concentrations in the winter and lower concentrations in the summer in Hong Kong. The total PAHs ratio of winter to summer was 8.6 at PU site and 7.5 at KT site, respectively. The ratios at the PU and KT sites were in accordance with results reported by other studies in Europe and in the USA: PAHs in the winter were generally higher by a factor of 1.5–10 than those in the summer (Baek et al., 1991; Harrison et al., 1996; Caricchia et al., 1999; Menichini et al., 1999). In Hong Kong, there is little seasonal variation in emissions from stationary sources since space heating is unnecessary. Thus, the higher PAH concentration in the winter was probably due to the contribution of outside sources. It is known that in winter the prevailing wind in Hong Kong is northeasterly, which brings in highly polluted air masses from the mainland to the sampling sites. On the contrary, in the summer, the Asian monsoon brings in clean oceanic air from the Tropics and unstable rainy weather. Thus, lower PAH levels were likely attributed to the combination of easier atmospheric dispersion of pollutants, washout effects, and to a lesser extent, photo degradation and higher percentage in the air in the vapor phase.

5.2.1.4. Diurnal variation

In some areas, the main source of PAHs is domestic emission from inhabitant activities. Thus, the distribution of PAHs may vary during the daytime and nighttime. This has been confirmed by some studies.

Qi et al. (2000) has reported that in Macao, the PAH concentrations during the daytime were generally 1.24–4.17 times higher than those during the nighttime at the same sampling site.

5.2.1.5. Vapor and particle phase distribution

PAHs can be further categorized as low and high molecular weight types (LMW and HMW) since the distribution and transport patterns of the two groups are distinct due to vapor pressure differences.

Guo et al. (2003b) observed that the winter and spring LMW and HMW were almost equally split (45.0 and 44.4%, respectively), while in the summer, the HMW PAHs dominated (72.0%). The difference in distribution was due to the gas-particle partitioning of these compounds in the atmosphere (Bidleman et al., 1986; Zheng & Fang, 2000; Zheng et al., 2000).

5.2.1.6. Vertical distribution

Because the construction of high-rises has become popular in urban residential areas in China in recent years, it is important to evaluate the vertical distributions of airborne pollutants to reveal the respiring exposure of residential population within those high buildings (Li et al., 2005).

In the study of Li et al. (2005), results showed clearly that there is a significant decrease in the concentrations of PAHs accompanied an increase in the height above the ground level. However, the decrease slowed down at the height of 24 m for PAHs, probably due to the existence of a quasi-equilibrium state at this height where the dilution and transformation processes of vehicular exhaust plume have already taken place. In addition, the trends for 4-through 7-ring PAHs at different heights were very similar.

Similarly, it was found that the level of PAHs measured at 25 m decreased to 30–50% of that measured at ground level (Bi et al., 2005).

5.2.1.7. Indoor and outdoor distribution

Indoor air pollution is a major global public health threat requiring greatly increased efforts in the area of research and policymaking, because people spend more than 80% of their time indoors, mostly in their homes (Li et al., 2005). The relationship between indoor and outdoor PAH concentrations is also an important part of the PAH distribution pattern. The results varied in the cities because of their different emission and ventilation patterns.

The study of Li et al. (2005) was conducted in Guangzhou, where direct air exchange between indoor and outdoor is common due to open doors and windows all year round with no residential heating. The total PAH concentrations ranged from 15.8 to 84.8 ng m^{-3} and from 14.2 to 77.9 ng m^{-3} in the outdoor and indoor samples, respectively. The contribution profiles of all individual PAHs were very similar in the indoor and outdoor samples, with 5–7-ring PAHs as the predominant contributors (79–90%). The indoor/outdoor (I/O) ratio, which is usually used to describe the I/O relationships of air pollutants for individual PAHs, was close to 1 (0.93–1.09), indicating that indoor concentrations of PAHs were dominated by outdoor sources.

5.2.1.8. Phase and particle size distribution

Once PAHs enter the atmosphere, they are distributed between gas and particle phases and subject to removal mechanisms, such as oxidative and photolytic reactions, as well as wet and dry deposition (Garban et al., 2002). The transport, deposition and chemical transformations of PAHs and other semi-volatile organic compounds are extensively controlled by their gas/particle-phase partitioning (Bi et al., 2005; Wu et al., 2005). Therefore, phase partitioning plays an important role in spatial distribution and transport. Low molecular weight PAHs (2–3-ring PAHs) are found mostly in the gas phase, whereas high molecular weight PAHs (4–6-ring PAHs) are typically associated with airborne particles (Gundel et al., 1995; Lighty et al., 2000).

Bi et al. (2005) measured 37 PAHs in both particulate and vapor phase samples. The average concentrations were in the range of 134.4–298.5 ng m^{-3} in the Liwan district of Guangzhou. Results showed that the mass distribution in air (including vapor and particulate phase) was dominated by phenanthrene, methylphenanthrene, fluoranthene, pyrene, chrysene, indeno[1,2,3-*cd*]pyrene and benzo[*g*,*h*,*i*]perylene, which together accounted for 69 and 77% of the total in samples from ground level sites and 25 m high level sites, respectively. Higher concentrations of low molecular weight compounds such as phenanthrene, fluoranthene and pyrene occurred in July vapor phase samples, exhibiting a positive correlation with air temperature, while the concentrations of HMW compounds, such as benzofluoranthene and benzopyrene, were negatively correlated with temperature. Higher concentration in particulate phase was present in April. The particle phase fraction ranged from 9.4% of the total PAHs in July to 44.8% in April. PAHs belong to the semi-volatile organic contaminant class and occur in both gaseous and particulate phases in the atmosphere. The vapor-particle partition exhibits a strong dependence on molecular weight. LMW PAHs tend to have a higher concentration in the vapor phase while HMW ones are often associated with the particles. The vapor-phase PAH chromatograms are characterized by strong peaks of congeners with 3–4 rings, of which fluorine, phenanthrene and their methylated derivatives, fluoranthene, and pyrene are the dominant PAH species, while HMW (>252) PAHs species were not detected in the vapor phase due to their low volatility. Higher molecular weight PAHs, from chrysene to coronen except perylene, dominated PAHs in the particulate phase with benzo[*g*,*h*,*i*]perylene as the highest.

Another study (Guo et al., 2003a) showed that the sum of 16 PAHs in PM_{10} was higher than that in $PM_{2.5}$ at two sites in the same season. For instance, at the PU site, in the summer, the total PAH concentration in $PM_{2.5}$ was 4.87 ng m^{-3} while in PM_{10} it was 5.82 ng m^{-3} (Table 5.1). At the KT site in the winter, the sum of PAHs in $PM_{2.5}$ was 27.9 ng m^{-3} and PAHs in PM_{10} was 38.6 ng m^{-3}. For individual PAHs, most at these two sites had similar patterns to $PM_{2.5}$ and PM_{10} except for benzo[*a*]pyrene and benzo[*k*] fluoranthene. The results indicate that most of the PAHs are in the $PM_{2.5}$ fraction. There was no statistical difference in ratios for individual PAHs in either season at the two sites. This reflects that the ratios of individual PAHs in $PM_{2.5}$ to that in PM_{10} in Hong Kong have common patterns, regardless of speciation, season and sampling locations.

5.2.1.9. Transport

Airborne particles may be delivered to surfaces by wet and dry deposition. Several transport mechanisms, such as turbulent diffusion, precipitation, sedimentation, Brownian diffusion, interception, and inertial migration, influence the dry deposition process of airborne particles. Large particles (dN10Am) are transported mainly by sedimentation; hence, large particulate PAHs tend to be deposited nearer the sources of emission Small particles (db1Am), which behave like gases, are often transported and deposited far from where they originated (Baek et al., 1991; Wu et al., 2005).

The transport pathway is severely influenced by meteorological conditions. In some northern cities, such as Tianjin, the dry deposition of airborne PAHs is highly likely to be the predominant mode of atmospheric loading to underlying surfaces (Wu et al., 2005). Wu et al. (2005) have studied the PAHs in dustfall in Tianjin; the total amount of PAH16 (sum of 16 PAH compounds) in the dustfall ranged from 1.0 to $48.2\,\mathrm{ng\,g^{-1}}$ with a mean of $6.6\,\mathrm{ng\,g^{-1}}$ for the nonheating season, and from 2.5 to $85.5\,\mathrm{ng\,g^{-1}}$ with a mean of $10.7\,\mathrm{ng\,g^{-1}}$ for the heating season. The profiles of the PAH compounds in the samples collected in different seasons are similar. The dominant species in the heating season were naphthalene, phenanthrene, fluoranthene, and chrysene in dustfall and naphthalene, fluorine, phenathrene and fluoranthene during the nonheating season. This corresponds to 79 and 76% of total PAH concentrations for heating and nonheating seasons, respectively. The concentrations of most individual PAH compounds in the heating season samples were higher than those in the nonheating season samples with the exceptions of acenaphthene, fluorine and fluoranthene. It should be emphasized, however, that these are general trends. The fractions of HMW PAHs (4–6 rings) in the bulk of the dustfall samples from the heating season were higher than those from the nonheating season except for samples collected from an industrial area in eastern Tianjin and those collected from locations near open coal storage sites and traffic roads. Seasonal variation in the ΣPAH456 values (sum of 4–6-ring PAHs) reflects the increase in fossil fuel consumption in winter. The deposition was highest in urban and east industrial areas during the heating season. Compared with those of the nonheating season, samples from the heating season were characterized by a higher fraction of high molecular weight PAHs with 4–6 rings, except for those from the east industrial area. The east industrial area had more significant correlations between individual PAH compounds, and more discrete triangular components of 3-, 4-, 5-, and 6-ring PAHs. The deposition fluxes of ΣPAH15 (sum of 15 PAHs except naphthalene), ΣPAH6 (sum of 6 carcinogenic PAHs recommended by IARC) and benzo[*a*]pyrene (BaP) from atmospheric deposition to the whole area were estimated to be 1911, 196 and 53 ng m^{-2} per year, respectively. Furthermore, the deposition contribution of PAHs during domestic heating season in winter was not significant relative to the annual inputs.

Qingdao is a coastal city in Shandong Province located down wind of the origin (Inner Mongolia and Hebei Province) of the Asian dust storms, which often occur in the spring, when northwesterly winds prevail. Guo et al. (2003b) measured PAHs in dust episodes in Qingdao. Results showed that the average level of PAHs in the Asian dust storm samples (52.8 ng m^{-3}) was higher than in the spring samples (13.1 ng m^{-3}) but lower than in the winter samples (177.2 ng m^{-3}). The ratio of individual PAHs in dust storm samples was the same as that in the spring samples, suggesting that the contribution of PAHs by the storm was insignificant.

Since the weather in the sub-tropical coast region of China is under the influence of the Asian monsoonal circulation, the northwest wind is predominant in the autumn and winter seasons, which may bring the PAHs emitted into atmosphere in the northern cities to the south. Hong Kong may act as a receptor of the huge anthropogenic emissions from this region by long- and medium-range transport, especially in winter (Guo et al., 2003a).

5.2.2. Factors affecting emissions of PAH

5.2.2.1. Source temperature

Source temperature plays an important role in PAH formation. The composition of PAHs varies depending on the combustion temperature. At low to moderate temperatures, such as in a wood stove, or from the combustion of coal, low molecular weight parent PAH compounds are abundant, and display a higher degree of alkylation. On the other hand, at high temperatures, such as in vehicle emissions, HMW parent PAH compounds are dominant, and display a higher number of unsubstituted species. As a result, nonalkylated/alkylated indices are high for pyrogenic PAH mixtures and low for petrogenic PAHs.

5.2.2.2. The rank of coal

The rank of coal (maturity) is an important factor that affects PAH emissions from residential combustion. PAH emission from various coals is found to have a relationship with their volatile contents, and the complete combustion of coals with a high volatile content is more difficult to achieve. Bituminous and sub-bituminous coals with high volatile content yield more PAHs when burned at low temperatures, such as residential combustion, while anthracite coal containing very little volatile matter can burn more completely and emit PAHs with a mass that is three orders of magnitude lower than bituminous coal. Smoky coal, which is burned as fuel for cooking and heating in unvented homes, produces combustion emissions composed primarily of parent PAHs and alkylated PAHs.

5.2.2.3. Burning conditions

Burning conditions also affect PAH emissions. For example, although most of the power plant fuels are bituminous coals, large-scale combustors such as power plants have very low PAH EFs, which are in the same order or even lower than that from anthracite in residential combustion. The poor air supply in residential burning may be another reason for the high production of PAHs. Ledesma et al. (2000) concluded that most of the PAH mass is produced when the oxygen ratio is under 30% during bituminous coal burning. This result indicates that it may be possible to decrease EFs by improving aeration conditions in residential combustion.

In cooking practice, Zhu and Wang (2003) found that during three different cooking practices (boiling, broiling and frying), boiling produced the least levels of PAHs. For fish, a low-fat food, frying it produced a larger amount of PAHs compared to broiling practice, except for pyrene and anthracene. Meanwhile, the production of PAHs from three common cooking oils (lard, rapeseed oil and soybean oil), lard produced more PAHs than rapeseed oil and soybean oil Additionally, an increase in cooking temperature generally increased the production of most PAHs.

5.2.2.4. Other factors

Other factors affecting the emission of PAHs include changes in emission patterns (stationary and vehicular) and meteorological conditions (daylight hours, ambient temperatures and pressure), which affect the volatilization and photochemical activity of PAHs. Zhu and Wang (2005) found that compared to those from gasoline engines, emissions from diesel engines were less toxic, although they might produce more PAHs. Of the same vehicular and oil type, automobiles with longer mileages produced more toxic PAHs. PAH distributions in the vehicular exhausts were related to the oil type. Large difference was found in the relative abundance of 3-, 5- and 6-ring PAHs between exhausts from gasoline and diesel oil engines. Diesel oil engines produced relatively lighter PAHs such as naphthalene, acenaphthene, and fluorine, while gasoline engines emitted heavier kinds such as benzo[*k*]flouranthene, indene and benzo[*g*,*h*,*i*]perylene. The automobile produced more PAHs with the increase of mileage, especially fluorine, pyrene, benzo[*a*]pyrene and benzo[*g*,*h*,*i*]perylene.

5.2.3. Identification of sources

The mixture of PAHs present in a particular sample in many cases mirrors the sources that produce them. Several methods can be used to qualitatively identify the probable sources of PAHs. Commonly used methods include the abundance ratios of individual compounds, the fossil fuel pollution index (FFPI), and diagnostic ratios indicative of sources (petrogenic vs. pyrogenic). Quantitative apportionment of sources needs sophisticated statistical approaches such as the chemical mass balance models (Li et al., 2003).

5.2.3.1. Abundance ratios of individual compounds

5.2.3.1.1. Phenanthrene/anthracene (Ph/An) and fluoranthene/pyrene (Fl/Pyr)

PAHs from different pollution sources have different compositions and relative ratios that can be used as indicators of pollution sources. Ph/An and Fl/Pyr ratios are most commonly used as clues to source and delivery routes of the PAHs (Okonkwo, 1997). The ratio of Ph/An within the 3-ring PAH group and Fl/Pyr within 4-ring PAH group were used to differentiate PAHs of different origins. Phenanthrene is more thermochemically stable than anthracene, and therefore at low maturation temperatures, much higher molar fraction of phenanthrene is produced compared to anthracene. The molar ratios of Ph/An at petroleum maturation temperatures lead to higher values. The ratios could be as high as 50 at 373 K. On the contrary, high temperature processes (800–1000 K), such as the incomplete combustion of organic materials (coal burning, wood burning, vehicular exhaust emission, waste crankcase oil, and asphalt roofing material), are characterized by low Ph/An ratio value.

Therefore, Ph/An $>$ 15 may point to petrogenic sources and Ph/An $<$ 10 to pyrolytic sources. Due to the wide range of values for this index found in the literature, values between 10 and 15 are considered indeterminate relative to source. In petroleum-derived PAHs, pyrene is more abundant than fluoranthene, while at higher combustion temperatures a predominance of fluoranthene over pyrene is characteristic. So the Fl/Pyr values greater than 1 are obviously related to pyrolytic sources, whereas values less than 1 are attributed to petrogenic sources. In order to avoid erroneous conclusions, the two ratios are often combined. When Ph/An $>$ 15 and Fl/Pyr $<$ 1, the PAH input is mainly from crude oil sources; and when Ph/An $<$ 10 and Fl/Pyr $>$ 1, the major input may be related to combustion (Wang et al., 2004b).

5.2.3.1.2. *Methylphenanthrenes/phenanthrene (MP/P)*

The ratio of alkylated PAH homologs to parent compounds is also characteristic of PAH sources. Generally, PAHs from a petrogenic source have LMWs with the depletion of those having HMW, while pyrogenic sources are abundant in HMW PAHs (Zakaria et al., 2002). Petrogenic PAHs are mainly alkylated homologs while pyrogenic are mainly parent PAHs (especially fluoranthene, pyrene). The methylphenanthrenes to phenanthrene (MP/P) ratio is widely used to express the abundance of alkyl homologs and to distinguish petrogenic from pyrogenic sources (Zakaria et al., 2002; Mai et al., 2003). MP/P ratios measured in combustion mixtures are generally lower than 1, whereas those in unburned fossil fuel PAH mixtures typically range from 2 to 6 (Zakaria et al., 2002).

5.2.3.1.3. *Perylene to ΣPAH (PER/ΣPAH)*

In most cases, identifying specific pollutant sources from complicated routes is a great challenge. Generally, in coastal areas, PAH congeners are divided into three categories: petrogenic, pyrogenic and biogenic, based upon diagnostic ratios or composition distributions of parental PAH compounds. Some PAHs, such as perylene, are derived from the diagenetic transformation of terrestrial precursors in the aquatic environment, and partially from petroleum or pyrolytic processes. Their concentrations have been found to vary dramatically from 100 to 4000 ng g^{-1} in marine and estuarine sediments (Venkatesan, 1988). Typically, for pyrogenic PAHs, perylene represents ~1–4% of the ΣPAH concentration (Wakeham et al., 1980; Wang et al., 1999). It has also been suggested that a concentration of perylene higher than 10% of the total pentaaromatics isomers can indicate a probable diagenetic input; if not, then a probable pyrogenic origin. In a study of core samples of four lake sediments, Wakeham et al. (1980) found perylene was usually the most abundant PAH, accounting for 70–90% of the ΣPAH concentration in deeper, older sediment layers where decreasingly anthropogenic PAHs were found.

5.2.3.1.4. Other ratios

Certain diagnostic ratios of alkylated dibenzothiophene and alkylated phenanthrene compounds were used to identify oil incineration residues. Furthermore, two ratios of dibenzothiophene and phenanthrene alkylated homologs, double ratios, were used to distinguish between Ixtoc-1 and non-Ixtoc-petroleum (Boehm et al., 1997). Page et al. (1996) also used double ratios to distinguish background petroleum hydrocarbons from the Exxon Valdez spill oil. Fang et al. (2003) found that the 4,6-dimethyldibenzothiophene/3,6-dimethyl-phenanthrene (4,6-C_2D/3, 6-C_2P) ratio was more useful than the MP/P ratio in tracing petrogenic PAHs from the inner harbor area to the adjacent coastal environment.

These ratios should be used in combination to avoid erroneous conclusions regarding origins of PAHs. For example, Lake et al. (1979) found that used motor oil exhibits Ph/An ratios as low as 3, which could easily be misinterpreted as a pyrogenic. Generally, in contrast to pyrogenic sources, petrogenic sources are characterized by high ratios of Ph/An ($\mathrm{Ph/An} > 15$) and MP/P ($\mathrm{MP/P} > 2$) in association with lower ratios of Fl/Pyr ($\mathrm{Fl/Pyr} < 1$) and benzo[*a*]anthracene/chrysene ($\mathrm{BaA/Chr} \leqslant 0.4$) (Readman et al., 2002). Fl/Pyr and BaA/Chr ratios are not sensitive enough to be used to distinguish petrogenic PAHs from pyrogenic PAHs in an area where pollutants come from multiple sources.

5.2.3.2. Fossil fuel pollution index (FFPI)

The FFPI is a diagnostic ratio designed to determine the approximate percentage of fossil fuel PAHs relative to the total PAH in a sample. The FFPI is calculated as:

$$\mathrm{FFPI} = \left[\frac{Ns + Ps + 0.5(Ps + C_1P) + Ds}{\sum \mathrm{PAH}}\right] \times 100,$$

where Ns, Ps and Ds are the sum of the naphthalene, phenanthrene and dibenzothiophene homolog series, respectively. These homolog series include the parent compound and the alkyl-substituted homologs. C_1P is methyl phenanthrene and ΣPAH is the sum of the 2–6-ring PAHs (Savinov et al., 2000).

5.2.3.3. Diagnostic ratios indicative of sources

The combustion/pyrolysis of fossil fuels yields PAH mixtures in which unsubstituted compounds in the higher molecular weight (MW) range

(MW > 178) prevail. PAHs in either fossil fuels or unburned fossil fuel residues are characterized by higher proportions of LMH PAHs and an increased abundance of alkylated homologs.

A concentration ratio of anthracene to the sum of anthracene and phenanthrene, An/(An + Ph) lower than 0.10 is usually taken as an indication of petroleum combustion and a ratio higher than 0.10 as dominance of heavy fuel combustion. Among PAHs with molecular mass of 228, the ratio of benzo[*a*]anthracene to the sum of benzo[*a*]anthracene and chrysene, BaA/(BaA + Chr) is also indicative of the sources. A ratio lower than 0.20 suggests a petroleum source, whereas a ratio from 0.20 to 0.35 indicates either a petroleum or combustion source, and any ratio higher than 0.35 signify a combustion origin. Similarly, petroleum sources may be suggested by a ratio of indeno(1,2,3-*cd*)pyrene to the sum of indeno(1,2,3-*cd*)pyrene and benzo[*g*,*h*,*i*]perylene, In/(In + BP), lower than 0.20. A ratio between 0.20 and 0.50 may indicate liquid fossil fuel (vehicle and crude oil) combustion, and a ratio higher than 0.50 suggests grass, wood and coal combustion (Chen et al., 2005a).

Another molecular ratio that has been proposed to differentiate the source of PAHs is fluoranthene to fluoranthene plus pyrene (Fl/Fl + Pyr) with 0.40 being defined as the petroleum/combustion transition point (Yunker et al., 2002). Most petroleum samples have Fl/Fl + Pyr ratio below 0.40 while those of most combustion generated PAHs are above 0.40. In addition, the ratio is further divided into two regions: a ratio between 0.40 and 0.50 is more characteristic of liquid fossil fuel (vehicle and crude oil) combustion whereas a ratio greater than 0.50 is characteristic of grass, wood, or coal combustion (Zhang et al., 2004a).

5.2.4. Fate of PAHs in the atmosphere

Once they enter the atmosphere, PAHs are redistributed between gas and particle phases and are subject to removal mechanisms such as oxidative and photolytic reactions and wet and dry deposition.

5.2.4.1. Atmospheric fallout

Although atmospheric PAHs are partitioned between particulate matter and gas phase, they are mainly associated with particulate matter. PAH concentrations found in the atmosphere are highly dependent on the size of particles, and the highest concentrations are found in inhalable particles.

Kaupp and McLachlan (2000) has investigated the distribution of PAHs within the full size range of atmospheric particles. The study showed that 97% of the PAHs with 5 or more rings, which were all more or less completely particle bound in the atmosphere, were associated with particles with aerodynamic diameters (d_{ae}) $<2.9\,\mu m$. The substance loading decreased steadily with increasing particle size. On average, only 3.4 and 1.2% of the $Cl_{7-8}DD/F$ and the PAHs with 5 or more rings, respectively, were found on large particles with $d_{ae} > 8.6\,\mu m$.

As semi-volatile organic compounds, PAHs are transported in the atmosphere as gas and/or particulate phases and scavenged according to various processes: (i) wet deposition: PAHs become associated with rain either by being dissolved in the raindrop or being incorporated as particles; (ii) dry deposition: they are associated with particles, whose transport is complex, depending on various physical factors; (iii) air–water exchange: they may be adsorbed and conversely volatilized when facing large aquatic systems.

Ollivon et al. (2002) has studied atmospheric deposition of PAHs to an urban site in Paris, France. They collected atmospheric fallout to analyze PAHs. The study showed that total PAH concentrations in bulk (dry plus wet) precipitation ranged from 51 to $995\,ng\,l^{-1}$ and were higher than those analyzed in rivers crossing the Paris area. The same trend was observed for PAH concentrations in bulk (gaseous plus particulate) air measured by the Laboratoire d'Hygiene de la Ville de Paris. Monthly fluxes ranged from $5.3\,\mu g m^{-2}$ in August to $63\,\mu g m^{-2}$ in December for total PAHs, with annual flux of $234\,\mu g m^{-2}$, corresponding to 2.1 and $27.7\,\mu g m^{-2}$ for the 6 PAHs of the WHO recommendations and $104\,\mu g m^{-2}$ for a year. The winter loading was two times higher than the summer one, and heating contribution was estimated to be 41% of the annual loading.

Garban et al. (2002) investigated the atmospheric bulk deposition of PAHs onto France. The study showed that atmospheric deposition was the main source of PAHs to terrestrial ecosystems and especially to soils.

5.2.4.2. Photo degradation

The photo degradation of PAHs is a topic of current interest worldwide. Information on the fate of particulate PAHs released to the atmosphere is at present fragmentary and unclear. It is generally assumed, however, that photochemical oxidation processes play an important role. Studies have shown that PAHs associated with atmospheric particulate matter decay rapidly in sunlight under appropriate atmospheric conditions. Their decay rates are strongly influenced by light intensity, temperature, water vapor concentration, and other atmospheric parameters (Kamens et al., 1988). A number of studies have demonstrated that the nature of solid particle surface strongly influences PAHs decay rates. Particle associated organic substances also have important effects on PAH decay (Buulter & Crossley, 1981; McDow et al., 1994; Odum et al., 1994; Jang & McDow, 1995).

Pan et al. (1999) reported detailed observations of PAH decay in aerosols under UV light of 253.7 nm. The study used a high volume sampler to collect the total suspended particles in air with quartz filters as the supporter. The results showed that the photo degradation of PAHs under UV radiation took place immediately, and was a first-order reaction. The photodegradation rate constant (k) is related to the oxidation half-wave potential ($E_{1/2}$) and the structure of the PAHs.

Wang et al. (1997) studied the photochemical behavior of selected PAHs, such as B(a)P, B(k)F and fluoranthene in coal smoke particles, using an indoor Teflon smog chamber. Experiments suggested that the photochemical reaction of PAHs is of first order. The obtained photodegradation rates of PAHs were proportional to light intensity and water vapor concentration. Temperature and PAH loading also influence PAH degradation rates. A model for PAH loss has been developed on the basis of these results and its simulations suggest that coal particle PAH half lives are of the order of a period of days in the winter and a few hours in the summer.

The spectral composition of sunlight reaching the Earth's surface can be characterized by spectral bands, which include the UV-B region (280–315 nm), the UV-A region (315–400 nm), visible light (400–780 nm) and the infrared band ($>$800 nm). Approximately 4% of the total energy from sunlight reaching the Earth's surface occurs in the UV band. Due to absorption by the stratospheric ozone layer, the minimum wavelength of terrestrial global radiation is approximately 290 nm. Although UV-B radiation contributes less than 1% of the total solar energy reaching the Earth's surface, it may play an important role in the photodegradation of organic pollutants in the environment due to its high photonic energy of approximately 4 eV.

Niu et al. (2004) investigated the photodegradation of PAHs sorbed on the surfaces of spruce (*Picea abies (L.) Karst.*) needles. The role of sunlight and, in particular, the role of short wavelength UV-B radiation was studied in a sun simulator under controlled environmental conditions. The photodegradation of PAHs followed first-order kinetics. No distinct phases of kinetics were observed for the PAHs. Direct photolysis dominated the photodegradation of PAHs.

However, the mechanism of photodegradation is still not well understood. It is suggested that it may be due to the photoreaction of OH free radical striking on the PAH molecules.

5.2.4.3. Reactions with other substances

The PAHs in the atmosphere can react with other substances, and the reaction products can have different toxicity compared with PAHs. For example, PAHs can react with fog, which has NO_X compounds. Their products have direct activity of mutation.

Guo et al. (2000) used the methods of chemical isolation and fluorescence to determine the binding reaction of the PAH fraction in the floating dust of Taiyuan City with DNA. The results showed that the PAH fraction from the floating dust in both day and night were capable of binding with DNA. However, the capacity in the day was stronger than in the night. The PAHs in the floating dust of Taiyuan City can react directly with DNA without being activated or metabolized by organisms. The reaction of PAHs in the day may be further strengthened by the increase in emissions from moving sources and the intensity of sunlight.

PAHs exist in the atmosphere in both vapor- and particulate-phases. PAHs with low molecular weights tend to be more concentrated in the vapor phase while the ones with higher molecular weights are often associated with particulates. Since they are emitted to the atmosphere as a result of incomplete combustion of fossil fuels and other organic materials, a large fraction of them are initially in the gas phase and then sorbed to existing particles. The fate, transport and removal of PAHs from the atmosphere by dry and wet deposition processes are strongly influenced by the gas-particle partitioning of PAHs. Understanding the gas-particle distribution of the PAHs is also helpful in assessing respiratory health effects, since these compounds have been found to be very harmful even at low concentrations. Particle size distributions of PAHs have been studied mostly in Europe and America. Distinct geographical locations and meteorological conditions can result in significant differences in aerosol size distribution. China is unique in many aspects because basic emission control technologies have not been intensively used yet, even though the eastern part of China, including the Pearl River Delta region, has developed quickly economically in the recent two decades.

5.3. PAHs in water and sediments

China has more than 50,000 rivers with catchment areas of some 100 km^2, of which 79 have catchment areas of more than 10,000 km^2. The rivers in China have a total length of 226,800 km and a total flow of more than 2,600,000 million m^3. With the rapid economic development and population increase that have occurred in recent years, the water quality of these rivers and lakes has decreased significantly. Even some drinking water sources are choked by nutriment as well as micropollution of toxic organic compounds. Among the toxic organic compounds existing in the water environment in China, PAHs are important pollutants. Li et al. (2006) reported significant PAH contamination in the middle and lower reaches of the Yellow River, with concentrations of benzo[*a*]pyrene above drinking water standards in most of the stations sampled. Qiao et al. (2006) also found PAH contamination in 25 surface sediment samples collected from Meiliang Bay, Taihu Lake, China, in 2003. Almost all large rivers in China belong to the exterior river system, which directly or indirectly empty into the sea. Therefore, any chemical input from these estuaries may cause unexpected marine environmental problems. Moreover, economy growth and urbanization have accelerated in the last two decades along the Chinese coastline as a result of drastic economic reform initiated in the early 1980s. Yuan et al. (2001) have already detected PAHs in sediment samples collected from three estuaries on the east coast of China from 1994 to 1999. Since sediments are the ultimate sinks and reservoirs of contaminants, it is essential to understand sediment pollution in order to assess the impact of anthropogenic activities on aquatic systems.

Due to their low solubility and hydrophobic nature, PAHs tend to be associated with particulate matter and accumulate in sediment. The contamination of PAHs in water is a complex phenomenon that involves various factors, such as water, suspended particulate matter (SPM) and sediment. Heemken et al. (2000) verified that 80–90% of the PAHs in the total water body is adsorbed to SPM, which emphasizes the importance of measuring particle-bound PAHs. However, the partition equilibrium between water and SPM is not usually available for wild situations due to weather, human activity and other impacts.

In this section, PAH contamination statuses in surface water and sediment were reviewed to gain insight into the possible sources of PAHs and the interaction between different environmental compartments. Additionally, investigations of the PAH homolog profile were conducted to provide useful information on possible pollution sources, and a comparison of PAH patterns in different places in China and abroad were also attempted.

5.3.1. PAH pollution of Yangtze River basins

The Yangtze River (also called Changjiang), the largest river in China, is the third largest river in the world. It is fed by hundreds of tributaries, wanders eastward across the mainland of China, flows through the provinces or autonomous regions of Qinghai, Tibet, Sichuan, Yunnan, Hubei, Hunan, Jiangxi, Anhui, and Jiangsu, and makes an incessant rush into the East China Sea in Shanghai. The Yangtze River has a length of 6300 km and a catchment area of 1.8 million km^2, which equivalent to 1/5 of the total land of China. In recent years, there has been great concern on the effects of increasing inputs of nutrient and organic compounds into the coastal regions of China, and the majority of these surveys focused on coastal seawater and estuarine water. However, few data are available for PAH contamination of the inland waters of China, which usually act as receptors for sewage, industrial effluents, and urban or rural runoff (Tables 5.2 and 5.3).

Zhu et al. (2004) reported the concentrations of 10 PAHs in four bodies of water in Hangzhou, China (July and November 1999–2002). The maximum levels of PAHs in the water bodies (34.4–67.7 $\mu g l^{-1}$) were found in July, while significantly lower PAH concentrations (4.7–15.3 $\mu g l^{-1}$) were measured in November. The measured PAH concentrations in sediments and soils, runoff water, and air particles were 224–4222 ng g^{-1}, 8.3 $\mu g l^{-1}$ and 2.3 $\mu g m^{-3}$, respectively. Clearly, such substantial contamination may lead to acute toxic effects on aquatic organisms. However, the erosion of soil material does not contribute significantly to the contamination of sediments. The atmospheric PAH deposition to water bodies in the city area of Hangzhou was estimated to be 530 tons/a, while the contribution of surface runoff water was

Table 5.2. PAHs concentration in water phase of Yangtze River Basin

Location	Year	ΣPAHs	Average ($\mu g\, l^{-1}$)	Range ($\mu g\, l^{-1}$)	Reference
Qiantang River, Hangzhou	July 1999–2002	10	67.70	49.46–71.03	Zhu et al. (2004)
	November 1999–2002		15.31	2.436–46.54	
Inland River, Hangzhou	July 1999–2002		34.43	15.76–58.06	
	November 1999–2002		8.837	1.520–38.71	
West Lake, Hangzhou	July 1999–2002		57.66	38.45–96.21	
	November 1999–2002		9.846	0.989–22.07	
Hangzhou Canal, Hangzhou	July 1999–2002		48.09	21.32–74.44	
	November 1999–2002		4.701	1.104–9.168	
Surface water in Hangzhou	December 2002	10	–	0.989–9.663	Chen et al. (2004)
Minjiang Estuary	November 1999	16	72.4	9.9–474	Zhang et al. (2004b)

Table 5.3. PAHs concentration in sediment of Yangtze River Basin

Location	Year	ΣPAHs	Average level ($ng\,g^{-1}$ dw l)	Range ($ng\,g^{-1}$ dw)	Reference
Meiliang Bay, Taihu Lake	2003	16	2563	1207–4754	Qiao et al. (2006)
Qiantang River, Hangzhou	November 2002	10	224.0	139.9–308.0	Zhu et al. (2004)
Inland River, Hangzhou	November 2002	10	674.2	141.4–1560.6	
West Lake, Hangzhou	November 2002	10	664.6	520.2–839.0	
Hangzhou Canal, Hangzhou	November 2002	10	4221.9	2342.2–342.6	
Surface water of Hangzhou	December 2002	10	–	132.7–7343	Chen et al. (2004)
Core sediment in Donghai, Yangtze Estuary	July 1998	7	–	61–7618	Xu et al. (2001)
Core sediment Baoshan, Yangtze Estuary	July 1998	7	–	5–2370	
Core sediment, Yangtze Estuary	September 1996	14	–	80–11,740 (parent PAHs and substituted naphthalene series)	Liu et al. (2000)
Surface sediment, Yangtze Estuary and adjacent East China Sea	–	11	–	22,000–18,2100	Bouloubassi et al. (2001)
Minjiang Estuary	November 1999	16	433	112–877	Zhang et al. (2004b)

estimated to be 30.7 tons/a. The value of PAH input via urban runoff into water was lower than PAH input via atmospheric particle deposition to urban and soil surfaces, suggesting that a great number of PAHs accumulated in soil and urban surfaces. Furthermore, it should be noted that PAH deposition from air to Hangzhou City water bodies was ~10 times larger than that in the Mediterranean Sea (Zhu et al., 2004).

Chen et al. (2004) collected 17 surface water samples and 11 sediment samples of four water bodies, and 3 soil samples near the water-body bank in Hangzhou, China in December 2002. The sum of PAH concentrations ranged from 989 to 9663 $\mu g l^{-1}$ in surface waters, from 132.7 to 7343 $ng\,g^{-1}$ dry wt. in sediments, and from 59.7 to 615.8 $ng\,g^{-1}$ dry wt. in soils. Obviously, the pollution status has not been alleviated compared to the situation in 1999–2002 (Zhu et al., 2004). Similar to the PAH composition of European rivers, 3-ring PAHs dominated in surface waters and soils, while 4-ring PAHs dominated sediments. Furthermore, Chen et al. also evaluated the sources of PAHs in different water bodies by comparing K_{oc} values in sediments of the river downstream with those in soils. PAHs released from industrial wastewater in the past was identified as the source for the PAHs in the Hangzhou section of the Great Canal, while present PAHs in sediment serve as sources of PAHs in surface water. PAHs in the Qiantang River were mostly from soil runoff, while PAHs in the West Lake were from municipal road runoff.

In the middle and lower reaches of the Yangtze River, many large lakes are connected, namely the Dongting Lake, the Poyanghu Lake, the Caohu Lake and the Taihu Lake. According to the GC-MS measurement report of 25 surface sediment samples collected from Meiliang Bay, Taihu Lake, China in 2003, total concentrations of 16 PAHs, identified as priority pollutants by the USEPA, ranged from 1207 to 4754 $ng\,g^{-1}$ dry wt. (Qiao et al., 2006). These PAH levels were higher than those in river sediments in China but were lower than those found in sediments of urban areas and harbors.

Since PAHs are highly hydrophobic, higher level of PAHs are expected in not only sediment but also pore water, possibly due to higher concentrations of dissolved organic carbon or colloids with which the hydrophobic pollutants were strongly associated. Xu et al. analyzed two sediment core samples of $\sim$50 cm long, which were collected from intertidal mud flats at the Baoshan site near a sewage outlet (Shidongkou) and at the Donghai site, the easternmost tidal flat of the Yangtze estuary. The total concentrations of PAHs in the two sediment samples ranged from 61 to 7618 $ng\,g^{-1}$ at the Baoshan site, and from 5 to 2370 $ng\,g^{-1}$ at the Donghai site. Total and individual PAH concentrations in sediment cores were characterized by at least one subsurface maximum, followed by decreased levels both to the surface and with increased depth (Xu et al., 2001). The author explained that this PAH abundance pattern indicated significant petroleum contamination in the Yangtze estuary due to incomplete combustion of fossil hydrocarbons. A few individual PAHs, such as acenaphthalene and anthracene in surface samples of the two cores, are in excess of current sediment quality criteria in the Yangtze estuary, implying significant anthropogenic input. Such PAH levels seem comparable to the published data of the same group in 2000 (Liu et al., 2000), in which the total concentration of PAHs ranged from 80 to 11,740 ng g^{-1}. The historical record of PAHs in the core is found to be in accordance with historical sewage discharge events during the 1980s and 1990s. The distribution of target molecule acenephthene, the fluoranthene/pyrene ratio, the proportion of 2–3- and 4–5-ring PAHs, and the ratio of alkylated naphthalene to parent naphthalene in the core sediments demonstrated that the sources in this area are characterized by petroleum-derived PAH contamination (mainly sewage discharge and the river runoff) and the incorporation of atmospheric inputs. Compared to the core sediment results, PAH contaminations in surface sediments from the Yangtze River estuary, East China Sea, were dominated by biogenic perylene at sampling stations receiving riverine input (Bouloubassi et al., 2001). Bouloubassi et al. found that anthropogenic PAHs released from combustion/pyrolysis processes varied from 17 to 157 ng g^{-1} and fossil PAH level located in 42–187 ng g^{-1}. However, the overall level of anthropogenic PAHs was rather low compared to those of relevant estuaries worldwide.

Compared to that of the main stream of Yangtze River, PAH pollution in some tributaries are more serious. According to the determination profile of 16 priority PAHs in water, pore water, sediment, soil and vegetable samples from the Minjiang River Estuary in China, total PAH concentrations varied from 9.9 to 474 μgl^{-1} in water, 82.1 to 239 μgl^{-1} in pore water, 112 to 877 ng g^{-1} dry wt. in surficial sediments, 128 to 465 ng g^{-1} dry wt. in soil, and 8600 to 111 000 ng g^{-1} dry wt. in Chinese vegetables (Zhang et al., 2004b). PAHs in sediment and soil are comparable to those found in many other similar environments, but the levels of these contaminants in surface water and Chinese vegetables were relatively high compared to data reported elsewhere. Moreover, the concentration gradient implies a potential flux of pollutants from sediment pore water to overlying water. The ratios of selected PAHs indicated that PAHs in the Minjiang River Estuary were mainly derived from incomplete combustion of fossil fuel.

Since toxic contaminants may disturb the biological condition of aquatic ecosystems, toxicological profiles of pollutants in surface water from an area in Taihu Lake, Yangtze Delta, was provided by analyzing genotoxic, hormone disrupting and Ah-receptor activity in water collected in January 1999 at Meiliang Bay, Taihu Lake, China, near the city of Wuxi in the Shanghai area. (Shen et al., 2001). The investigation used an array of in vitro tests, and the results indicated considerable contamination with genotoxic, dioxin-like and hormonal active compounds released into the environment by human activities, to which PAHs might have contributed.

Qiao et al. (2006) indicated that contamination levels of PAHs at most studied sites in Meiliang Bay, except some sites in the northern part of the bay, might not lead to adverse biological effects of the waterbody on the basis of the numerical effect-based sediment quality guideline (SQGs) of the United States. However, the carcinogenic potential of PAH pollution in water should not be neglected. The author used B[*a*]P toxicity equivalents (TEQs$^{\text{carc}}$) to express the total PAH levels since there is a good correlation between the benzo[*a*]pyrene level and the total PAH concentration ($r = 0.97$). The average TEQ$^{\text{carc}}$ value was 407 ng g^{-1} dry wt., and the maximum total TEQ$^{\text{carc}}$ value of 856 ng g^{-1} dry wt. was found at northern site 22. Compared with those of other sediments of other literature-reported sites, such as the bottom sediments from Guba Pechenga, Barents Sea, Russia (Savinov et al., 2003), TEQs$^{\text{carc}}$ values were higher in sediments of Meiliang Bay. Moreover, benzo[*a*]pyrene, a well-known carcinogen, astonishingly accounted for 60% of total TEQ$^{\text{carc}}$.

5.3.2. PAH pollution of Yellow River Basins

The Yellow River rises on the northern slopes of the Bayankela Mountains of Qinghai and traverses nine provinces or autonomous regions including Qinghai, Gansu, Sichuan, Ningxia, Inner Mongolia, Shaanxi, Shanxi, Henan, and Shandong. It is the second largest river in China and falls 4450 m over a length of 5465 km with a drainage area of 795,000 km^2. Similar to the Yangtze River, the Yellow River is a pivotal water supply for northern China and in recent years, has suffered from low water yields and water pollution. Moreover, national petrochemical industrial plants, mines, metallurgy factories and many other pollution sources are located in the middle and lower reaches of the river (Li et al., 1996; Li et al., 2006), and the contamination of PAHs has become one of the major problems in the Yellow River (Gao et al., 2001; Liu et al., 2004; Wang et al., 2004a).

The Yellow River possesses a notable feature that cannot be ignored: it is the largest loess deposit in the world. Because of intense soil erosion, the Yellow River far exceeds any of the world's large rivers in terms of annual sediment transport and is the most turbid large river in the world. Such high suspended-sediment content in water may affect the fate and effect of PAHs in the river to a considerable extent.

Recently, Li et al. (2006) assessed PAH concentrations, distribution between different phases, and transition along the middle and lower reaches of the Yellow River Concentrations of PAHs in water samples from the main stream of Yellow River ranged between 179 and

369 ng l^{-1} for the 15 PAHs with a mean value of 248.2 ng l^{-1}. The relative proportions of the 15 PAHs in all stations of the main stream were similar, and exhibited in the following order: naphthalene (50.5% on average) > phenanthrene (11.4%) > pyrene (7.8%) > fluoranthene (6.3%) > fluorine (6.0%) > dibenzo[*a*,*h*]anthracene (5.1%) > benzo[*g*,*h*,*i*]perylene (2.8%) > indeno[1,2,3-*cd*]pyrene (2.6%) > benzo[*a*]anthracene + chrysene (2.3%) > benzo[*a*]pyrene (1.9%) > benzo[*b*]fluoranthene (1.6%) > benzo[*k*]fluoranthene (1.0%) > anthracene (0.7%). Similar to that of the Yangtze River, the concentration of naphthalene was the highest (137 ng l^{-1}) among the PAHs, possibly because of its popular use in industries and households. Surprisingly, benzo[*a*]pyrene was also detected in high concentrations in main stream of the Yellow River, which exceeded the Environmental Quality Standard for Surface Water of China (2.8 ng l^{-1}, GB3838-2002) in all the stations at the main stream except the one in the Jiaogong Bridge. Like the Yangtze River, PAH concentrations in tributaries were higher than those in the corresponding sites in the main stream. Concentrations of PAHs in the tributaries ranged from 185 to 2182 ng l^{-1} in water for the 15 PAHs, in which the Mengzhou Channel had the highest levels of PAHs, which were almost 10 times higher than that of the main stream. Such a gradient mainly resulted from low water flow and direct wastewater discharge into the channel. However, the author excluded the possibility that PAHs in the main stream of the lower and middle reaches of the Yellow River come from its tributaries because the water flows of the tributaries were not significant enough to cause such pollution. Consequently, the PAHs in the water of the main river of the lower and middle reach of the Yellow River mainly came from the upper reach. The detected concentrations of PAHs in suspended particles were from 54 to 155 mg kg^{-1} dry wt. The relative proportions of the 13 PAHs in all stations of the main river were similar. Just like the situation of the Yangtze River, the proportion of higher molecular weight (5- to 6-ring) PAHs were found to be much higher in suspended particles than that in the water phase. PAH concentrations of suspended particles were mainly correlated with contents of total organic carbon. The average value of total PAHs in sediments from the main stream of Yellow River was 76.8 mg kg^{-1}, among which phenathrene occupied the largest proportion. In contrast to water and suspended particles, the proportions of PAHs in sediment samples from different stations of the main river varied significantly, and PAH levels in sediments were mainly correlated with the volume of particles smaller than 0.01 mm. PAHs in yellow River mainly originated from coal burning, although in some tributaries, PAH inputs could come from the combustion of petroleum (Li et al., 2006).

High sediment load may significantly change the behavior of PAHs in the river. Xia et al. (2006) reported the effect of sediment on biodegradation of chrysene, benzo[*a*]pyrene and benzo[*g*,*h*,*i*]perylene with phenanthrene as a co-metabolite substrate in natural waters from the Yellow River. They found that the biodegradation rates of PAHs increased with the sediment content in the water. Further studies indicated that the enhanced biodegradation rate in the presence of sediment might have been caused by three kinds of mechanisms: sediment enhancement in bacteria population growth, PAHs sorption on the sediment phase described by the dual adsorption–partition model, and the increase in PAH bioavailability by desorption (Xia et al., 2006).

5.3.3. PAH pollution of Pearl River Basins

The Pearl River is one of the largest rivers in the south and among the seven major rivers in China. The river is composed of the West, the North, and the East Rivers and the Pearl River Delta waterway network with a catchment area of 453,700 km^2. Intrigued by the open policy initiated in the early 1980s, the Pearl River Delta has become the most developed region in China in economic terms. The population has increased from 50.6 millions in 1979 to 69.0 millions in 1996, while the gross domestic production in 1997 experienced a 13.5% annual increase in the region compared to an average increase of 7.8% nationwide (Luo et al., 2006). There are many coal, aluminum, tungsten, tin and ferric sulfide mines standing along the waterways in the Pearl River Valley, Commercial/industrial cities such as Guangzhou and Nanning, especially the cities of Shenzhen, Zhuhai, which are listed in the special economic zones, have developed very quickly for the last 20 years that contribute to the boost of the local economy. The industrialization of the areas has resulted in severe environmental problems. Pollution has put the local water environment under very high pressure. Approximately 85% of SPM brought by the Pearl River is deposited in the estuary, and the rest is deposited in the rivers within the Pearl River Delta. Therefore, large amounts of particle-associated contaminants, such as PAHs, generated in the Pearl River Delta may accumulate in the sediments of the estuary and the South China Sea (Luo et al., 2006).

Luo et al. (2004) measured the PAH concentrations in suspended particles and dissolved phase from Baiertang water column and the Macao water column samples collected from the Guangzhou channel of the Pearl River and the Macao harbor. Total PAH concentrations varied from 189 to 637 $ng\,g^{-1}$ in sediments and 422 to 1850 $ng\,g^{-1}$ in SPM. 5,6-ring PAH compounds dominated in sediments and 2,3-ring compounds in SPM samples. While total PAH concentrations varied from 987.1 to 2878.5 ng l^{-1} in the Baiertang water column samples and from 944.0 to 6654.6 ng l^{-1} in the Macao water column samples (Luo et al., 2004). The vertical distribution profiles of pollutants and the partitioning of pollutants between particles and dissolved phases indicate that the pollutants in the water of this region mainly originated from the release and re-suspension of contaminants residing in the sediments. Compared to those of the Jiulong River estuariy and the Minjiang River estuary, the concentrations of PAHs in the Pearl River estuary were relatively higher. Relatively high values of PAHs appeared in sediments, SPM and bivalves at the outlet of the river, waterway and harbor during 1994 and 1997 (Hong et al., 2000). Mai et al. (2003) have made a comprehensive assessment of the input sources and transport pathways of PAHs found in the coastal sediments of Macao, based on measurements of 48 2–7-ring PAHs and 7 sulfur/oxygenated (S/O) PAH derivatives in 45 sediment, 13 street dust, and 68 aerosol samples. Total sediment PAH concentrations ranged from 294 to 12,741 ng g^{-1}, categorized as moderate contamination compared to other regions of Asia and the world. However, the total concentrations of 16 PAHs varied from 4228 to 29,325 ng l^{-1} in water, and from 115 to 1134 ng g^{-1} dry wt. in sediments in samples collected from Daya Bay (Zhou & Maskaoui, 2003). In comparison to many other marine systems studied, the PAH levels in Daya Bay waters were relatively high, and at six sites they were sufficiently high (>10 ng l^{-1}) to cause acute toxicity. The PAH composition pattern in sediments suggest dominance by medium to HMW compounds, and the ratio of certain related PAHs indicate important pyrolytic and petrogenic sources. The author analyzed the distribution coefficient (K_d) of PAHs and indicated that the K_d increased with the particular organic carbon content of the sediments, which is consistent with the PAH partitioning theory. The organic carbon normalized distribution coefficients (K_{oc}) also increased with the compounds' octanol/water partition coefficients (K_{ow}). The concentrations of total polycyclic aromatic hydrocarbons (ΣPAHs) and 15 individual PAH compounds in 20 surface sediments collected from four mangrove swamps in Hong Kong showed that ΣPAH concentrations ranged from 356 to 11,098 ng g^{-1} dry wt. with mean and median values of 1992 and 114.2 ng g^{-1}, respectively. These values were significantly higher than those of marine bottom sediments of Hong Kong harbors, suggesting that mangrove surface sediments accumulate more PAHs. The concentrations of ΣPAHs as well as individual PAH compounds varied significantly among mangrove swamps. The swamps heavily polluted by livestock and industrial sewage, such as Ho Chung and Mai Po, had much higher concentrations of total PAHs and individual PAHs than the other swamps (Tam et al., 2001).

In order to evaluate the risk of PAHs pollution in water to human health, PAHs in sediment and biotic samples including tilapia (*Oreochromis mossambicus*), bighead carp (*Aristichthys nobilis*), grass carp (*Ctenopharyngodon idellus*), crucian carp (*Carassius auratus*) and mandarin fish/fresh water grouper (*Siniperca chuatsi*) collected from different fishponds in the Pearl River Delta (Tanzhou, Sanjiao, Guangzhou, Shipai, Changan and Mai Po) were analyzed (Kong et al., 2005b). Mandarin fish, which belongs to the highest trophic level, accumulated the highest concentrations of PAHs among all fish species. Levels of PAHs in fish samples ranged from 1.91 to 224.03 $\mathrm{ng\,g^{-1}}$ (wet wt.). However, the potency-weighted total concentrations of PAHs in all muscle tissues were below the guideline value of 0.67 $\mathrm{ng\,g^{-1}}$ (wet wt.) for human consumption set by US EPA. In comparison with tilapia fish (*Tilapia mossambicus*) collected from the fishponds in Hong Kong, PAHs concentrations in fish from Pearl River Delta was relatively higher, which indicates that the fishponds in the mainland are more polluted than those in Hong Kong as a result of rapid socioeconomic growth in the region during the past 20 years (Kong et al., 2005a). Because of the bioaccumualation, concentrations of trace organic pollutants in the bivalves were 2–300 times higher than those in the sediments (Hong et al., 2000).

In the assessment of PAH sources, PAH isomer pair ratios were usually used. Ratio values of specific PAH compounds such as Ph/An and Fl/Pyr, were calculated to identify the possible source of PAHs. Values of Fl/Pyr ratio of 1.3–1.7 have been recorded for sediments at remote sites and ca. 1.0 for sites near urban centers (Helfrich & Armstrong, 1986). Values of Ph/An in the range of 3–11 are indicative of urbanized areas, especially of those most impacted by urban runoff, while ratios greater than 11 are indicative of remote sites that are primarily influenced by atmospheric deposition. This may be due to the selective photooxidation of anthracene during long-range transport (Qu et al., 2002). The spatial and temporal variability of PAH pollution in surface sediments and dated core sediments from the Pearl river and estuary in China revealed that the sediments from the sampling stations in the Guangzhou channel have the highest concentrations of PAHs. This may be due to contributions from the large amount of urban/industrial discharges from the city of Guangzhou (Mai et al., 2001). The pyrogenic (combustion) source, characterized by the abundance of parent PAHs, were predominant in the heavily contaminated station near the aging industrial area, and the petrogenic (petroleum-derived) PAHs were more abundant in the stations adjacent to the petrochemical plant and shipping harbor. Biomass and coal combustion are the major PAH sources of the outer part of the Pearl River estuary sediments and that petroleum combustion is the major PAH source of the inner part of estuary sediments (Luo et al., 2006). The SPM samples indicated multiple PAH sources (petroleum, petroleum combustion, and biomass and coal combustion). The distribution of perylene in the SPM samples indicated that the river was the dominant source of perylene in SPM. Compositional analysis and principal component analysis (PCA) suggested that different classes of PAHs in the coastal sediments of Macao might have been derived from different input sources via various transport pathways (Mai et al., 2003). The significant decrease of PAH concentrations in sediments from the Shiziyang channel is mainly attributed to the increasing degradation and desorption of low molecular weight PAHs and alkyl PAHs, and dilution by less contaminated water acid particles from the East river. The PAH contaminants were concentrated on the western side in the Lingding Bay of the Pearl River estuary because of the hydrodynamic and sedimentation conditions. Perylene is a naturally derived PAH. The high concentration of perylene in the sediment was indicative of an in situ biogenic origin. Dating of the sediment cores using Pb-210 indicated that higher PAH concentrations occurred in the sediments deposited after 1980, and higher fluxes of PAHs discharged into the Pearl River were found after 1990. The PAH profiles in four mangrove swamps in Hong Kong showed similar pattern, and were dominated by 2-ring naphthalene, and 3-ring fluorine and phenanthrene (Tam et al., 2001). The mangrove sediments had higher percentages of low molecular weight PAHs. These indicated that PAHs in mangrove sediments might originate from oil or sewage contamination (petrogenic input). Ratio values of Phe/Ant and Flu/Pyr were calculated to evaluate the possible source of PAH contamination in mangrove sediments. These ratios varied among samples, suggesting that mangrove sediments might have a mixed pattern of pyrolytic and petrogenic inputs of PAHs. Sediments collected from Ho Chung mangrove swamp appeared to be more dominated by pyrolytic input while those from Tolo showed strong petrogenic contamination.

5.4. PAHs in soil and plants

5.4.1. Distribution of PAHs in soil

PAHs in soil can be attributed to natural processes and human activities. Individual PAH concentrations in soils produced by natural processes like vegetation fires and volcanic exhalations have been estimated to be in the range of 1–10 $\mu g\,kg^{-1}$. Anthropogenic contribution has greatly affected the soil PAH concentrations. At present, even the lowest measured PAH concentrations in temperate soils are ~10 times higher than the concentrations assumed to have been present prior to industrialization. Generally, PAH concentrations in soil increase with increasing impact of industry, traffic, and domestic heating. PAH concentrations in topsoils increase in the order of arable soils < mineral soils under forest < permanent grassland < urban soils < specifically contaminated sites (Wilcke et al., 2000). The soil system seems to be the important repository for atmospheric PAHs. Once deposited, PAHs can reside for more than 20 years. The accumulation of PAHs in soil may lead to contamination of food chains, and then cause direct or indirect exposure to humans. Moreover, soil PAHs may transport to atmosphere and groundwater through leaching, evaporation and migration. Although soil pollution by PAHs has not been surveyed systematically in China, limited research has revealed the general trends of contamination in the soil of China. Agricultural soil in remote areas is usually uncontaminated. However, suburban and urban soil around big cities like Beijing may contain various kinds of pollutants because of sewage irrigation and air and water discharge of pollutants from industries Cities with PAH concentrations in soil reported in the literature are listed in Table 5.4. A brief scan of the table reveals that PAH concentration in the soil of China varied greatly according to the location and utilities of the sampling site. Generally, urban soil is more heavily contaminated with PAHs than suburban soil. For instance, in Beijing, the PAH concentration is 366–27,825 ng g^{-1} in urban soil while in suburban soil it is less than 7.84 ng g^{-1} (Tang et al., 2005, Ma et al., 2003, 2005a,b). The most heavily contaminated site is the wastewater irrigation area in Shengyang with PAHs content as unbelievably high as 900–27,378 mg kg^{-1} (Song et al., 2005). Because of the number of samples was usually very limited, some of the data may need to be considered with care. The contamination distribution pattern for whole country cannot be built at this stage.

5.4.1.1. *PAH contamination in urban soil and suburban soil*

Because anthropogenic activities are the main sources of PAHs, the levels of PAHs in soils in urban areas are approximately 2–10 times higher than those in rural areas. An extensive and systematic survey has been undertaken by Tang et al. (2005) to evaluate the PAH contamination of urban soils in Beijing, China. Soil samples were collected from campuses of universities, schools and kindergartens, public squares, fallow land, and roadsides, and were analyzed for 16 PAHs by GC-MS. There was a high variability in the total PAHs (ΣPAHs) concentrations, ranging from less

Table 5.4. PAH concentrations in soil of China

Cities	Sampling site	PAH concentration in soil (ng g^{-1})	No. of samples	Literature
Beijing, urban soils	Campuses of universities, schools and kindergartens, public squares, fallow land, and roadsides	366–27,825		Tang et al. (2005)
Beijing, suburban Soil	Subsoil	n.d.–0.982	45	Ma et al. (2005a)
	Topsoil	0.016–3.884	45	Ma et al. (2005b)
	Greenhouse soil	1.92–7.84		Ma et al. (2003)
Tianjin	Bulk soil	1.08–6.25	2	Tao et al. (2004)
	Rhizosphere	2.25–7.82	2	
	Wastewater irrigated paddy field	3900		Tao et al. (2002)
Hangzhou		59.71–615.8	3	Chen et al. (2004)
Guangzhou	Vegetable land	42–3077	43	Chen et al. (2005a)
Guiyang	Urban	247–1560	8	Hu et al. (2006)
	Suburban	61–511	5	
Xiamen	Jiulong agricultural catchment	0.50–0.95		Maskaoui et al. (2006)
Yangtze Delta Region	Area with copper- and zinc-smelting factory	0–530	65	Xing et al. (2006)
Shenyang	Waste water irrigation area	900,160–2,737,910		Song et al. (2005)

than 366 to 27,825 ng g^{-1}. The highest ΣPAHs concentrations were found at roadsides and industrial sites. Compared to urban soil, suburban soil is much cleaner.

In Guiyang City in Southern China, the total concentration of 16 priority PAHs in the soil of 13 sampling sites varied from 61 to 1560 ng g^{-1} (Hu et al., 2006). Urban samples and suburban samples showed drastically different PAH levels. The concentrations of 16 PAHs for urban soils are at a similar level as those in Beijing—between 247 and 1560 ng g^{-1}—while the concentrations of 16 PAHs for suburban soils are 61–511 ng g^{-1}. In all the samples, PAHs are dominantly composed of 4- and 5-ring species. Three of the samples (sample 8, 12 and 13) have 4-ring PAHs concentrations lower than 5-ring ones, which may be affected by the same pollution source. The other ten samples have 4-ring concentrations higher than 5-ring ones, and they may be affected by other different sources.

5.4.1.2. PAHs in surface soil and subsoil

PAHs usually distribute in different depths of soil, reflecting the source contribution. The concentrations of PAHs frequently increase from the horizon consisting of little decomposed organic material to the lowermost organic horizon, which directly overlays the uppermost mineral soil. The organic material and preferential flow can enhance the transport of organic pollutants in topsoil to the deeper layer. If the upland soil is frequently irrigated or saturated with water for a significant period of the year, the leaching potential of PAHs from the zone of contaminated sites to deeper layers may increase significantly, and the groundwater quality may be endangered. Ma et al. (2005a,b) have carried out a wide survey of PAH contamination in soils in Beijing. Analysis of PAH content in 47 surface soils and 45 pooled subsoil samples collected from the outskirts of Beijing revealed the distribution map of total PAH contents as a contour plot. PAHs in most of the subsoil were lower than those in the topsoil. The concentration range of 16 PAHs in surface soils varied by over two orders of magnitude from 0.016 ng g^{-1} in rural soils to 3.884 ng g^{-1} in suburban soils with the relatively standard deviation of 70.5%. The pollution extent of PAHs at various sampling sites differed greatly. The sum of 17 PAH concentrations varied from not detected to 0.982 ng g^{-1} in subsoil. It was notable that the concentration of BaP in surface soils was 0.005–0.270 ng g^{-1} with a mean of 0.055 ng g^{-1}. The distribution of PAHs in topsoil centered on the HMW PAHs. The 4–6-ring PAHs represented ~66–70% of the total PAHs found in topsoil samples. Source identification of PAHs with the selected marked compounds by PCA and pair ratios of special PAHs (Ph/An vs. Flu/Pyr; ΣCOMB/ΣEPA—PAHs) suggest that pyrogenic origins, especially traffic exhausts, are the dominant sources of PAHs in Beijing outskirt soils. In subsoil, the dominating PAHs were perylene > benzo[*a*]pyrene > benzo[*g*,*h*,*i*]perylene > indeno (1,2,3-*cd*)pyrene. The important fact was that the content of 8 carcinogenic PAHs represented 47% of the total priority PAHs among which the concentration of benzo[*a*]pyrene in the subsoil was comparable to that in the topsoil. Analysis of perylene content and the Flu/Pyr ratio shows that the sources of PAHs in the subsoil are combustion and incorporation of the diagenetic PAHs.

5.4.1.3. PAHs in wastewater irrigation field

The water resources in China are distributed unevenly in both space and time, especially in the northern part of China, where sewage and industrial effluents from biological treatment plant have been widely used for agricultural irrigation to compensate for the water shortage. Because of poor control of the wastewater quality and long-term application, pollutant accumulation and relevant ecotoxicological effects may occur, especially for persistent pollutants and permanently bound chemical residues. The total 16 PAHs in a composite sample collected from a wastewater irrigated paddy field near Tianjin was 3.90 mg kg^{-1}, which is ~500 times higher than that in common soils in the same region (Tao et al., 2002). Field surveys for PAH pollution in farmlands irrigated by effluents from biological treatment plants in a suburb of Beijing also showed severe PAH accumulation. Significantly higher concentrations of PAHs were observed in the sampling sites close to the entrance of main wastewater irrigation channels (157–297 ng g^{-1}) in contrast to those along branches (5.14–80.7 ng g^{-1}) and the reference sites (14.8–23.4 ng g^{-1}) (Chen et al., 2005b). Main components of PAHs in these sites were benzo[*b*]fluorathene, benzo [*a*]pyrane, indeno[1,2,3-*cd*]pyrene, dibenzo[*a*,*h*]anthracene and benzo [*g*,*h*,*i*]perylene. Among these PAHs, concentrations of benzo[*a*]pyrane (45.6 ng g^{-1}), indeno[1,2,3-*cd*]pyrene (IcP, 86.3 ng g^{-1}) and benzo[*g*,*h*,*i*] perylene (BgP, 66.9 ng g^{-1}) exceeded the limits of the Netherlands soil quality standard for biodegraded soils. In identification of the sources, the IcP/BgP values of PAHs in soils were closer to that in air particulates from coal/coke source (1.09 + /−0.03 ng g^{-1}). Therefore, both of the PAHs residues in effluents and emission from a nearby coal/coke plant were responsible.

Shenyang is a famous industrial center in northern China. It also has a long history of wastewater irrigation because of its lack of water. Accumulation of PAHs in soil samples collected from seven sites in the upper, middle, and lower reaches along and nearby the wastewater irrigation channel in western Shenyang had unbelievably high concentrations of 900–2738 mg kg^{-1} (Song, et al., 2005). Toxicity effects of contaminated soils on seedling emergence (root length of wheat) and on earthworms mortality and inhibition of body weight showed that the root elongation was inhibited from −20 to 40%, the mortality rates of earthworms ranged from 0 to 40% from the exposure period of two weeks to eight weeks, and earthworm growth rates were inhibited from −19.36 to 34.53%.

5.4.1.4. PAHs in agriculture soil and plants

Crops and vegetables grown in a PAH contaminated agriculture field may uptake the pollutants from the soil causing PAH accumulation in the agriculture products. PAH contamination in agriculture soil and vegetables in Xiamen, Tianjin, and Beijing were reported. The main PAHs found in soil samples were the low molecular weight compounds in Xiamen region (Maskaoui et al., 2006). The total PAHs detected in soil samples ranged from 0.50 to 0.95 ng g^{-1} soil. The highest values of PAHs, which range from 236 to 249 ng g^{-1} soil were detected in the orange tree leaves, showing recent atmospheric inputs of these volatile pollutants. The distribution of PAHs in vegetables were monitored; the concentrations were high and ranged from 8.24 to 58.9 ng g^{-1}. The total concentrations of PAH16 in bulk soil from two sites in Tianjin were 1.08 and 6.25 ng g^{-1}, respectively, with similar patterns (Tao et al., 2004, 2006a). Greenhouses are used widely in agriculture in China. Soils in the greenhouse may also be contaminated by pollutants. The total concentrations of PAHs determined in greenhouse soils from Beijing suburbs were 1.92–7.84 ng g^{-1}. The contamination of PAHs was relatively serious and the most abundant compounds were 4-, 5- and 6-ring unsubstituted PAHs. The profiles reflect the important contributions of traffic on PAHs in greenhouse soils (Ma et al., 2003). The concentrations of PAH16 and individual compounds in the rhizosphere were significantly higher than those in the bulk soil, with mean values of 2.25 and 7.82 ng g^{-1} for the two sites, respectively. Among the eight types of vegetables studied, the highest concentration of PAHs was found in cauliflower. By average, the concentration of PAH16 in the aerial part of vegetables was 6.5 times higher as that in vegetable root, suggesting that foliar uptake is the primary transfer pathway of PAHs from environment to vegetables. Almost all PAH compounds studied were detected in both roots and aerial parts of the vegetables studied. The abundance of higher molecular weight PAHs in vegetables, however, was lower than that in soil. It appears that agricultural soils and vegetables in Tianjin, especially those from the site located immediately next to an urban district and irrigated with wastewater for several decades, were severely contaminated by PAHs (Tao et al., 2004).

PAHs uptaken by plants could be affected by the growing states of the plants and could also be transferred to different parts of the plants. In order to show the relationship of the PAH uptake pathway from the environment, PAHs in cabbages were studied in detail (Tao et al., 2006a). PAH concentrations in cabbages were positively correlated to either gas or particle-bound PAHs in air. A multivariate linear regression with cabbage PAHs as a function of both gas and particle-bound PAHs in air was established to quantitatively characterize the relationship between them. Inclusion of soil PAH concentrations would not improve the model, indicating that the contribution of soil PAHs to cabbage (aerial part) accumulation was insignificant. Investigation of PAH concentrations in various tissues of rice plants sampled from a PAH contaminated site in Tianjin revealed that the levels of PAHs were much higher in roots than in the exposed tissues (Tao et al., 2006b). Grains and internodes accumulated much smaller amounts of PAHs than leaves, hulls or ear axes. No specific gradient trends along roots, stem, ear axes, and grains were observed, suggesting that systematic translocation among them is unlikely. Over the ripening period, PAH concentrations were increased in rice roots and decreased in most above-ground tissues. Significant correlations between PAH and lipid contents can only be observed during full mature stage. The spectra of individual PAH compounds in rice organs including roots were similar to those in air, rather than those in soil. There was also a significant correlation between bioconcentration factor (plant over air) and octanol/air partitioning coefficient (K_{oa}).

5.4.2. Spatial distribution and source of PAHs in soil

The spatial distribution patterns of PAHs in soil are important to regional environmental assessment. Tianjin, a large city located in northern China adjacent to Beijing, has been studied systematically for the spatial distribution and source apportionment of soil PAHs. The city is highly urbanized and industrialized, while a large portion of the surrounding land is used for agriculture. Tianjin contains one main urban district, seven suburban districts and five counties. Soil in the area is heavily contaminated by many kinds of pollutants, including PAHs. Wang, et al. (2003) have studied the spatial structural features of 16 priority PAH compounds in the topsoil of Tianjin area, as well as soil properties. Spherical models with sills could be used to fit all experimental variograms. The spatial structures of PAH contents demonstrated significant anisotropy. Air precipitation caused by the combustion of coal was the key factor in the formation of the spatial structural patterns of PAHs in the topsoil of the Tianjin area. In most cases, PAHs in soils in urban areas of Beijing were found, using the Phe/Ant and Flu/Pyr ratios, to be pyrogenic. These sources included motor vehicle exhausts, industrial activities and coal burning (Tang et al., 2005). Due to the wide variety of emission sources of PAHs and their different tranportation and transformation pathways to soil, commonly used methods for identifying the source of PAHs in the atmosphere, which compare the ratios of concentrations of selected pairs of PAH congeners in the source emissions to the ratios in the contaminated environmental media, may cause great deviation for the source apportionment of PAHs in soil. These ratios can be altered significantly due to differences in the transport of the PAH compounds in a multimedia environment. To examine such changes, a fugacity model was applied to PAH ratios in a model environment (Zhang et al., 2005). The bulk media studied included air, water, soil, and sediment. For air and water, only the solid fractions were considered. The major influences affecting the diagnostic ratio were evaluated, and the uncertainty of the model results was assessed. The model was verified by comparing model calculations with the actual changes in ratio of PAHs as contaminants moved from the sources of the emissions to the surface soil in Tianjin, China. A linear relationship between the rate of emission and the bulk media concentration was identified for each PAH compound in an environmental medium at a steady state and was quantified by a receptor-to-source ratio (R-RS). It was demonstrated that the R-RS values of the two congeners usually differ significantly. Consequentially, PAH ratios changed remarkably from the source emissions to various environmental media. A site-specific rectification factor was defined as the ratio of the two R-RS values of the paired congeners for a specific PAH ratio in a given medium, which can be applied to account for the ratio changes in a multimedia environment. The sensitivity analysis revealed that PAH ratios of the low molecular weight compounds were less stable. The most influential parameters controlling PAH ratios were those pertaining to dry precipitation, surface-to-air diffusion, degradation in air and water, and exchange between water and sediment. The same group of researchers has also used the multivariate spatial analysis in scale-based distribution and source study of PAHs in the topsoil of Tianjin, China (Wang et al., 2006). Data from 188 topsoil samples collected in the Tianjin area were used for the study. The contents of 16 PAHs and soil background properties were determined for all samples. Results show that coal combustion was the major source for the spatial distribution patterns of PAHs in the topsoil of the studied area. It worked mainly at the short-range scale (5–10 km). Significant spatial variation patterns were identified. In contrast, no significant spatial distribution trends at the nugget (0–5 km) or long-range scales (10–50 km) were seen. Long-range transport and site contamination of PAHs might not be key contributors in forming the distribution pattern of PAHs in the topsoil of Tianjin area. Soil organic carbon was one of the important factors that can influence the concentrations of PAHs in soils. It was found that concentrations of ΣPAHs were significantly correlated with that of soil organic carbon (Tang et al., 2005).

The spatial distribution of soil PAHs and the relationship between current soil PAH levels and land use patterns in the Yangtze River Delta in Southeast China were reported by Xing et al. (2006). Many privately owned and so called township enterprises have been established over the last 20 years in rural locations in the Yangtse River Delta, specializing in metal smelting, production of construction materials, and paper manufacturing. Based on a survey for PAHs in surface soils in the area containing 15 small copper- and zinc-smelting furnaces, 65 topsoil (0–20 cm) samples were collected and 16 PAHs were determined. The average total amount of the 16 PAHs ranged from 0 to 530 $\mu g\,kg^{-1}$ (oven dry basis), with a mean concentration of 33.2 $\mu g\,kg^{-1}$. Benzo[*a*]pyrene and indeno[1, 2, 3-*cd*]pyrene were the two main PAHs present at high concentrations, while pyrene and fluorine had very low concentrations. PAH concentrations were higher in uncultivated than in cultivated soils, and areas of woods and shrubbery had the lowest soil PAH contents. The average PAH-homolog concentrations ranked as follows: 5-rings > 3-rings, 4-rings > 6-rings > 2-rings. Much higher concentrations of PAHs were found in the southern part of the sampling area, perhaps due to deposition of airborne particles by the southeasterly winds in the winter and the spring. The author concluded that small smelting furnaces were the dominant source of PAHs that accumulated in the soils, and the southeasterly winds led to the spatial distribution of PAHs in the topsoils. Land vegetation cover and soil utilization patterns also affected the accumulation and distribution of soil PAHs.

In Guiyang city, coal is widely used for industrial and domestic purposes and the number of the vehicle is growing, so PAH contamination from these sources is very important. It was reported that a large proportion of HMW parent PAHs is a typical characteristic of combustion sources and the enrichment of low molecular weight PAHs is common in fresh fuels (Femandes et al., 1997; Baumard et al., 1998). Analysis of PAHs from 13 samples collected in different sites of Guiyang city revealed that PAHs of three samples (8; 12 and 13) may dominantly originate from coal combustion, and PAHs of the other ten samples may dominantly originate from diffusion of traffic exhaust and coal combustion. This opinion is consistent with the details of the three sample sites that are affected by coal combustion sources. The other ten samples are not close to any obvious point source of PAHs and show a feature of 4-ring higher than 5-ring; thus, they may reflect an impact of gaseous diffusion and deposition of mixed PAHs sources, such as traffic exhaust and coal combustion (Hu et al., 2006).

5.4.3. Phase distribution

PAHs are emitted mainly into the atmosphere and have been detected at long distances from their sources. Because of their low vapor pressures, compounds with 5 or more aromatic rings exist mainly adsorbed to airborne particulate matter, such as fly ash and soot. Those with 4 or fewer rings will occur both in the vapor phase and particulate phase. PAHs reach the hydrosphere and pedosphere mainly by dry and wet deposition and road runoff but additionally from industrial wastes containing PAHs and leaching from creosote-impregnated wood. PAHs are adsorbed strongly to the organic fraction of sediments and soils. Sediments and soils are usually considered as the main sinks for PAHs in the environment. In the past 20 years, numerous important studies focused on transport of POPs in multimedia environment (Chiou et al., 1998; Karickhoff et al., 1979), for example, between vapor phase/particle phase in atmosphere, sediment/water, soil/water, biota/water and water/air. It is believed that POP sorption into soil or sediment was dominated by partition into solid organic matter (Chiou et al., 1998; Karickhoff et al., 1979). Small changes of POP mass in the soils/sediments had a major impact on concentrations in 'adjacent' media, such as air or water. The partition coefficients of POPs with soils and sediments (i.e., K_d) are important parameters to characterize the mobility and fate of POPs in soil/sediment–water systems.

To investigate the distribution of PAHs in different environmental media, the concentrations of 10 PAHs in water, sediments, soils, runoff water and atmospheric particles of Hangzhou, China were simultaneously measured five times (July and November 1999–2002) (Zhu et al., 2004). Comparison of PAH levels in sediments and soils led to the conclusion that the erosion of soil material does not contribute significantly to the contamination of sediments. The atmospheric PAH deposition to water bodies in the city area of Hangzhou was estimated to be 530 tons/a, while the contribution of surface runoff water was estimated to be 30.7 tons/a. Analysis of the composition pattern of PAHs by ring size in water, sediment and soil revealed that 3-ring PAHs dominated in surface waters and soils; meanwhile, sediments were mostly dominated by 4-ring PAHs (Chen et al., 2004). The difference pattern of PAH abundance in surface waters, sediments and soils were contributed to two factors. First, water column and soil receives direct PAH inputs from various sources. Second, high molecular mass PAHs undergo sorption in sediment more easily and are resistant to degradation. With the calculated PAH apparent distribution coefficients (K_d) and solid f(oc)-normalized K_d (e.g., $K_{oc} = K_d/\text{f(oc)}$), the sources of PAHs in different water bodies were evaluated by comparison of K_{oc} values in sediments of the river downstream with that in soils. The ratio of K_{oc} of sediment to that of soil is the ratio of PAHs in sediment to that in soil (organic carbon content normalized). In the Qiantang River, the ratio of $K_{oc\ sedi}/K_{oc\ soil}$ and ratio foc_{sedi}/foc_{soil} approximate to 1, suggesting that PAHs in Qiantang River were mainly obtained from soil runoff. In the Hangzhou Canal, a $K_{\mathrm{oc\ sedi}}$ larger than K_{oc} (equilibrium partition coefficients of PAHs) and a ratio of $K_{\mathrm{oc\ sedi}}/K_{\mathrm{oc\ soil}}$ much larger than 1 indicated that the Hangzhou Canal was heavily polluted by PAHs released from industrial wastewater in the past years, and now PAHs in sediment may serve as significant sources of PAHs in surface water. In the West Lake, $K_{\mathrm{oc\ sedi}}$ values near the bank is larger than those far from the bank, indicating that municipal road runoff mainly contributed to West Lake PAHs.

Zhang et al. (2004b) studied the levels of 16 priority PAHs in water, pore water, sediment, soil and vegetable samples from Minjiang River Estuary, China. Total PAH concentrations varied from 9.9 to 474 ng l^{-1} in water, 82.1 to 239 ng l^{-1} in pore water, 112 to 877 ng g^{-1} dry wt. in surficial sediments, 128 to 465 ng g^{-1} dry wt. in soil and 8600 to 111 000 ng g^{-1} dry wt. in Chinese vegetables. Overall, the mean concentrations of PAHs were present in higher levels in pore water than those in surface water, due possibly to higher concentrations of dissolved organic carbon or colloids with which the hydrophobic pollutants were strongly associated. Such a concentration gradient implies a potential flux of pollutants from sediment pore water to overlying water. Contamination was dominated by high molecular mass PAH compounds in all samples, indicating combustion-derived sources (e.g., pyrolysis at high temperature). The levels of PAHs in water and vegetables were relatively high in comparison to other studies, although PAHs in sediment and soil were comparable to those found in many other similar environments. The ratios of selected PAHs indicated again that PAHs in Minjiang River Estuary were mainly derived from incomplete combustion of fossil fuel.

5.4.4. Transportation of PAHs in soil

PAHs in soil may partition into soil organic matter (SOM) or adsorb on soil minerals. The sorptive properties of SOM fractions for organic contaminants in soil play an important role on the transportation of PAHs in soil. Xiao et al. (2004) has reported that soil/sediment organic matter can be fractionated into four fractions with a combined wet chemical procedure and that kerogen and black carbon (BC) are major SOM components in soil/sediment samples collected from the industrialized suburban areas of Guangzhou, China. Phenanthrene and naphthalene were used as the sorbates to study PAH's sorption isotherms on four original and four Soxhlet-extracted soil/sediment samples, 15 isolated SOM fractions, and a char as the sorbents. The sorption isotherms of phenanthrene and naphthalene on all the sorbents were variously nonlinear. The particulate kerogen and black carbon (KB) fractions dominated the observed overall sorption by the tested soils and sediments and exhibited more nonlinear sorption with much higher organic carbon-normalized capacities for both sorbates. KB fractions are expected to be the most important soil components affecting bioavailability and the ultimate fate of hydrophobic organic contaminants (HOCs). The isolated KB fractions exhibited much higher sorption capacities than when they were associated with soil/sediment matrixes. It is suggested that a large fraction of the particulate kerogen and BC was not accessible to sorbing HOCs. Encapsulation within soil aggregates and surface coverage by inorganic and organic coatings may have caused large variations in the accessibility of fine kerogen and BC particles to HOCs and hence lowered the sorption capacity of the soil. This variability posts an ultimate challenge for precisely predicting HOC sorption by soils from the contents of different types of SOM. The isolated humic acid exhibited significantly nonlinear sorption, but its contribution to the overall isotherm nonlinearity and sorption capacity of the original soil was insignificant because of its low content in the tested soils and sediments.

Organic matter contents in soils can also influence the accumulation of PAHs in plants. Tao et al. (2006c) have developed a rapid chemical method for determining the bioavailability of PAHs. Four PAHs naphthalene, acenaphthylene, fluorine, and phenanthrene were used to evaluate the extent of bioaccumulation by the roots of wheat plants (Triticum aestivum L.) in soil. The extractabilities of PAHs in the soil were tested by a sequential extraction scheme using accelerated solvent extraction with water, *n*-hexane, and a mixture of dichloromethane and acetone as solvents. The water or *n*-hexane-extractable PAHs were positively correlated to dissolved organic matter (DOM) and negatively correlated to total organic matter (TOM), indicating mobilization and immobilization effects of DOM and TOM on soil PAHs, respectively. The apparent accumulation of PAHs by wheat roots was also positively and negatively correlated to DOM and TOM, respectively. As a result, there were positive correlations between the amounts of PAHs extracted by water or *n*-hexane and the quantities accumulated in plant roots, suggesting the feasibility of using water or *n*-hexanes-extractable fractions as indicators of PAH availability to plants.

5.5. Emission estimation of PAHs in China

In order to evaluate the evolution of PAH contamination in China, it is necessary to estimate their emission. For emission estimation of a pollutant, an emission inventory of a particular activity can be compiled by multiplying the activity rate by the corresponding EF (Xu et al., 2006). The PAH emission sources included (1) industrial coal combustion, including thermoelectric power station and heat plants; (2) domestic coal combustion, including residential and commercial sectors; (3) coke production; (4) nontransport oil combustion; (5) transport oil combustion; (6) straw burning; (7) firewood burning; and (8) primary aluminum production. Source-specific production (aluminum) and consumption (other sources) data for the period 1980–2003 in China were collected from officially published sources. It was estimated that the total emission of PAH16 and total emission of seven carcinogenic PAH components among them (PAH7: BaA, CHR, BbF, BkF, BaP, IcdP and DahA) were 25,300 and 3460 tons, respectively, in China in 2003. Although the emission of PAH16 in 2003 in China was very close to the amount emitted in the United States in 1990 (26,500 tons), the emission of PAH7 from China was much higher than that emitted from the United States in 1990 (2000 tons) or 1996 (1400 tons), respectively. The relatively higher fraction of carcinogenic species in the PAH emission profile in China was closely related to the emission source pattern. The relatively higher portion of HMW species with carcinogenic potential in the emission profile can be attributed to large contributions of domestic coal and coking industry in China. The major sources of PAH emission in China were identified as industrial and domestic coal combustion, coke production, primary aluminum production, transport and nontransport oil combustion, and biomass burning, including straw and firewood. PAH emission profiles were greatly different between China and the other countries, such as the United Kingdom and the United States. In terms of PAH16, biomass burning contributed 60% of the total in China, which is much higher than those in the United Kingdom and the United States. Domestic coal combustion was another important PAH source in China, which contributed 20% of the total and was a unique feature in the emission profile compared with the United States and United Kingdom. The coking industry in China also accounted for a considerable share (16% for PAH16) of the total PAH emission. Compared to the PAH emission from coal consumption, petroleum was not a major contributor. Only 2.2% of the total PAH16 emission was from this source.

Because of the enormous differences in economic development, population density, and size of different provinces in China, total emission, emission density, emission intensity, and emission per capita showed geographical variations. In general, the southeastern provinces were characterized by higher emission density, while those in western and northern China featured higher emission intensity and population-normalized emission. The annual PAH emissions at the provincial level ranged from

253 tons in Sichuan to 0.7 tons in Macao, and the source patterns varied widely. Sichuan contributed the largest portion of PAH emission in China with 79% of the total from biomass burning, which is a typical feature of agricultural provinces. Shanxi ranked second in the emission with a source pattern totally different from that of Sichuan. Shanxi produced 452 million tons of coal and 67 million tons of coke in 2003, accounting for 27 and 38% of those produced in China, respectively. Consequently, the coking industry alone was responsible for 69% of the total PAH emission in the province. Domestic coal combustion was a major PAH source in Beijing and other northern provinces in China, and Qinghai was among a few provinces where aluminum production had a significant contribution to PAH emission. PAH emission density in the southeastern provinces was one order of magnitude higher than that of the other provinces in the west.

China has undergone a rapid population and economic expansion in the last 20 years. With the increase in domestic coal consumption, emission of PAH16 and BaP in China increased 28 and 40%, respectively during the period from 1980 to 1990. As the new round of industrialization and urbanization occurred in the past several years, small and medium size cities and towns with population less than 1 million became the centers of urbanization. Population growth in these agglomerations accounted for over 75% of the total increment in urban population in China. A direct consequence was that domestic coal consumption increased, bringing the PAH emission up again. Increase in coke production was another reason that caused increased PAH emission, particularly the carcinogenic species. The annual production of coke jumped from 122 million tons in 2000 to 178 million tons in 2003, in response to rapidly growing demands both nationally and internationally. It was estimated that coke production would continually increase from 178 million tons in 2003 to 260 million tons in 2005. Obviously, the emission of PAHs from the coke industry will continue to increase rapidly if no measures are taken, either to reduce the production or to reduce the emission during manufacture. Although energy consumption in China went up continuously during the past two decades, annual emission of PAHs fluctuated depending on the amount of domestic coal consumption, coke production, and the efficiency of energy utilization.

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Chapter 6

Sources and Occurrence of Persistent Organic Pollutants in the Pearl River Delta, South China

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Abstract

The Pearl River Delta is a fast-developing economic zone in South China. Relatively abundant monitoring data of POPs are available in the regional environment. DDT is still the most priority POP widely occurred at high concentrations in the air, wild fishes and human breast milk. Fast-increasing municipal waste incinerators, as well as electronic waste cycling activities in the region are important potential sources for PBDEs and PCDD/Fs. Atmosphere and aquatic biota are suggested to be the priority environmental media for monitoring POPs in the subtropical environment, and regional collaboration between mainland China, Hong Kong and Macau on the monitoring and inventory of POPs are of critical need in the Pearl River Delta.

6.1. Introduction: The Pearl River Delta

Low-latitude regions may be important source regions for persistent organic pollutants (POPs), and may also play an important role in the global atmospheric transport of these pollutants. In developed countries, the production and application of many important POPs, in particular those of organochlorine pesticides (OCPs), have been prohibited or well controlled/managed, and their distribution in the environment is relatively uniform (Jaward et al., 2004). However, in most developing countries, in particular those located in the low-latitude regions, there may still be new sources and current application of some POPs, as a result of exemption of the Stockholm Convention, illegal local use, as well as potential transfer of industries and electronic wastes from developed countries to developing countries (BAN, 2002). On the other hand, owing to their volatility, many POPs are capable of migrating in the atmosphere

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across a long distance, from warmer places to colder regions (Wania and Mackay, 1996). Therefore, the current situation of POPs contamination in the low-latitude regions is of interest in the context of their global sources, inventories and transport.

Located in the low-latitude region, below the Tropic of Cancer, the Pearl River Delta (PRD) is one of the most important metropolitan areas in China. The PRD has a land area of ca. 41,700 km^2, a population of over 40.2 millions. Large and important cities in the PRD include Guangzhou, Hong Kong, Shenzhen, Fushan, Macau, Zhuhai, Zhongshan, Dongguan etc. (Fig. 6.1). Administratively, the mainland part of the PRD is affiliated to Guangdong Province. Owing to the fast industrialization during the last 25 years, the PRD contributes more than 10% of the country's gross domestic product (GDP, excluding Hong Kong and Macau). The annual average air temperature and precipitation in the PRD are 21–22°C and 1690–1900 mm, respectively. The Pearl River is the third largest river in China, with an average discharge of 174 billion m^3/year and an associated suspended load of 37.3 million tones (Hong et al., 1999). Being the habitat of more than 320 fish species, the Pearl River estuary (PRE) has an area of 2110 km^2, forming one of the key ecosystems in south China costal area.

6.2. Concerned sources of POPs in the PRD

6.2.1. Organochlorine pesticides (OCPs)

The PRD had a long history of agricultural application of large amounts of technical DDTs and HCHs until their official ban implemented in 1983. In the PRD, it is estimated that OCPs usage was ~76,000–100,000 tons annually from 1972 to 1982 (Hua and Shan, 1996). The application rate of these chemicals has been averaged from 1.8 to 2.7 kg/metric acre in the agricultural zones around the Delta (Mai et al., 2003). The residues from the past usage in soil and sediment were believed to be the secondary sources for DDTs and HCHs in the contemporary environment, via evaporation, desorption and with land runoffs, enhanced by the intensifying human activities and land transform in the fast-developing region (Zhang et al., 2002).

An acaricide in wide application, dicofol, was suspected to be a new source of DDTs in China (Qiu et al., 2003). Dicofol is synthesized by using DDT as a key intermediate. The residue of DDTs is controlled to be $<0.1\%$ in many developed countries. However, due to the less advanced industrial technology, the concentration of DDT residue in dicofol in China is still high. According to a report, the average contents of

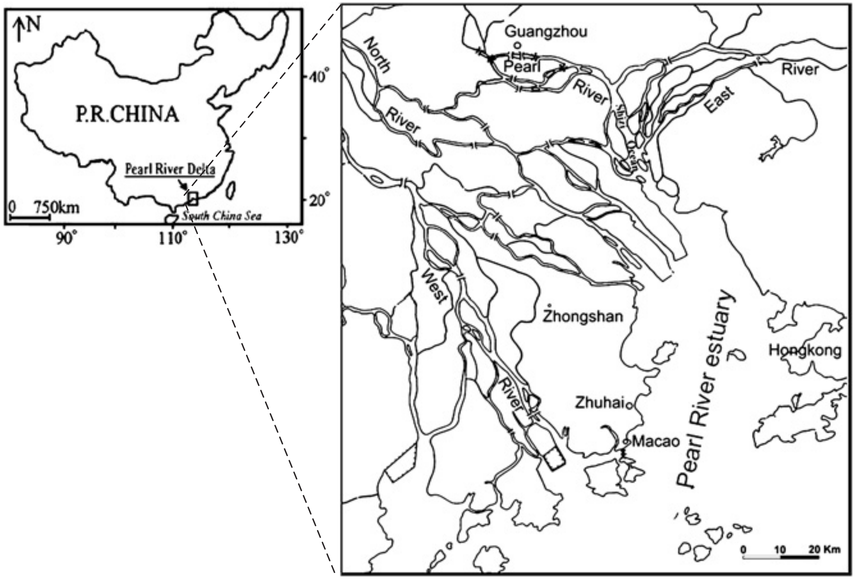

Figure 6.1. Map showing the Pearl River Delta, South China.

o,p′-DDT, *p,p′*-Cl-DDT, *o,p′*-DDE, and *p,p′*-DDT in some commercial available samples were 114, 69, 44, and 17 g kg^{-1} dicofol, respectively. On the basis of a production and distribution survey, the total input of DDTs to the environment from the dicofol use in China was estimated to be 8770 tons between 1988 and 2002 (Qiu et al., 2005). Dicofol is also applied in the PRD. A commercially available dicofol product on the market in Guangzhou contains ca. 5% of *p,p′*-DDE, 4.5% of *o,p′*-DDT and 5% of *p,p′*-DDT (Li Jun et al., 2003, unpublished data). In 2003, an average of 14.4 tons of dicofol (as pure product) were applied in the PRD (An et al., 2005), corresponding to the introduction of ca. 2 tons of DDTs (sum of *p,p′*-DDE, *o,p′*-DDT and *p,p′*-DDT) to the environment.

Another potentially important regional source of DDT in the PRD may be from antifouling paints used on fishing boats. The average annual production of DDT was 4519 tons during 2000–2003 in China, and there was no DDT import from other countries. Approximately 4% of total DDT production was used as the additive for the production of antifouling paint for fishing ships. It is estimated that ~150–300 tons of DDT per annum is emitted through antifouling paint usage in China, corresponding to roughly 5% by weight DDT content in the product. The coastal area of Guangdong province has ca. 60,000 fishing ships, which is ~1/5 of the total number in China. Roughly it can be estimated that ~30–60 tons of DDT may be introduced to the coastal environment of Guangdong, including the PRD. As most of this DDT is expected to be released directly to coastal waters, their potential ecological risk needs to be further evaluated.

The γ-isomer of HCH, as the active component in Lindane, is widely used as a pesticide in the mainland part of the PRD (Hong Kong banned Lindane in 1991; AFCD, 2001), both in agriculture and household. It has been reported that conversion of γ-HCH to α-HCH in the environment is possible (Walker et al., 1999), and this point will need to be considered when analyzing the potential source of HCH in the environment.

Chlordane and Mirex were widely used in the PRD for termite control. Chlordane was strictly banned by the local government in 2001, while Mirex is still in use in Guangdong due to the lack of less toxic substitutes. The estimated average annual application of Mirex in the PRD was ca. 44 tons in the PRD in 2000 (An et al., 2005).

6.2.2. Industrial chemicals: Polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs)

PCBs can be contained in industrial products manufactured in the past, and/or formed as by-products during combustion processes. In the context of industrial PCBs, China issued a “Relevant Regulations for

Stopping the Production of PCBs" in 1974, and issued a "Circular on Preventing the Pollution of Hazardous Substances of PCBs" in 1979. Approximately 10,000 tons of PCBs were manufactured, and of these, 9000 tons were trichlorobiphenyl applied in transformers and capacitors. The remaining 1000 tons were pentachlorobiphenyl mainly applied in paints, inks and lubricants as an additive. In Guangdong, most of the PCB-containing capacitors were replaced and sealed/stored for more than 20 years. They have been further treated safely in recent years gradually by the local government. Until 1999, the remaining untreated PCB-containing capacitors were estimated to be a few hundreds (Li, 1999).

PBDE is another group of industrial POPs. It is used as brominated flame retardants through the addition to or reaction with plastics and synthetic fibers. These fire retardants often make up a considerable proportion of product weight: plastic can contain up to 15% PBDEs, and polyurethane foam (PUF) up to 30% PBDEs (WHO, 1994; EU, 2003). The total global consumption of PBDEs in 2001 was 67,440 tons, among them deca-BDE accounted for more than 80% and octa-BDE more than 12%. The PRD has become an important manufacturing base in the world since the 1980s, for the production of electronics, appliances, personal computers and peripheral devices, textile and furniture. In particular, it is one of the three electronic manufacturing bases in China, accounted for more than 40% (ca. 100 billion US$ in 2002) of the total production of electronic products in the country. Therefore, the application amount of PBDEs in the PRD is estimated to be high. However, as the regional industry began to thrive largely in the 1990s, when the production of PBDEs was shifted from penta- and octa-BDE to deca-BDE, the major PBDE product applied is believed to be deca-BDE, as would be consistent with the use of PBDE products in Asia (50,710, 331, 3307 tons of deca-, penta-, and octa-BDE, respectively, in 2001). It should be noted that, in 2003, EU announced the new Regulation of Hazardous Substances (RoHS), which came into force on July 1, 2006. RoHS strictly regulates PBDE residues in electronic products exported to EU, and has consequently limited the PBDE application in the PRD, from where a large portion of electronic products are exported to EU. In addition, China will also implement its domestic RoHS, mainly targeting electronic products, in 2007, which is believed to further limit the industrial application of PBDEs.

6.2.3. Unintentional by-products: Polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans (PCDD/Fs), PCBs and PBDEs etc.

PCDD/Fs have various sources and are produced as unintentional by-products of many manufacturing and combustion processes involving the use, production or disposal of chlorine or chlorine-derived chemicals, notably, polyvinyl chloride (PVC) polymers. Sources of significant environmental concern for PCDD/Fs include waste incineration, combustion of landfill gases, open burning, and many organochlorine production processes. Other sources include steel industry, ceramic industry, power generation etc. PCDD/Fs are also found as impurities in 2,4-D and pentachlorophenol (PCP). Hong Kong assembled its PCDD/Fs inventory in 2003. However, until now, there is no regional inventory of PCDD/Fs in the PRD as a whole.

Incineration is one of the major waste treatment options in the PRD under the huge burden of municipal solid waste (MSW). Small waste incinerators with capacity less than 300 ton/day have been strictly regulated since 2001, and most of them have been closed in recent years. However, until 2006, there were nine large MSW incinerator power plants located in Shenzhen, Guangzhou, Zhuhai, Fushan and Dongguan, treating 6640 tons of MSW daily, and there are other eight incinerators being built for an extra capacity of 6150 tons/day. It is planned that, before 2010, there will be a total of 27 large MSW incinerator power plants in the PRD, treating 23,490 tons of MSW, which account for 73.87% of the total MSW generated daily in the region. Most of the incinerator power plants adopted advanced technologies from European countries. It is estimated that 70% of the light industrial waste consists of PVC plastics, rubber, leather and cloth etc. (Fu et al., 2003). Although concentrations of PCDD/Fs in the emission of these large incinerators are still not available, it could be estimated that they may contribute significantly to the total environmental loadings of PCDD/Fs in the PRD.

Illegal electronic waste (e-waste) recycling is believed to be another important source for unintentional POP emissions, in particular for PBDEs, PCBs, PCDD/Fs (Soderstrom and Marklund, 2002; Wang et al., 2005; Cai and Jiang, 2006), and polycyclic aromatic hydrocarbons (PAHs; Yu et al., 2006a, b). The hazardous e-wastes include computers, electronic appliances and transformer carcasses. In the e-waste sites, recycling operations consist of toner sweeping, dismantling electronic equipment, selling computer monitor yokes to copper recovery corporations, plastic chipping and melting, burning wires to recover copper, melting circuit boards over open fires and using acid chemical strippers to recover gold and other metals (Cai and Jiang, 2006). It was estimated that more than 70% of the e-waste from North America is shipped/smuggled to Asia, most of them to the southeastern coastal China (BAN, 2002). In addition, it was estimated that more than 200 million sets of electronic appliances, mainly TV sets and electronic fans, were retired/disposed of in Guangdong. There are three large scale e-waste recycling towns in the province, among them two are located in the PRD. Despite the potential importance of e-waste recycling as a source of PCDD/Fs, PCBs and PBDEs, the POP emission factors associated with the process of e-waste burning and recycling without sound management, as well as its contribution to POPs in the environment, are still largely unknown in the region.

6.3. Occurrence of POPs in the environment of the PRD

6.3.1. Organochlorine pesticides (OCPs)

6.3.1.1. Air

A screening of POPs in the atmosphere in East Asia using passive atmosphere samplers (PAS) showed that the PRD was among the regions with the highest concentrations of DDTs and HCB in Asia (Jaward et al., 2005). Nevertheless, there are only limited studies reporting levels, based on active high-volume samplers, of POPs in the air of the PRD. Cheng et al. (2000) analyzed OCPs in a few aerosol samples in this area, the results showed high concentrations of DDTs in Guangzhou (up to 109.38 pg m^{-3}). Louis and Sin (2003) collected air samples, using modified Anderson high-volume samplers, during the winter of 2000/2001 at the Tai Mo Shan weather station in Hong Kong. OCPs were found at relatively low concentrations of ~0.02–0.23 ng m^{-3}. Recently, a study was conducted to measure the atmospheric concentrations of OCPs in Guangzhou and Hong Kong fortnightly from December 2003 to December 2004. The results showed that the atmospheric DDT concentrations in the PRD were much high (Li et al., 2007) when compared with other places in the world (Table 6.1). The average concentrations of α- and γ-hexachlorocyclohexane (HCH), *trans*-chlordane (TC), *cis*-chlordane (CC), *p,p′*-DDT, *p,p′*-DDE, *p,p′*-DDD, *o,p′*-DDT, endosulfan-α and -β in the air of Guangzhou were 134, 539, 871, 1340, 627, 207, 93, 846, 246, and 60 pg m^{-3}, respectively; and in Hong Kong were 46, 51, 389, 380, 358, 56, 53, 191, 148, and 20 pg m^{-3}, respectively. In general, the concentrations of OCPs increased from winter to summer except for α-HCH, which showed no clear seasonal pattern.

6.3.1.2. Water

Significant amounts of OCPs were found in water of rivers, estuaries and seas, and generally, sewage water concentrations > river concentrations > estuary concentrations > sea concentrations. Levels of OCPs in sewage from Guangzhou had the highest concentrations of DDTs and HCHs

Table 6.1. Comparison of organochlorine pesticide concentrations (pg/m^3) in the atmosphere of Guangzhou and Hong Kong with reference data (Li et al., 2007)

	α-HCH	γ-HCH	TC	CC	*p,p′*-DDE	*p,p′*-DDD	*p,p′*-DDT	*o,p′*-DDT	End 1	Reference
Hong Kong	46±28	51±63	389±381	380±358	56±26	53±58	358±718	191±188	148±212	Li et al. (2007)
	(5–108)	(5–261)	(7–1602)	(7–1496)	(8–151)	(3–235)	(6–2625)	(7–673)	(<LOD–840)	
Guangzhou	134±70	539±797	871±443	1335±989	207±151	93±85	627±740	846±618	246±291	Li et al. (2007)
	(41–313)	(5–2639)	(127–1789)	(129–4185)	(28–579)	(8–378)	(22–2836)	(86–2014)	(<LOD–1083)	
South India	(530–27400)	(380–8170)			(400–5790)	(140–520)	(60–1020)	(0–150)		Rajendran et al. (1999)
Korea	169±250	50.5±86.6	5.0±9.4	3.7±7.1	34.6±51.3	6.2±18.3	21.0±34.6			Yeo et al. (2003)
	(20.6–830)	(4.8–326)	(0.2–35.0)	(0.1–26.1)	(2.6–185)	(<5.6–67.0)	(<1.0–121)			
Japan	103±67	40±22	70±89	61±76	5.3±4.2	<2	6±7			Murayama et al. (2003)
	(14–281)	(10–98)	(2–401)	(<1–329)	(<0.3–17.8)	(<2–<2)	(<2–25)			
Chicago	110±40	150±80	130±80	120±70		100±50	70±60			Bidleman et al. (1998)
Belize, Central America		63±22	34±39	32±42	458±127	35±45	556±356	145±45		Alegria et al. (2000)

(up to 1200 ng l^{-1}), and the total OCPs in river waters were from 130 to 1200 ng l^{-1} (Yang et al., 1997). The OCP concentrations in estuary water were significantly lower than those of river. For example, total OCP concentrations in estuary near Macao were from 25.2 to 67.8 ng l^{-1} (Luo et al., 2004). A survey of OCPs in surface sea waters in 2005 was carried out in the South China Sea (SCS). A total of nine 100 L surface seawater samples were collected, and relatively low concentrations of total OCPs with 1.3–7.4 ng l^{-1} were found (Zhang et al., 2007).

6.3.1.3. Sediment

The concentrations of total HCHs (t-HCHs) ranged from 0.08 to 1.38 ng g^{-1} with a mean value of 0.36 ng g^{-1}, which were comparable to those of Kyeonggi Bay, Korea (<0.15–1.2 ng g^{-1}) and Xiamen Harbor (0.14–1.12 ng g^{-1}), but were lower than those of the Yangtze River Estuary and its nearby coastal area (n.d.–30.4 ng g^{-1}). The levels of total DDTs (t-DDT; sum of *p,p′*-DDD, -DDE, and-DDT) ranged from 0.04 to 2.48 ng g^{-1} with an average of 0.87 ng g^{-1}. The mean concentration (1.54 ng g^{-1}) of t-DDTs within the PRE was slightly lower than the mean concentration of 2.84 ng g^{-1} obtained in the same area by Hong et al. (1999). Again, the DDT levels were lower than those reported for Kyeonggi Bay, Korea (0.048–32 ng g^{-1}), but were higher than the levels in the Yangtze River Estuary and its nearby coastal area (n.d.–0.57 ng g^{-1}). The concentrations of t-OCPs (sum of t-HCHs, t-DDTs, and heptachlor) exhibited positive correlations with the TOC contents ($r = 0.76$ with $p < 0.001$), suggesting that TOC was a significant factor controlling the contaminant distribution in sediments (Chen et al., 2006a, b, and references therein).

6.3.1.4. Soil

A survey of OCPs in surface soils was carried out recently in the PRD (Li et al, 2006). A total 74 soil samples containing crop, paddy and natural soils were collected. The concentrations and enantiomeric compositions of HCH, DDT, and chlordane were analyzed. Detailed information on the concentrations in the soils is shown in Table 6.2. The mean concentrations of total HCHs and DDTs in descending order were: crop soils > paddy soils > natural soils; whereas, only pesticides in the natural soils were significantly ($p < 0.001$) lower than crop soils and paddy soils. The spatial distribution of HCHs and DDTs was similar, with higher levels found at the center of the PRD. The DDT concentrations in crop (mean 54 ng g^{-1} dw) and paddy soils (mean 47 ng g^{-1} dw) in the PRD were similar to those reported in paddy soils in Dehradun of

Table 6.2. OCP concentrations in soils of different land uses in the Pearl River Delta (Li et al., 2006)

Subgroup	ng g^{-1}	α-HCH	β-HCH	γ-HCH	δ-HCH	*p,p′*-DDE	*p,p′*-DDD	*p,p′*-DDT	*o,p′*-DDT	TC	CC
Crop soils (37)	Mean	1.08	2.49	0.90	0.50	21.9	7.22	20.9	6.34	0.62	0.71
	Median	0.80	1.26	0.54	0.42	7.82	2.70	4.64	0.80	0.42	0.40
	Range	<DL–3.48	0.05–16.0	<DL–4.43	<DL–1.28	0.14–231	0.06–73.8	0.07–305	<DL–96.7	<DL–6.13	0.10–7.74
Paddy soils (14)	Mean	0.89	1.76	0.62	0.38	19.4	23.4	2.98	0.91	0.42	0.36
	Median	0.78	1.14	0.45	0.26	12.6	7.64	1.05	0.33	0.47	0.40
	Range	<DL–2.76	<DL–7.01	<DL–2.03	<DL–1.02	1.64–66.6	0.07–163	0.19–22.4	0.12–4.92	<DL–0.76	<DL–0.56
	Mean	0.25	0.27	0.11	0.20	0.82	0.53	1.40	0.46	1.53	1.61
Natural soils (23)	Median	0.17	0.11	0.04	0.14	0.71	0.48	1.12	0.41	0.45	0.38
	Range	<DL–1.46	<DL–1.11	<DL–0.75	<DL–0.70	<DL–2.22	0.05–1.40	0.09–4.20	0.05–1.22	<DL–13.7	<DL–15.5

India 13–238 ng g^{-1} (Babu et al., 2003), lower than those reported in soils in urban Guangzhou (ranged from 3.58 to 831 ng g^{-1}) (Chen et al., 2005), Tianjin (628.1–2840.5 ng g^{-1}) (Gong et al., 2002), Vietnam (averaged 110 ng g^{-1}) (Thao et al., 1993), the US Corn Belt (n.d.–11,800 ng g^{-1}) (Aigner et al., 1998), and Romania (9.0–1542.2 ng g^{-1}) (Covaci et al., 2001). Another independent survey of OCPs in soils conducted recently in Hong Kong (Zhang et al., 2006) found much lower concentrations of DDTs (0.52 ng g^{-1} dw) and HCHs (6.19 ng g^{-1} dw).

6.3.1.5. Biota

There have been limited reports on OCP levels in aquatic organisms in the PRD. OCP concentrations were reported in mussels from Hong Kong waters (Phillips, 1985; Fang et al., 2001), fishes from the Hong Kong market (Chan et al., 1999), fishes (Tilapia) from Hong Kong inland waters (Zhou et al.,1999) and from aquacultural fishponds in the PRD (Zhou and Wong, 2004). The concentrations in freshwater fishes were 0.01–7.8 ng g^{-1} lipid for HCHs, and 22.3–381 ng g^{-1} lipid for DDTs (Zhou and Wong, 2004). In a recent survey of OCPs in demersal fishes in the PRE and Daya Bay, 50 samples (34 fishes, 4 shrimps, 6 crabs) were collected and analyzed with GC-MS. The average concentrations of t-DDTs, t-HCH, and t-Chlordane in the fishes were 73.36 ± 102.37, 0.30 ± 0.18, 0.87 ± 0.35 ng g^{-1} ww in Daya Bay, and 123.68 ± 100.66, 0.41 ± 0.48, 12.23 ± 26.85 ng g^{-1} ww in the PRE, respectively. Concentrations of HCHs and chlordanes were comparable to those reported in other region, while DDTs levels were higher (Guo et al., 2007). The results suggested that DDT is still the priority pesticidal POP in the aquatic ecosystem of the PRD.

The mean concentration of total HCHs was 1164.7 ng g^{-1} ww, in the blubber of five live Indo-Pacific humpback dolphins in Hong Kong, 36 times greater than that of Zhuhai (32.8 ng g^{-1}). For total chlordanes, the Hong Kong samples (258.6 ng g^{-1}) had concentrations comparable to those of the Xiamen (249.5 ng g^{-1}) and Zhuhai (221.7 ng g^{-1}). However, the mean total DDT concentration in Hong Kong samples, 9110.5 ng g^{-1} ww, was lower than those of Xiamen and Zhuhai (Leung et al., 2005).

6.3.2. PCBs

6.3.2.1. Air

Limited reports are available on PCBs in the atmosphere of the PRD. The total PCB levels measured in a background site (Tai Mo Shan) in

Hong Kong ranged from 10 to 1910 (mean 480) pg m^{-3} (Louie and Sin, 2003). In 2005, air samples were collected at four urban sites in Guangzhou for the analysis of 64 PCB congeners. The study reported similar total PCB concentrations (sum of 64 congeners) of 363–1961 pg m^{-3} (Chen et al., 2006). This was similar to the range of 20–1700 pg m^{-3} in Europe as determined by PAS technology by Jaward et al. (2004), but much higher than the range in Asia (5–340 pg m^{-3}, by PAS, Jaward et al., 2005). The PCBs in the air of Guangzhou were dominated by congeners with 3–4 chlorine atoms (Chen et al., 2006).

6.3.2.2. Water

Nie et al. (2005) reported PCB concentrations from water samples collected from four major river outlets of the Pearl River. The concentrations of total PCBs in surface water ranged from 2.47 to 6.75 ng l^{-1}, with an average of 3.92 ng l^{-1}. There were no significant differences between various sampling sites. These levels were 100 times higher than the samples collected from the uncontaminated Atlantic Ocean (0.035–0.072 ng l^{-1}; Connel et al., 1999), close to the level obtained in Humber estuary, UK (1.0 ng l^{-1}; Zhou et al., 1996), but much lower than those observed in Daya Bay in China (313.6 ng l^{-1}; Zhou et al., 2001a, b) and in Minjiang River Estuary, Southeast China (214–1819 ng l^{-1}; Zhang et al., 2003). In terms of the pattern of congener composition in water, PCB-153, 180, 119, and 49 (with 6, 7, 5, and 4 chlorine atoms, respectively) were dominant.

6.3.2.3. Sediment

The levels of PCBs in the PRD sediments have been compared with those from other parts of the world in recent studies (Mai et al., 2002; Fu et al., 2003). The sediments in Zhujiang River (48.3–486 ng g^{-1}) and Macao Harbor (339 ng g^{-1}) were thought to be moderately to strongly contaminated by PCBs, when compared to the world-wide concentrations (0.2–400 ng g^{-1}) of near-shore surface sediments (Fowler, 1990). PCB levels in sediment from Shiziyang (10–30.3 ng g^{-1}) and Xijiang (11–13.6 ng g^{-1}) Rivers, and Lingding Bay (10.2–13.5 ng g^{-1}) were comparable to those of sediments from Canadian Mid-latitude and Arctic lake sediments (2.4–39 ng g^{-1}) (Muir et al., 1996). The DDT concentration (1629 ng g^{-1}) in sediment from Macao Inner Harbor is higher than those obtained in other heavily polluted locations, such as Rhone Prodelta in the north-west Mediterranean region (124–657 ng g^{-1}) (Tolosa et al., 1995). DDTs levels in sediments of Zhujiang (35.1–91.0 ng g^{-1}) and

Shiziyang (22.9–40.4 ng g^{-1}) rivers were in the high end of the world-wide concentration range, and comparable to those of moderately polluted locations, such as Ebro prodelta in the NW Mediterranean region (23–89 ng g^{-1}) (Tolosa et al., 1995). Nie et al. (2005) reported that the concentrations of total PCBs (36 congeners) in the sediments were 23.23, 17.82, 13.65, and 11.13 ng g^{-1} dw for Humen, Hengmen, Jiaomen, and Modaomen, respectively, and these concentrations were within the ranges of the above-mentioned studies (Mai et al., 2002; Fu et al., 2003). Another study conducted in Deep Bay of the PRE reported a total PCB (28 congeners) concentration range of 6.0–290 ng g^{-1} dw (Fung et al., 2005), which is also within the regional range (Mai et al., 2002; Fu et al., 2003).

6.3.2.4. Biota

The concentrations of PCBs in 71 fishes in the PRE were reported by Nie et al. (2005). The total PCB concentrations (38 congeners) ranged from 68.64 to 316.85 ng g^{-1}, lipid in fish. The concentration of PCBs in fish in this study were higher than that of shellfish ($<$6.78 ng g^{-1} dw) from Minjiang estuary (Chen et al., 2002), close to that of shrimp and fish from Mai Po Marshes in Hong Kong, and lower than or close to the concentration of PCBs in green-lipped mussels (*Perna viridis*, 82.8–615.1 ng g^{-1}, lipid) from the PRE (Fang et al., 2001). However, by comparison with other places in the world, the concentrations of PCBs in fish from the PRE were lower, well below the 2000 ng g^{-1} on a wet weight basis of maximum concentration of total PCBs in edible seafood allowable by the Food and Drug Administration. Notwithstanding, the PCB concentrations in some species exceeded the standard in meat, eggs, poultry and related products at 200 ng g^{-1} lipids set by the European Directive 1999/788/CE (Binelli and Provini, 2003). It was found that the feeding habits of fish were very significant in influencing the accumulation of polychlorinated biphenyls and their congeneric pattern. Carnivorous and benthic fishes such as eel (*Anguilla japonica*) and Chinese sea catfish (*Arius sinensis*) were found to have high concentrations of polychlorinated biphenyls (mainly of high chlorinated congeners), while herbivores such as shad (*Clupanodon punctatus*) and mullet (*Mugil cephalus*) exhibited an opposite trend. Congeners PCB-153, 138, 118, 87/81, 170, and 52 were found frequently in most fish samples. Another study investigated the PCB concentrations in 61 freshwater fish samples (Tilapia, common carp, big head, silver carp, and grass carp) from the PRD (Zhou et al., 2004), which reported total PCB concentration ranges of 60–480 ng g^{-1} lipid, similar to those in the estuarine fishes (Nie et al., 2005), and 16% of fish collected from the PRD exceeded the US EPA guideline concentration for PCBs. Concentrations of total PCBs ranged from 5.3 to 40.8 μg g^{-1} ww (mean 19.6), in the blubber of five live Indo-Pacific humpback dolphins in Hong Kong, and 0.07 μg g^{-1} ww in a dolphin from Zhuhai (Leung et al., 2005).

6.3.3. PBDEs

6.3.3.1. Air

There have been two noteworthy studies of PBDE measurements in air of the PRD. One using high volume air samplers in the urban city of Guangzhou in June of 2004 (Chen et al., 2006) and the other using PUF passive air samplers in three locations (Dinghushan, Guangzhou and Hong Kong) of the PRD from Sept. to Nov. 2004 (Jaward et al., 2005). The concentrations of Σ_{10}PBDEs in air samples (particle plus gas phases) collected from Guangzhou ranged from 88.8 pg m^{-3} at an urban site to ~3672 pg m^{-3} near an industrial area, while BDE 209 ranged from 263.8 pg m^{-3} to ~4200 pg m^{-3}. The arithmetic mean atmospheric concentrations of ΣPBDEs (sum of all target PBDE congeners except for BDE 209) in samples from the urban and city background sites in this study were comparable to or slightly higher than those from other places around the world. The arithmetic mean atmospheric concentrations of BDE 209, however, were higher than those in North America and Europe, and similar to the values from Japan. Congeneric compositions were dominated by BDE 209 in all ($>70\%$) but an industrial site, with an average abundance of 48% for BDE 209. The PBDE congeneric profiles in air samples indicated that deca- and penta-BDE were the main source mixtures consistent with the results from the sediments. In a study of air across Asia, the PBDE concentrations (sum of BDE 17, 28, 32, 47, 49, 75, 99, 100) in PUF samplers from three locations of the PRD region ranged from 3.97 to 23.8 pg/sample, and these were generally lower than those in developed countries (Jaward et al., 2005).

6.3.3.2. Water

Very few data is available for PBDEs in water of the PRD. A recent study reported PBDE concentrations in five paired subsurface layer (1 m) and micro-surface layer water samples in Hong Kong. The total PBDE (eight congeners) concentrations ranged from 11.3 to 62.3 pg^{-1} in the dissolved phase and from 26.2 to 32.5 pg^{-1} in the suspended particulate matter. BDE 28, 47, and 100 were the most abundant congeners, with no BDE 209 detected. This was different from those reported in San Francisco

Bay in the US, where BDE 47, 99, and 209 were found to be the most abundant congeners (Oros et al., 2005).

6.3.3.3. Sediment

There have been several studies of PBDE concentrations in sediments of the PRD (Zheng et al., 2004; Liu et al., 2005a, b; Mai et al., 2005a, b). A total of 66 river and estuarine surface sediment samples from the PRD region have been analyzed for PBDEs in a recent study (Mai et al., 2005). The Σ_{10}PBDEs (BDE 28, 47, 66, 100, 99, 85, 154, 153, 138, 183) and BDE 209 concentrations in surface sediments ranged from 0.04 to 94.7 ng g^{-1} dw with an average of 9.9 ng g^{-1} dw and from 0.4 to 7340.8 ng g^{-1} dw with an average of 465 ng g^{-1} dw, respectively. In general, the concentrations of BDE 209 were one to two orders of magnitude higher than those of ΣPBDEs. The mean concentrations of ΣPBDEs decreased in the order of Dongjiang River > Zhujiang River > Macao coast > the PRE > the SCS > Xijiang River for ΣPBDEs, while those of BDE 209 decreased in the order of Dongjiang River > Zhujiang River > Macao coast > the PRE > Xijiang River > the SCS. The Σ_{10}PBDEs concentrations in most surface sediments are well within in the range of the world riverine and coastal sediments (<50 ng g^{-1}), while the BDE 209 concentrations in Zhujiang and Dongjiang rivers were at the high end of the worldwide figures for BDE 209 in sediments. Congeneric profiles were dominated by BDE 209 (72.6–99.7%), consistent with deca-BDE as the main source mixture, followed by the congeners from the penta-BDE mixture (BDE 99: 4.34%, DE 47: 2.87%, BDE 153: 0.83%, BDE 100: 0.60%, and BDE 154: 0.58%) and some octa-BDEs (BDE 183: 0.52% and BDE 138: 0.30%).

6.3.3.4. Biota

There is limited PBDE data in literature on the levels in organisms from the PRD. Small cetacean samples collected from Hong Kong waters during 1995–2001 had PBDE concentrations ranging from 230 to 6000 ng g^{-1} lw (Ramu et al., 2005), which were apparently higher when compared to northern fur seals from the Pacific coast of Japan (Kajiwara et al., 2004). The levels observed in cetaceans from Hong Kong were comparable to harbor seals from San Francisco Bay (She et al., 2000) and harbor porpoises from British Columbia (Ikonomou et al., 2002). Congeneric profiles in cetaceans showed that BDE 47, 99, and 100 made up 90% on an average of the total PBDE load. Another study has analyzed PBDEs in green mussel samples collected from nine locations along

Hong Kong marine waters (Liu et al., 2005). The Σ_{15}PBDEs (BDE 3, 15, 28, 47, 60, 85, 99, 100, 138, 153, 154, 183, 197, 207, 209) in Hong Kong mussels ranged from 27.0 to 83.7 ng g^{-1} dw.

A recent study compared PBDE concentrations in demersal organisms from the PRE and Daya Bay (Guo et al., 2007). The PBDE concentrations in fishes from the PRE (21–170 ng g^{-1} lipid, 0.2–4.2 ng g^{-1} ww) were generally within the reported ranges in literature, while those from Daya Bay were at the low end of the worldwide figures. Relatively higher total PBDE concentrations were observed in tank gorby (*Glossogobius giuris*, 170), robust tonguefish (*Cynoglossus robustus*, 140), and thread herring (*Clupanodon thrissa*, 100 ng g^{-1} lipid) from the estuary. Among the 15 PBDEs analyzed in this study, BDE 47 was the most abundant congener, accounting for 39 and 50% of total PBDEs in fishes from the PRE and from Daya Bay, respectively. BDE 100 accounted for 10% and 14% in fishes from the estuary and Daya Bay, respectively. Despite the large quantity of BDE 209 used in Asia/China (Ueno et al., 2004) as well as its high concentrations in some of the sediments from the PRD (Mai et al., 2005), BDE 209 comprised only $<3\%$ of the total PBDEs in the fishes. This may imply that BDE 209 has a low bioaccumulation potential to fishes (Sellström et al., 1998; Boon et al., 2002).

6.3.4. PCDD/Fs

Published data on PCDD/Fs in the environment of the PRD is still limited. A short-term sampling scheme was conducted to determine the levels of particle-bound polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in Guangzhou atmosphere and evaluate the impact of PCDD/Fs to inhabitants. Samples were collected from four different districts of Guangzhou. The results showed that industrial activities had more influences on levels of PCDD/Fs in the sampled districts. The mean PCDD/Fs concentrations (i.e., mean I-TEQ values) of Huadu district, Liwan district, Tianhe district and Huangpu district were 3815–26,530 fg m^{-3} (104.6–769.3 fgI-TEQ m^{-3}). Emission source analysis indicated that small diffuse sources were relatively important (Yu et al., 2006).

Atmospheric deposition of PCDD/Fs was also investigated at four locations in Guangzhou. The annual deposition fluxes of tetra- to octa-CDD/Fs (total PCDD/Fs) were found to range from 170 to 3000 (mean 1500) pg m^{-2} day, and the fluxes of total 2,3,7,8-substituted PCDD/F congeners ranged from 2.1 to 41 (mean 20) WHO-TEQ m^{-2} day. The average deposition fluxes of total 2,3,7,8-substituted PCDD/F congeners in rainy season were found to be 27–37 pg WHO-TEQ m^{-2} day, and the PCDD/F deposition fluxes were obviously higher in rainy season than in dry season. Results from regression analysis showed that number of rainy days, the amount of wet precipitation, PCDD/F concentrations in particles and organic carbon content played important roles in accounting for the variation of PCDD/F deposition fluxes. It was found that the profiles of PCDD/F homologues or congeners in the samples were the same either spatially or temporally, indicating that the PCDD/F emission sources were similar to one another. It was suggested that vehicle exhaust might be an important source for PCDD/Fs in Guangzhou, and that atmospheric deposition possibly tended to remove lower chlorinated DD/Fs from air and was one of sources for PCDD/Fs in soils (Ren et al., 2007).

An investigation of PCDD/Fs in soils across the PRD was conducted by the same research group. A total of 61 samples including 58 soils and 3 sediments were analyzed for PCDD/PCDFs with the isotope dilution method using a high resolution gas chromatograph/high resolution mass spectrometer (HRGC/HRMS). The results showed that the total concentrations of PCDD/PCDFs were 85.5–14,525 pg g^{-1} dw, and the concentrations of 2,3,7,8-tetrachlorinated dibenzo-*p*-dioxin (TCDD) equivalents (I-TEQ) were 0.09–19.7 pg g^{-1} dw. According to the German and the USA guidelines for I-TEQ concentrations, 14 in the 58 samples contained TEQs between 5 and 40 pg g^{-1} dw, and may be a cause for concern. The relative higher total concentrations and I-TEQ of PCDD/DFs in selected samples indicated the presence of potential point-source pollution. The homologue profile of PCDD/DFs and the spatial distribution suggested that the sources of PCDD/DFs were mixed in soils, but the uses of HCH and PCP were possibly the main sources in the samples that contained high concentration of PCDD/DFs. PCDD/DFs were also detected in soils from three mountain tops, suggesting wide dispersal of PCDD/DFs in this region via dry and wet deposition (Zhang, 2006).

6.4. Human exposure to POPs

POPs in human breast milk may directly reflect human exposure to POPs in the environment. A survey was conducted to examine *p,p′*-DDT, *p,p′*-DDE, β-HCH, and PCB concentrations in human breast milk, one of the most reliable bioaccumulation indicators. Milk samples (115 from Hong Kong and 54 from Guangzhou), in the lactation period from 3 to 5 weeks were analyzed. The results demonstrated that the mean levels of *p,p′*-DDT (Hong Kong: 0.39; Guangzhou: 0.70 μg g^{-1} of fat), *p,p′*-DDE (2.48; 2.85), and β-HCH (0.95; 1.11) were 2–15-fold higher when compared with studies conducted elsewhere (i.e., United Kingdom, Germany, Sweden, Spain, and Canada). In contrast the concentration of PCBs (0.035; 0.031) was ~10 times lower. When compared to a similar study conducted 10 years ago in Hong Kong (*p,p′*-DDT: 2.17 μg g^{-1} of fat, *p,p′*-DDE: 11.67, β-HCH: 15.96, and PCB: 0.64), a considerable reduction in the levels of these contaminants was observed (Wong et al., 2002).

A recent study investigated PBDEs in 21 paired maternal and fetal blood, and 27 breast milk, with most of the samples collected in Guangzhou (Bi et al., 2006). The concentrations of total PBDEs ranged from 1.5 to 17 ng g^{-1} in the samples, and were within the range reported in European samples for a similar population, but lower than the human tissue levels in North America. BDE 47 and 153 were the dominant PBDE congeners in all samples and accounted for 60% of the total PBDEs.

6.5. Regional cycling and time trends of POPs

Natural archives of POPs, such as sediment cores, serve as an important source to retrieve the past POP contamination. Contrary to the decreasing trends observed in studies in many developed countries, OCPs, PCBs, and PAHs all displayed surface/sub-surface layer enrichment along the sediment cores in the PRD. The DDT and HCH concentrations increased sharply in the sediment layers deposited in the early 1990s, which correspond to the sharp cultivated land loss as a result of fast urbanization in the region, implying that soil runoff enhanced by the large scale land transformation may have mobilized these pesticides from the soil to the water environment (Zhang et al., 1999, 2002). The PCB concentrations in the sediment cores also displayed an up-profile increasing trend in relation to the regional GDP and cultivated land area loss during the same period when fast development of regional economy took place (Mai et al., 2003). The up-profile increase in PAH concentrations was also concurrent with the development of power generation, vehicle numbers in the PRD (Liu et al., 2005). Though most POPs trapped in the sediment may be immobilized, vertical migration of lighter PCBs with 3–4 chlorine atoms was observed in two cores (Mai et al., 2003). The POP pollution history reconstructed by sediment cores reflected that the intensive anthropogenic activities, typically during the last two decades in the PRD, which may have a strong impact on the sources and biogeochemical cycling of POPs in the region.

6.6. Conclusion remarks

Compared to other regions in China, the environmental occurrence and fate of POPs in the PRD have been more extensively characterized. In view of the potential negative impact on human health, DDTs in the air and wild fishes in the region occur in very high concentrations, and should be taken as the first priority POP in the context of current source reduction. In particular, the DDT-containing dicofol application and antifouling paints for fishing ships should be paid a great attention. Secondly, PCDD/Fs were found at high levels in the urban environment. It is suggested that monitoring and assessment measurements should be taken urgently to enable a sound management of the MSW incinerators, the number of which is sharply increasing in the region. Thirdly, for PCBs and PBDEs, although they were generally within the concentration levels around the world and less important at a regional scale, distinctively high concentrations were found in several e-waste recycling sites. This calls for a better management and best applicable technology to be applied in the e-waste recycling industry, as well as characterization and remediation of relevant potential contaminated sites. Fourthly, a sound management/control/reduction of POPs at a regional scale cannot be made without a good understanding of the regional inventories of POPs, on which the knowledge and information is still very limited in the PRD. A regional collaboration between Guangdong province and Hong Kong is of great importance.

It is worth pointing out that, although high concentrations of DDT and PCDD/Fs were evident in the atmosphere, their concentrations in other abiotic compartments, i.e., soil, sediment and water, were generally comparable to other regions around the world. This is likely to be resulted from the high temperature in the tropical-subtropical region, and may generally be applicable to other low-latitude regions. It is thus suggested that atmosphere and aquatic organisms might be the priority environmental media for regional monitoring of POPs in the PRD, to elucidate their regional sources and future time trends.

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Chapter 7

Persistent Organic Pollutants in Hong Kong

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Abstract

The Stockholm Convention on Persistent Organic Pollutants commits the international community to protecting human health and the environment from harmful effects of persistent organic pollutants (POPs) and aims to end global use and release of 12 most toxic POPs. A POPs inventory in Hong Kong has been compiled for the period 2000–2004 for assessing POPs' potential impacts on the local environment and human health. None of the nine POPs pesticides (i.e., aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, HCB, mirex and toxaphene) are now registered for use in Hong Kong. The inventory indicates that only a small quantity of PCBs in PCB-containing equipment was in local use/stockpile in 2004. The estimated total annual release of dioxins/furans to the environment in 2003 was 20.3 g TEQ which on a "per capita" basis, was the 2nd lowest in air emission among 26 countries/regions in Asia, Europe, North America and Australia compared. The level of POPs contamination in the local environment was generally comparable to the range reported in most other urban locations worldwide. The estimated total exposure of Hong Kong residents to dioxins/furans in 2003 via the dietary and inhalation routes was 0.93 pg TEQ kg^{-1} bw d^{-1}, falling at the lower end of the range of tolerable daily intake (1–4 pg TEQ kg^{-1} bw d^{-1}) set by the WHO (1998). Overall, the current level of POPs contamination was found to pose no unacceptable risk of potential toxicological concern to the local environment or human health.

7.1. Introduction

Persistent organic pollutants (POPs) are organochlorine compounds widely used as pesticides and/or industrial chemicals. These chemicals share four common properties: highly toxic, persistent, capable of long-range transport and bio-accumulation in the fatty tissues of living

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organisms. Their "grasshopper" movement within environmental compartments and global circulation often result in serious threat to the people and the wildlife near and distant from their origin of production. To respond to the increasing global concern about POPs' potentially harmful effects and to better safeguard public health and the environment, the international community has stepped up its efforts to control, ban or restrict the trade, manufacture, use or release of some of the most toxic POPs worldwide by adopting the Stockholm Convention on Persistent Organic Pollutants which entered into force on May 17, 2004. As at January 15, 2006, 117 countries have become Parties to the Convention (http://www.pops.int).

The Stockholm Convention is a global treaty committing the international community to protecting human health and the environment from the potentially harmful effects of POPs (UNEP Chemicals, 2005). The United Nations Environment Programme (UNEP) has identified 12 most toxic POPs (the "Dirty Dozen") for control under the Convention, including 10 intentionally produced POPs pesticides/industrial chemicals (aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), mirex, toxaphene and polychlorinated biphenyls (PCBs)) and two unintentionally produced POPs by-products (polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)). In implementing the Convention, Parties to the Convention will take measures to restrict the trade, production and use of the intentional POPs and to reduce and, where possible, to ultimately eliminate the production and release of the unintentional POPs by-products.

The Stockholm Convention became effective to the People's Republic of China (PRC), including the Hong Kong Special Administrative Region (HKSAR), on November 11, 2004. Under the Convention, the PRC will submit a National Implementation Plan (NIP), which includes the Hong Kong Special Administrative Region Implementation Plan (HKSARIP), to the Conference of the Parties of the Stockholm Convention within two years of ratification of the Convention. In preparing the HKSARIP, the Environmental Protection Department (EPD) of the HKSAR Government conducted a thorough review of the current POPs situation and compiled a comprehensive POPs inventory on the 12 most toxic POPs regulated by the Stockholm Convention in Hong Kong. The inventory provided a scientific basis for assessing the environmental and human health impacts of POPs and supported the policy-makers' development of an effective POPs management and implementation strategy for the HKSAR. This chapter presents the POPs inventory in Hong Kong for the period 2000–2004 and the findings of a science-based assessment of their potential impacts on the local environment and human health.

7.2. The HKSAR basic profile

The HKSAR is a sub-tropical city situated in the Pearl River Delta (PRD) at the south-eastern tip of Mainland China. It has a total area of 1104 km^2, comprising Hong Kong Island, the Kowloon Peninsula, the New Territories and 262 outlying islands (Fig. 7.1).

Hong Kong has one of the finest deep-water ports in the world and is a well-established international financial, trading and business centre. It is widely recognized as the world's freest economy (Heritage Foundation's 2005 Index of Economic Freedom) and one of the most competitive economies in the world (International Institute for Management Development's World Competitiveness Yearbook 2005). Over the past few decades, there has been a structural transformation of the Hong Kong economy from manufacturing to service orientation. The local industrial activities have shrunk to a substantial extent in both variety and size as manufacturing enterprises have progressively relocated their production lines to the Mainland. On the other hand, trading and logistics, finance and banking, tourism and a wide range of business services are steadily gaining importance.

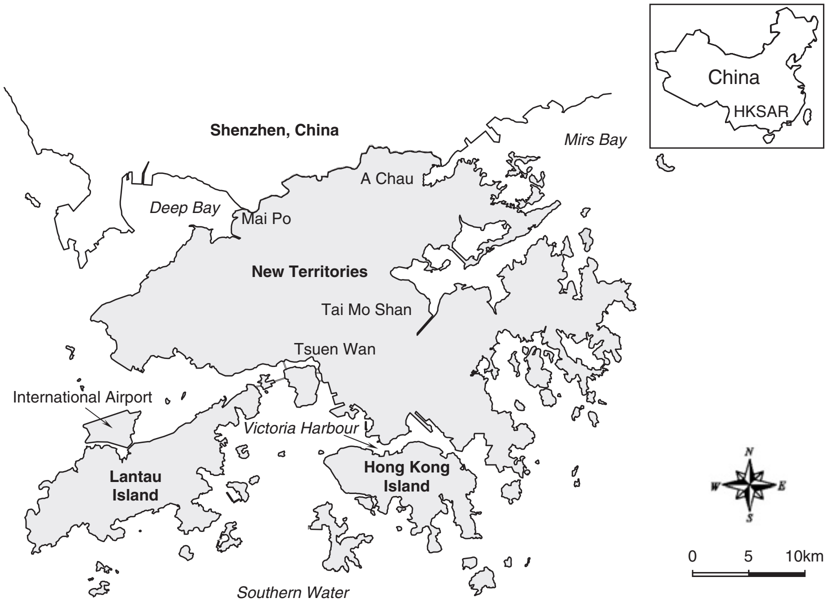

Figure 7.1. Map of the Hong Kong Special Administrative Region (HKSAR), China.

With a population of 6.9 million, Hong Kong is one of the world's most densely populated cities (6380 persons per km^2 according to data of the Census and Statistics Department, the HKSAR Government) (CSD, 2004). Over the years, Hong Kong has developed an efficient wholesale and retail network to cater for the growing consumption needs of a more affluent population. The dense population coupled with a high level of dynamic economic activities has exerted intense pressure on Hong Kong's environment. This is further compounded by the effects of immense economic growth in the PRD, one of the fastest developing regions in the world. Since the 1980s, the HKSAR Government has been implementing various plans and programmes to meet the local environmental challenges. Pollution by toxic substances including POPs is a relatively new area of focus in Hong Kong, but has received increased attention in recent years. Programmes for monitoring air and water toxic pollutants have been established to assess background pollution and to better safeguard the environment and human health (EPD 2004a, 2005a).

7.3. Source inventories of POPs

The source inventories of POPs in Hong Kong were developed in accordance with relevant UNEP guidance documents (UNEP Chemicals, 2003a,b) and compiled based on existing information gathered from all available sources to represent the broadest possible sweep of relevant local data. The main sources of information included annual government reports of routine monitoring and inspection programmes, relevant reports of ad hoc and case studies, and government-funded consultancy studies. The manufacture, use and stockpile inventory of pesticides was reported for a five-year period (2000–2004) for which data were available. The dioxin/furan emission inventory was compiled for the year 2003, the most recent year of complete data entries.

Data screening and quality assurance checking were conducted at initial information retrieval and all data entries cross-checked during subsequent data compilation. Production/activity levels were verified against different information sources including annual records, self-monitoring reports and ad hoc study reports. There was inadequate documentation of local industrial/commercial/urban activities and/or limited analytical data on the level of POPs contamination in some classes of emission sources. These were identified as inventory data gaps for follow-up actions.

7.3.1. Trade, production and use of intentional POPs

7.3.1.1. Pesticides

In Hong Kong, the nine intentional POPs pesticides (aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, HCB, mirex and toxaphene) targeted for global elimination or restricted production and use were not registered, or their registration status had been cancelled for many years due to toxicological or environmental concern.

Aldrin	Chlordane	DDT	Dieldrin	Endrin	Heptachlor	HCB	Mirex	Toxaphene
1988[a]	1991[a]	1988[a]	1988[a]	NR	NR	NR	1997[a]	1984[a]

Note: NR = Not registered.
[a]The year in which all use and trade activity were prohibited unless under a pesticide permit granted in exceptional circumstances.

Table 7.1 presents the local source characterization and quantification of the nine intentional POPs pesticides. There was neither import, export, manufacture nor use and no stockpiling of any of these pesticides in Hong Kong for the past five years (2000–2004). Transhipment of DDT was reported in 2000–2003 but not in 2004, while transhipment of mirex was recorded in 2004 only.

7.3.1.2. Polychlorinated biphenyls

Stockpiles of PCBs contained in PCB-products manufactured from past industrial activities exist. Results of periodic PCB-equipment surveys conducted by EPD in 1994/1995, 2001/2002 and 2004 are presented in Table 7.2. There has been no PCB-containing transformer stockpile in Hong Kong since 2001/2002 and the number of PCB-capacitor units dropped significantly from 830 in 1994/1995 to 303 in 2001/2002. In 2004, the number of PCB-capacitor units further dropped to 191. Most of these capacitor units were small. Of the 191 capacitor units, only 85 were still in use and 106 were stockpiles being stored in the workplace to be disposed of anytime. The total quantity of PCBs in use/stockpile was estimated to be 422 kg. Phased out PCB-containing equipment is classified as a chemical waste in Hong Kong, the disposal of which is governed by the Waste Disposal Ordinance. Small PCB-containing equipment and PCB-fluid removed from large PCB-containing equipment are incinerated at the Chemical Waste Treatment Centre (CWTC). The PCB-contaminated

Table 7.1. Source characterization and quantification of POP-pesticides in Hong Kong in 2000–2004

Chemical	Import ($\mathrm{t\ a^{-1}}$)	Export ($\mathrm{t\ a^{-1}}$)	Manufacture ($\mathrm{t\ a^{-1}}$)	Use ($\mathrm{t\ a^{-1}}$)	Stockpile (kg)	Transhipment (kg)				
					2000–2004	2000	2001	2002	2003	2004
Aldrin	0	0	0	0	0	0	0	0	0	
Chlordane	0	0	0	0	0	0	0	0	0	
DDT	0	0	0	0	0	112,600	274,228	153,118	123,440	0
Dieldrin	0	0	0	0	0	0	0	0	0	
Endrin	0	0	0	0	0	0	0	0	0	
Heptachlor	0	0	0	0	0	0	0	0	0	
Hexachlorobenzene	0	0	0	0	0	0	0	0	0	
Mirex	0	0	0	0	0	0	0	0	0	125
Toxaphene	0	0	0	0	0	0	0	0	0	

Table 7.2. Domestic use of PCBs and PCB waste disposal in Hong Kong for the period 1994–2004

PCB-containing equipment	1994/1995	2001/2002	2004
High voltage transformer (no. of units)	13	0	0
Power plants/power stations			
Railway/mass transit railway			
High voltage capacitor (no. of units)	830	303	191
Factories/old buildings			
High voltage capacitor in use (no. of units)			85
Industries			27
Dockyard			48
Hospital			3
Estate management			7
High voltage capacitor stockpile (no. of units)			106
Total PCB in use/stockpile (kg)			422*

PCB-waste disposal	1994–2001 (kg)	2002–2004 (kg)
PCB-fluid waste disposed of at CWTC	25,305	2
PCB-containing solid waste disposed of at CWTC	16,379	3210
PCB-contaminated solid waste disposed of at landfills	48,225	0

*The PCB content of individual capacitor unit was calculated based on its unit volume, assuming a capacitor of size (60 cm × 30 cm × 15 cm) would contain 1.4 kg of 100% PCB fluid.

solid waste is disposed of at landfills. The total quantities of PCB-waste disposed of during 1994–2001 and 2002–2004 are shown in Table 7.2.

It was noted that PCBs might also be present in minute quantities in some consumer products such as small old electrical appliances/parts, electronics, impact papers, adhesives, sealants, plastic materials and paints. The 2003 Hong Kong Census and Statistic figures showed local trading activities of these consumer products. However, in the absence of information on the product content of PCBs, no estimate of total PCBs in semi-closed and open application could be made. The relative contribution from this category to total PCB use was likely to be insignificant.

7.3.2. Release of unintentional POPs as by-products

7.3.2.1. Development of the dioxin/furan release inventory

PCDDs and PCDFs are unintentional by-products of industrial and combustion processes. The 2003 dioxin/furan release inventory in Hong Kong was generated based on the "UNEP Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases" (UNEP Chemicals, 2003b). The known potential local sources of environmental releases of dioxins/furans were divided into nine major emission categories, each containing a number of subcategories and classes of similar processes. For each identified process with a known local activity, the estimated average annual release of dioxins/furans to individual vector (air, water, land, products and residues) was calculated using the following basic equation:

$$\text{Annual emission or release} = \text{emission factor} \times \text{production or activity rate}$$

If locally measured emission data were available for a process, a local emission factor (EF) specific to Hong Kong was derived to provide a more accurate estimate of its local annual release. For all other processes, the generic EFs published in the Toolkit (UNEP Chemicals, 2003b) were adopted. It was noted that where available, local EFs were generally lower than the corresponding UNEP default values for the same processes.

7.3.2.2. The 2003 dioxin/furan release inventory in Hong Kong

A summary of the 2003 local dioxin/furan emission profile is presented in Table 7.3. The annual release of dioxins/furans to the environment via all vectors was estimated to be 20.3 g TEQ. Figure 7.2a shows the relative contribution of different emission categories. The top three contributing categories were "Ferrous and Non-Ferrous Metal Production" (39.3%), "Disposal/Landfill" (28.7%) and "Power Generation and Heating/Cooking" (25.9%). Together, they represented 93.9% of the total annual dioxin/furan emission in 2003. A "zero" emission value was assigned to Category 7 "Production of Chemicals, Consumer Goods" due to a general lack of local data on the contamination level of dioxins/furans in consumer goods.

On a vector basis (Fig. 7.2b), the major route of release was "residues", responsible for 82.4% of the total, followed by "air" (12.9%) and "water" (4.2%). The "land" and "products" together contributed to only 0.5% of the total annual release. It was observed that for the "land" and "products" vectors, a "blank" release value was assigned to many classes of potential emission sources due to a general lack of data on EFs.

The 2003 annual dioxin/furan release to the atmosphere was 2.61 g TEQ. The relative contribution of different source categories to total air emission is shown in Fig. 7.2c. The top four contributing classes of local emission sources were: (a) "coal fired power boilers plants" (45.3%); (b) "crematoria" (13.4%); (c) "aluminium production (secondary)" (10.3%) and (d) "accidental fires—houses, factories and vehicles" (9.6%). These

Table 7.3. The 2003 inventory of annual dioxin/furan (PCDD/F) emissions in Hong Kong—a breakdown on subcatergories and individual classes of activity

Cat.	Source categories	Production (t a^{-1})	Potential release route (μg TEQ t^{-1})					Annual release (g TEQ a^{-1})†					All routes† (g TEQ a^{-1})
			Air	Water	Land	Products	Residues	Air	Water	Land	Products	Residues	
1.	**Waste incineration**							**0.008**	**0.000**	**0.000**	**0.000**	**0.057**	**0.065**
	Hazardous waste incineration	10,507	*0.3*				*2.27* (BA)	0.003				0.024	0.027
	Medical/hospital waste incineration	36	*125*				*920* (FA)	0.005				0.034	0.038
2.	**Ferrous and non-ferrous metal production**							**0.272**	**0.000**	**0.000**	**0.000**	**7.700**	**7.972**
	Iron/steel foundries and brass/bronze production	15,570	*0.13*					0.002					0.002
	Aluminum production (secondary)	77,000	3.5				100	0.270				7.700	7.970
3.	**Power generation and heating/cooking**							**1.549**	**0.000**	**0.000**	**0.000**	**3.692**	**5.242**
	Fossil fuel power plants	320,424						1.214				3.692	4.907
	Coal fires power boilers plants	263,737	*4.48*				14	1.182				3.692	
	Heavy fuel fired power boilers	1,851	2.5					0.005					
	Light fuel oil/natural gas fired power boilers	54,836	0.5					0.027					
	Landfill and biogas combustion							0.037					0.037
	Biogas-fired boilers, motors/turbines and flaring	4,627	8					0.037					
	Domestic heating—fossil fuels	57,029						0.298					0.298
	Coal fired stoves	242	70				5 μg TEQ kg^{-1} ash	0.017				ND	
	Oil fired stoves	23,053	10					0.231					
	Natural gas fired stoves	33,734	1.5					0.051					
4.	**Production of Mineral Products**							**0.009**	**0.000**	**0.000**	**0.000**	0.074	0.082
	Asphalt mixing	1,230,000	0.007				0.06	0.009				0.074	0.082
5.	**Transport***							**0.117***	**0.000**	**0.000**	**0.000**	**0.000**	**0.117***
	4-Stroke engines	355,992						0.002					0.002

Table 7.3. (*Continued*)

Cat.	Source categories	Production (t a^{-1})	Potential release route (μg TEQ t^{-1})					Annual release (g TEQ a^{-1})†					All routes† (g TEQ a^{-1})
			Air	Water	Land	Products	Residues	Air	Water	Land	Products	Residues	
	Unleaded fuel without catalyst	18,682	0.1					0.002					
	Unleaded fuel with catalyst	337,310	0.00										
	2-Stroke engines	143						0.0004					0.0004
	Unleaded fuel without catalyst	143	2.5					0.0004					
	Diesel engines	1,144,969	0.1					0.114					0.114
	Heavy oil fired engines (all types)*	3,021,753	4					12.087*					12.087*
6.	**Uncontrolled combustion processes**							**0.312**	**0.000**	**0.048**	**0.000**	**0.213**	**0.573**
	Fires/burnings—biomass	12,076						0.060		0.048			0.109
	Forest fires	6,038	5		4			0.030		0.024			
	Grassland and moor fires	6,038	5		4			0.030		0.024			
	Fires, waste burning, landfill fires, industrial fires, accidental fires	1,020						0.251				0.213	0.464
	Accidental fires in houses, factories	510	400				400	0.204				0.204	
	Accidental fires in vehicles (per vehicle)	485	94				18	0.046				0.009	
	Open burning of wood (construction/demolition)	25	60				10	0.002				0.000	
7.	**Production of chemicals, consumer goods**							**0.000**	**0.000**	**0.000**	**ND**	**0.000**	**0.000**
	Textile plants	ND									ND		
	Leather plants	ND									ND		
8.	**Miscellaneous**							**0.347**	**0.000**	**0.000**	**0.000**	**0.065**	**0.412**
	Crematoria[a]	30,161						0.347				0.065	0.412
	No control plants[a]	4,182	*52.47*					0.219					
	Medium control plants[a]	16,127	*7.89*				2.5	0.127				0.040	
	Optimal control plants[a]	9,852	*0.01*				2.5	0.000				0.025	
	Dry cleaning residues	17					50					0.0009	
	Tobacco smoking[b]	4,216,948,889						0.0004					0.0004
	Cigar[b]	11,820,820	0.3					0.000					
	Cigarette[b]	4,205,128,070	0.1					0.000					

9.	**Disposal/landfill**							**0.000**	**0.855**	**0.000**	**0.062**	**4.895**	**5.812**
	Landfill leachate	1,469,174							0.005				0.005
	Non-hazardous waste[c]	1,469,174		*3.62*					0.005				
	Sewage/sewage treatment								0.850			4.895	5.745
	Sewage-Mixed industrial, commercial, and domestic	944,984,329							0.850				
	-No sludge removal[c]	276,198,167		*2.86*					0.790				
	-With sludge removal[c,d]	668,786,162		*0.09*					0.060				
	Sludge-Mixed industrial, commercial, and domestic	97,890										4.895	
	-CEPT[e]	72,067					50					3.603	
	-Secondary treatment[e]	25,823					50					1.291	
	Open water dumping	ND							ND				
	Composting	4,112									0.062		0.062
	Livestock wastes	4,112				15					0.062		
1–9.	**Total (g TEQ a^{-1}) (excluding Cat. 5d—bunker fuel consumption)**							**2.613**	**0.855**	**0.048**	**0.062**	**16.696**	**20.274**

Note: BA = bottom ash; FA = fly ash.

ND = no data; figures in Italic represent HK data.

[†] Values may not add up to ''total'' due to rounding.

[*] Not included in the annual dioxin emission estimate 2003; the sale of bunker fuel to international ocean-going vessels is not considered representative of local fuel consumption.

[a] Production = annual no. of cremations; unit of EF = μg TEQ/cremation.

[b] Production = annual consumption of tobacco items; unit of EF = pg TEQ/item.

[c] Unit of EF = ng TEQ t^{-1}.

[d] Local EF for chemically enhanced primary treatment (CEPT) used for all sewage with sludge removal (CEPT + secondary) in the absence of reliable dataset on secondary treated sewage, assuming that sewage quality after secondary treatment would be equal/better than that of primary treatment.

[e] Unit of sludge production = t dw a^{-1}; unit of residue EF = μg TEQ t^{-1} dw.

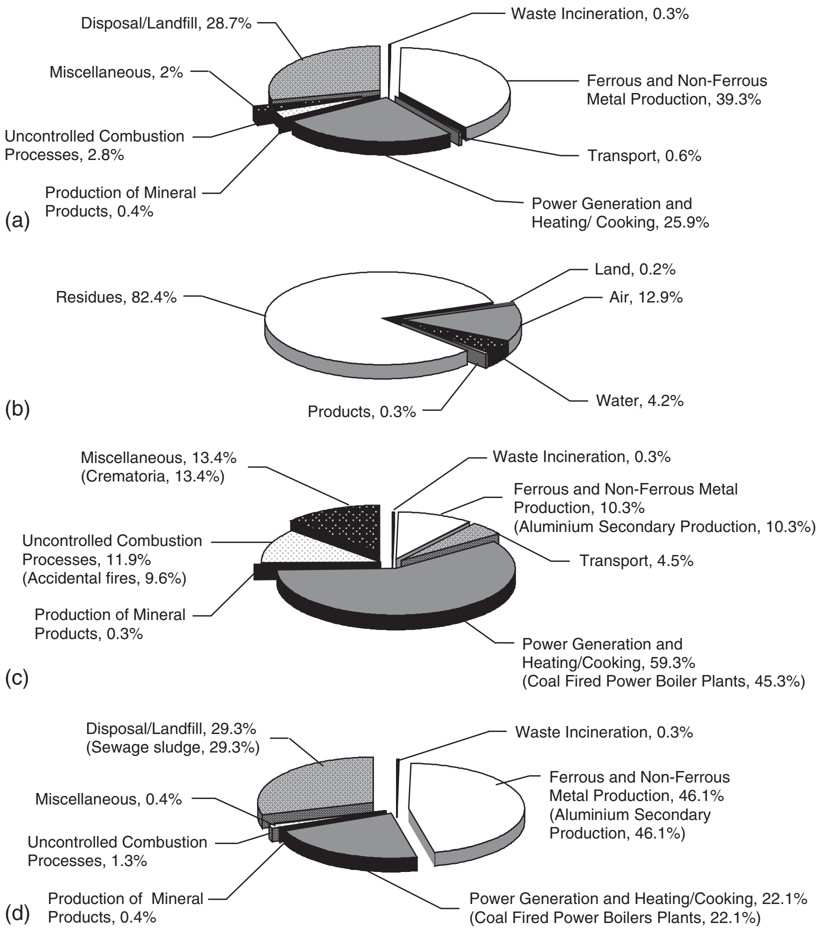

Figure 7.2. Percentage contribution of individual source categories to annual dioxin/furan emission in 2003 (a) total emission; (b) on a vector basis; (c) emission to air and (d) emission to residues.

four classes of activities together accounted for 78.6% of the total annual air emission while the other 18 classes were responsible for the remaining 21.4%. Contributions from the "coal fired power boilers plants" and "crematoria" were well characterized and the emissions were calculated based on locally developed EFs. Estimation of local dioxin/furan emission from the "aluminium production (secondary)" and "accidental fires" activities was made by adopting the more conservative, generic EFs published in the UNEP Standardized Toolkit (2003). Considering that the reported local annual aluminium production (secondary) activity also appeared unusually high compared with the values reported in other Asian and European regions, the annual dioxin/furan emission from this class of industrial activity would be likely to be over-estimated. While the contribution from ''accidental fires'' could hardly be controlled, efforts to establish a more representative local annual activity and emission level from the ''aluminium production (secondary)'' process would be necessary to better understand and assess the performance of the industry and its contribution to local air dioxin/furan release.

The 2003 annual dioxin/furan release to the local marine environment was 0.86 g TEQ, contributed solely by the ''Disposal/Landfill'' category. Within this category, the two major contributing classes of emission sources were ''sewage with no sludge removal'' (92.4%) and ''sewage with sludge removal'' (7.0%), while the landfill leachate contributed to only a minor 0.6%. Given the limited local data available and considering the large quantity of annual sewage production in Hong Kong, further analysis of sewage discharge at source would be warranted for a better estimate of its contribution to the local annual dioxin/furan release.

For release ''to land'', the only category with an EF available was ''Uncontrolled Combustion Processes''. Burning of biomass in forest/grassland fires contributed to the total annual land dioxin/furan release of 0.05 g TEQ. There was a general lack of information on other potential local land sources of dioxin/furan release.

The 2003 annual dioxin/furan release ''in products'' was 0.06 g TEQ, contributed solely by the composting of livestock wastes process within the ''Disposal/Landfill'' category. Release from composting of livestock wastes was estimated using a UNEP generic EF for composting of garden and kitchen wastes as surrogate. A local EF specific to livestock waste would need to be determined for a better estimate of contribution from this class of emission source. The compost was used as product for landscaping and horticulture work. There was a general lack of information on other potential local sources of dioxin/furan release in products.

The 2003 annual dioxin/furan release ''in residues'' was 16.7 g TEQ. The relative contribution of different source categories to emission in residues is presented in Fig. 7.2d. The top three contributing classes were: (a) ''aluminium production (secondary)'' (46.1%); (b) ''disposal of sludge from sewage treatment works'' (29.3%) and (c) ''coal fired power boilers plants'' (22.1%). These three classes of activities together accounted for 97.5% of the total local annual dioxin/furan release in residues. Estimates of annual dioxin/furan release from the ''aluminium production (secondary)'', ''sludge disposal'' and ''coal fired power boiler plants'' activities were made by adopting the conservative, generic EFs published in the UNEP Standardized Toolkit (2003). Hong Kong specific, local EFs should be generated to better estimate their relative contribution to the annual dioxin/furan release profile in residues.

7.3.2.3. Annual release of dioxins/furans per capita

In 2003, the calculated annual release of dioxins/furans in Hong Kong per capita was 2.96×10^{-6}. A comparison with the five Asian countries that participated in the 2003 Asian UNEP Toolkit Project (UNEP Chemicals, 2003c) indicated that the total annual dioxin/furan release per capita in Hong Kong was similar to that of Jordon, Lebanon, the Philippines or Vietnam, but significantly lower than that reported in Brunei (Fig. 7.3). On a vector basis, Hong Kong's annual air dioxin/furan emission per capita was ranked the 2nd lowest among 26 countries/regions in Asia (UNEP Chemicals, 2003c; Government of Japan, 2004), North America (Environment Canada, 2005; USEPA, 2005), Europe (European Commission, 2000) and Australia (Australian Government, 2004a). The local annual water or residue dioxin/furan releases per capita was generally comparable to the range reported in most countries/regions under comparison.

7.3.2.4. Release of polychlorinated biphenyls as by-products

There was comparatively little information on the release of PCBs as unintentionally produced POPs. PCBs are known to be produced as unintentional combustion by-products of incineration and combustion processes. The current UNEP Toolkit (2003) does not give EFs for PCBs. There was little information on the release of PCBs from known local emission sources. A few measured emission data were available from a number of incinerators, crematoria and power plants to permit local EFs to be derived and the annual release of dioxin-like PCBs to be estimated for these processes. Results indicated that the measured total annual air emission of dioxin-like PCBs was very low (less than 0.1 g TEQ). Compilation of the local dioxin-like PCB emission profile would await further emission data from other potential sources.

7.4. Environmental levels of POPs

"POPs in the environment" has been an area of increasing global concern in recent years and has received close attention in Hong Kong. The environmental POPs inventory (2000–2004) was compiled to give an overview of the existing status of POPs contamination in the environment of Hong Kong and to provide the basis for assessing their environmental and human health impacts (EPD, 2005b). The major sources of

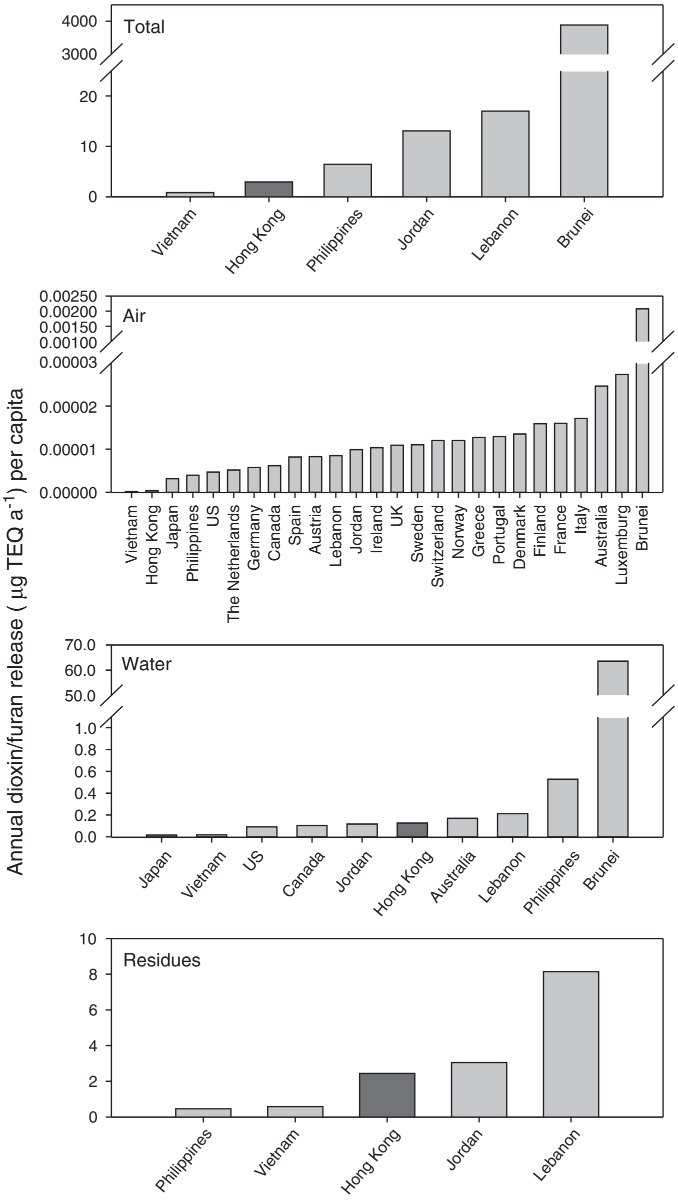

Figure 7.3. Comparison of annual dioxin/furan release on a "per capita" basis in Hong Kong and other countries.

information that contributed to the inventory were reports of the EPD routine monitoring programmes and government-funded consultancy studies. Study reports generated by local academia and relevant publications in the open literature were also critically reviewed for their suitability to be included in the inventory.

7.4.1. Contamination levels of POPs in environmental media

A summary of the levels of POPs contamination reported in the environmental media (ambient air, surface water, sediment and soil, and vegetation) of Hong Kong in 2000–2004 is presented in Table 7.4. The mean environmental levels of POPs were weighted arithmetic sample means calculated based on samples analyzed and reported in individual studies. If the level of a POP chemical was found to be below the analytical method detection limit (DL) in all samples analyzed in a particular medium, the mean value was reported as "0". If a measurable level (i.e., $>$DL) of a POP chemical was reported in some or all samples analyzed in a particular medium, the mean value was calculated by assuming a value of 0.5DL for sample levels of $<$DL, unless stated otherwise.

7.4.1.1. Ambient air

Ambient levels of total PCBs and dioxins/furans had been routinely monitored at two general urban locations (Tsuen Wan and Central & Western) in Hong Kong since mid-1997 (EPD, 2004a). The 24-hour ambient air samples were collected monthly and analyzed for PCBs and dioxins/furans to provide the annual and seasonal trends of their presence in the atmosphere. In addition, dioxin data collected from a year-round dioxin-monitoring project that targeted suspected local emission sources at Tsing Yi (where the CWTC is located) (2000–2004) and from an ad hoc study conducted at Tai Mo Shan (a rural site at the highest point in Hong Kong) (2000–2001) were included in the calculation of the mean local ambient air dioxin/furan concentration (Sin et al., 2002; Louie and Sin, 2003). The average ambient air concentration of PCBs and dioxins/furans measured for the period 2000–2004 was 0.48 ng m^{-3} and 0.06 pg I-TEQ m^{-3}, respectively. Data on the level of local ambient air POPs pesticides were very limited. The few data on ambient air POPs pesticides concentrations reported in the inventory were from ad hoc measurements taken in a single sampling event at the Tai Mo Shan Station. Relatively low concentrations of DDT (0.05 ng m^{-3}), heptachlor (0.03 ng m^{-3}) and HCB (0.16 ng m^{-3}) were found.

Table 7.5 compares the reported ambient air concentrations of dioxins/furans in Hong Kong and other urban locations worldwide. Overall, the mean local ambient air dioxin concentration of 0.06 pg I-TEQ m^{-3} measured in 2000–2004 was highly comparable to the range reported in most other urban locations in Asia (Government of Japan, 2005), Europe (Buckland et al., 1999; Gras and Müller, 2004), Australia (Taucher et al., 1992), New Zealand (Buckland et al., 1999) and the US (Riggs et al., 1996), and was lower than that reported in Korea (Park and Kim, 2002) or Spain (Gras and Müller, 2004).

7.4.1.2. Surface water

Data on marine water POPs were mainly generated from two consultancy studies on toxic substances pollution in Hong Kong commissioned by the EPD (EPD, 2003a,b). The 2004 EPD in-house toxic substance monitoring programme (EPD, 2005a) also contributed to the inventory, especially on the marine water levels of DDT, PCBs and dioxins/furans. None of the nine POPs pesticides was detected at any of the sampling sites. PCBs was found to be below DL in all 180 water samples analyzed from 38 sites located throughout Hong Kong. The 2,3,7,8-TCDD was not detected in any of the 104 local marine water samples analyzed in 2000–2004. The calculated mean concentration of dioxins/furans was 0.55 (lower bound, assuming zero for individual congener level $<$DL) and 5.21 (upper bound, assuming 1/2DL for individual congener level $<$DL) pg I-TEQ L^{-1}, respectively. There were no data available on the level of POPs in inland waters of Hong Kong.

The calculated mean (lower bound) dioxin/furan concentration of 0.55 pg TEQ L^{-1} fell at the high end of the range (0.24–0.40 pg TEQ L^{-1}) reported in public waters of Japan in 1998–2000 (Government of Japan, 2002). Little other marine water dioxin/furan data from elsewhere were available for comparison.

7.4.1.3. Surface sediment

Contamination of local marine sediment by toxic chemical pollutants has been relatively well documented. The marine sediment POPs inventory was compiled based primarily on data generated from a major consultancy study on local toxic substances pollution (EPD, 2003a), EPD routine and ad hoc marine monitoring programmes of 2003/2004 and study reports published by local academia (Zheng et al., 2000; Müller et al., 2002; Tam and Yao, 2002; Wong et al., 2001, 2005). With the exception of mirex and toxaphene, all other POPs pesticides were detected in the

Table 7.4. Mean levels of POPs contamination in the environment of Hong Kong in 2000–2004

Chemical	Ambient air (ng m^{-3})			Surface water (ng L^{-1})			Surface sediment (µg kg^{-1} dw)			
				Marine water			Marine sediment			River Sediment
	No. of sites	No. of samples	Mean[b] (min–max)	No. of sites	No. of samples	Mean[c] (min–max)	No. of sites	No. of samples	Mean[c] (min–max)	No. of sites
Aldrin	1	4	0	22	84	0	28	54	4.7 (1.30–9.2)	
Chlordane				22	84	0	28	54	4.2 ($<$0.01–$<$10.0)	
DDT	1	4	0.05 (0–0.10)	32	104	0	46	168	6.81 (0.30–33.1)	5
Dieldrin	1	4	0	22	84	0	28	54	5.19 (2.40–11.0)	
Endrin	1	4	0	22	84	0	28	54	3.86 ($<$0.01–$<$10.0)	
Heptachlor	1	4	0.03 (0–0.09)	22	84	0	28	54	4.48 ($<$0.01–$<$100)	
HCB	1	4	0.16 (0.05–0.23)	22	84	0	22	54	5.98 (0.05–23.8)	
Mirex				20	80	0	20	40	0	
Toxaphene				22	84	0	20	40	0	
PCBs	2	209	0.48 (0.01–1.81)	38	180	0	118	381	24.1 (0.63–330)	5
Dioxins/furans[a]	4	271	0.06 (0.04–0.35)	32	104	0.55[d], 5.21[e] (0.0005–24.4)	52	89	9.1 (2.28–38.7)	

[a] Unit of dioxins/furans in ambient air = pg I-TEQ m^{-3}; in surface water = pg I-TEQ L^{-1}; in surface sediment/surface soil/vegetation = ng I-TEQ kg^{-1} dw.

[b] "0" indicates values were $<$DL; DL of pesticides in ambient air = 0.02 ng m^{-3}; if mixed values of $>$DL and $<$DL were recorded in a sample pool, mean value was calculated by assuming "0" for samples $<$DL calculated by assuming "0.5DL" for samples $<$DL.

[c] "0" indicates values were $<$DL; DL DDT, all other pesticides and PCB in marine water = 15, 10 and 100 ng L^{-1}, respectively; DL of mirex and toxaphene in marine sediment = 10 µg kg^{-1} dw; if mixed values of $>$DL and $<$DL were recorded in a sample pool, mean values was calculated by assuming "0.5DL" for samples $<$DL.

[d] The value was calculated assuming zero for individual congener level $<$DL. 2,3,7,8-TCDD$<$DL in all 104 samples.

[e] The value was calculated assuming 0.5DL for individual congener level $<$DL.

Surface sediment (µg kg^{-1} dw)		Surface soil (µg kg^{-1} dw)			Vegetation (µg kg^{-1} dw)					
River Sediment					Ground vegetation			Tree bark		
No. of samples	Mean (min–max)	No. of sites	No. of samples	Mean[c] (min–max)	No. of sites	No. of samples	Mean (min–max)	No. of sites	No. of samples	Mean (min–max)
15	4.96 (2.82–8.63)	46	46	0.52 (<0.004–6.00)						
		46	46	0.01 (<0.004–0.10)						
		46	46	0.01 (<0.001–0.30)						
15	193 (43.0–461)	46	46	0.1 (<0.004–0.16)						
		5	40	5.33 (0.35–32.8)	5	40	2.13 (0.29–14.1)	5	10	1.47 (0.49–3.57)

Table 7.5. Comparison of ambient air concentrations of dioxins/furans (PCDD/Fs) in Hong Kong and other urban locations

Location	Period	Concentrations of PCDD/Fs (pg I-TEQ m^{-3}) mean (min–max)	Reference
Hong Kong, China	2000–2004	0.06 (0.04–0.35)	EPD, 2005b
Australia	1992	0.02–0.06	Taucher et al., 1992
Belgium	1993	0.02–0.59	Wevers et al., 1993
Germany	1993–1997	0.071 (0.009–0.231)	Buckley-Golder, 1999
Japan	2003	0.068 (0.0066–0.72)	Government of Japan, 2005
Korea	2000–2001	0.282 (0.017–0.803)	Park and Kim, 2002
New Zealand	1996–1997	0.0536 (0.00699–0.234)	Buckland et al., 1999
Portugal	1998	0.036–0.49	Gras and Müller, 2004
Spain	1994–2000	0.158–0.264	Gras and Müller, 2004
UK	1998	0.02–0.51	Gras and Müller, 2004
USA	1996	0.09–0.45	Riggs et al., 1996

marine sediment sampled at over 20 locations throughout Hong Kong. The mean sediment pesticide concentrations ranged <DL–6.81 μg kg^{-1} dw. DDT (6.81 μg kg^{-1} g dw), HCB (5.98 μg kg^{-1} dw) and dieldrin (5.19 μg kg^{-1} dw) were found to be the major POPs pesticide contaminants. PCBs and dioxins/furans were widely distributed, with sediment levels ranging 0.63–330 μg kg^{-1} dw and 2.28–38.7 ng I-TEQ kg^{-1} dw for PCBs and dioxins/furans, respectively.

Information on POPs in local river sediments was sketchy. One ad hoc study of the inland water systems in Hong Kong was available and the study data were reported in this inventory (Zhou et al., 1999). River sediment samples were taken at 15 sites along the 3 main local rivers (Shing Mun River, Tai Po River and Lam Tsuen River in the New Territories) and analyzed for DDT and PCBs. The mean level of DDT contamination was 4.96 μg kg^{-1} dw, while that of PCB contamination was 193 μg kg^{-1} dw.

Comparison of the level of POPs contamination in marine sediment of Hong Kong and other countries/regions was made based on best available data and the results are summarized in Table 7.6. Overall, the level of POPs measured in local marine surface sediment was comparable to those reported in most other locations around the world. For DDT, a POPs pesticides of regional interest, the level of mean local sediment contamination was found to be well within the range reported in the Pearl River Estuary (Li et al., 2001), the east coast estuaries of China (Yuan et al., 2001), the coast of Argentina (Menone et al., 2001), the Netherlands (Stronkhorst and Hattum, 2003) and Pakistan (Sanpera et al., 2003), and

Table 7.6. Comparison of the level of POPs contamination in marine sediment of Hong Kong and other urban locations

Location	Period	DDT[b]	Dieldrin[b]	Endrin[b]	Heptachlor[b]	HCB[b]	PCBs[b]	PCDD/Fs[c]	Reference
Hong Kong, China	2000–2004	6.81 (0.30–33.1)	5.19 (2.40–11.0)	3.86 (<0.01–<10.0)	4.48 (<0.01–<10.0)	5.98 (0.05–23.8)	24.1 (0.63–330)	9.10 (2.28–38.7)	EPD, 2005b
Argentina	1996	0.77–3.14	0.10–0.24	0.05–0.26	10.7–12.3	<0.0013–0.053	0.31–1.61		Menone et al., 2001
Australia	2001–2002							0.67 (0.000002–3.9)	Australian Government, 2004b
Baltic Sea	1993							26–71	Koistinen et al., 1997
China									
East Coast Estuaries	1996, 1999	6.17–73.7					1.69–14.3		Yuan et al., 2001
Pearl River Delta	1997						26.7–32.0		Mai et al., 2005
Pearl River Estuary	1997	1.56–26.5	ND–0.19	ND–0.61	0.47–1.62				Li et al., 2001
Dutch	1999–2000	<1–40				<1–67			Stronkhorst and Hattum, 2003
Finland	1999							0.70–100	Fiedler et al., 1999
Japan, Tokyo Bay	2003[a]							3.30–52.0	Hosomi et al., 2003
Korea	2000							0.01–5.50	Moon et al., 2001
New Zealand	1999[a]							0.53 (0.081–2.71)	Scobie et al., 1999
North Sea	1994[a]							0.60–2.80	Tyler et al., 1994
Pakistan	1999–2000	7.80					2.20		Sanpera et al., 2003
South Africa	2003[a]							0.20–22.0	Vosloo and Bouwman, 2003
Sweden	1999							0.80–207	Fiedler et al., 1999
USA									
Florida Bay	2003[a]							0.50–77.8	Hemming et al., 2003
Santa Monica Bay	1997	31.0–290					2.50–924		Bay et al., 2003
Tampa Bay	1995–1999		0.33	0.18	0.78				Grabe and Barran, 2004
New York Harbour	1994–1996						80–1410		Huan et al., 1998
	2003[a]							23–880	Litten et al., 2003

Note: ND = not detected.

[a] Year of data reporting.

[b] Expressed as mean (min–max); unit = $\mu g\ kg^{-1}$ dw.

[c] Expressed as mean (min–max); unit = ng I-TEQ kg^{-1} dw.

much lower than that in the California coast (Bay et al., 2003). For PCBs, the mean local sediment contamination level fell at the lower end of the range reported in New York Harbour (Huan et al., 1998) and the Californian coast (Bay et al., 2003), was comparable to that found in the PRD (Mai et al., 2005) and higher than that reported in the coast of Argentina (Menone et al., 2001) and Pakistan (Sanpera et al., 2003). For dioxins/furans, the measured local sediment contamination level was comparable to that found in Tokyo Bay (Hosomi et al., 2003) or the coast of South Africa (Vosloo and Bouwman, 2003), at the higher end of the range reported in Australia (Australian Government, 2004b), Korea (Moon et al., 2001), New Zealand (Scobie et al., 1999) and the North Sea (Tyler et al., 1994), but much lower than that reported in New York Harbour (Litten et al., 2003), the coast of Sweden and Finland (Fiedler et al., 1999) and the Baltic Sea (Koistinen et al., 1997).

7.4.1.4. Surface soil

The soil POPs pesticide inventory was compiled based on one ad hoc territory-wide background monitoring of surface soil in Hong Kong (NISS/CAS and HKBU, 2004). Rural surface soil samples were collected from 46 locations across the region, mostly woodland and grassland and analyzed for DDT, endrin, HCB and PCBs. The level of POPs pesticides contamination in the soil was generally very low, with mean values ranging from 0.01 (endrin and HCB) to 0.52 $\mu g\ kg^{-1}$ dw (DDT). The mean soil PCBs concentration (0.1 $\mu g\ kg^{-1}$ dw) was found to be 241 times and 1930 times lower than that found in the local marine and river sediments, respectively. Dioxins/furans were measured in an EPD-commissioned monitoring consultancy study in 2001/2002 that targeted potential local dioxin emission sources (EPD, 2004b). Forty soil samples were taken from five locations near landfill sites, the CWTC and livestock waste composting sites. Low soil dioxin/furan concentrations ranging 0.35–32.8 ng I-TEQ kg^{-1} dw were recorded.

The level of DDT contamination of surface soil in Hong Kong recorded in 2000–2004 was found to be the lowest among those reported in most other urban locations of Mainland China (Chau, 2005; Nakata et al., 2005), in Cuba (UNEP Chemicals, 2003d), India (UNEP Chemicals, 2003d), the subtropical Atlantic (Ribes and Grimalt, 2002) and the US (Aigner et al., 1998) (Table 7.7). While the mean local soil PCBs concentration was generally comparable to that found in most other urban locations of China (Nakata et al., 2005), it was at the lower end of the range reported in the subtropical Atlantic (Ribes and Grimalt, 2002), Amazon (Buckland et al., 1998a) and Panama regions (Meijer et al., 2003).

Table 7.7. Comparison of the level of POPs contamination in surface soil of Hong Kong and other urban locations

Location	Period	DDTs[b]	PCBs[b]	PCDD/Fs[c]	Reference
Hong Kong, China	2000–2004	0.52 (<0.004–6.00)	0.10 (<0.004–0.16)	5.33 (0.35–32.8)	EPD, 2005b
Amazon	1998[a]		0.1–7.7		Buckland et al., 1998a
	1998[a]			0.02–0.4	Buckland et al., 1998a
China					
Haining	2001	83±83			Nakata et al., 2005
	2001		0.05±0.01		Nakata et al., 2005
Pearl River Delta	2005[a]	15–125			Chau, 2005
Shanghai	2001	34±23			Nakata et al., 2005
	2001		0.41±0.20		Nakata et al., 2005
Shaoxing	2001	0.70±0.39			Nakata et al., 2005
	2001		<0.01		Nakata et al., 2005
Cuba	1983	60–350			UNEP Chemicals, 2003d
France	1998			0.2–17	UNEP Chemicals, 2002
India	2003[a]	5–49			UNEP Chemicals, 2003d
Italy	2002[a]			1.0–6.2	UNEP Chemicals, 2002
New Zealand	1998[a]			0.26–6.67	Buckland et al., 1998a
Panama	2003[a]		0.026–97		Meijer et al., 2003
Portugal	2002[a]			2.04–16.4	Coutinho et al., 2002
Spain	2001[a]			0.15–24.2	Eljarrat et al., 2001
Subtropical Atlantic	2002[a]	5.4 (0.01–40)			Ribes and Grimalt, 2002
	2002[a]		1.2 (0.04–9.2)		Ribes and Grimalt, 2002
USA, Corn Belt	1995–1996	9.63			Aigner et al., 1998

[a] Year of data reporting.
[b] Expressed as mean (min–max); unit = μg kg^{-1} dw.
[c] Expressed as mean (min–max); unit = ng I-TEQ kg^{-1} dw.

For dioxins/furans, the mean level of contamination of local soil was comparable to that reported in most European countries (Eljarrat et al., 2001; Coutinho et al., 2002; UNEP Chemicals, 2002) and higher than that found in the Amazon region (Buckland et al., 1998a).

7.4.1.5. Vegetation

The level of dioxin/furan contamination of ground vegetation and tree barks was measured in an EPD-commissioned monitoring consultancy study in 2001/2002 that targeted suspected local dioxin emission sources (EPD, 2004b). Forty samples of ground vegetation and 10 tree bark samples were taken from 5 locations near landfills, the CWTC and livestock waste composting sites. The mean level of dioxin/furan contamination of ground vegetation and tree barks in the vicinity of potential local sources of dioxin emission was 2.13 and 1.47 ng I-TEQ kg^{-1} dw, respectively. No data on POPs pesticides contamination of local vegetation were available.

7.4.2. Contamination levels of POPs in aquatic biota

Table 7.8 summarizes the level of POPs contamination reported in representative freshwater and marine biota (fish, shellfish, water bird eggs and marine mammals) of Hong Kong in 2000–2004. The mean tissue levels of POPs were weighted arithmetic means calculated based on tissue samples analyzed and reported in individual studies.

7.4.2.1. Freshwater fish

There was a general paucity of information on POPs in local freshwater biota. Ad hoc studies reported by local academia contributed to all the data compiled in this section of the inventory (Zhou et al., 1999; Kong, 2004). Four freshwater fishes from a few (1–3) sampling sites were analyzed. DDT was the only POPs pesticide detected, with a mean tissue concentration of 6.78 μg kg^{-1} ww. PCBs was measured in only one fish species from two locations and a mean tissue level of 57.8 μg kg^{-1} ww was reported.

7.4.2.2. Marine fish and shellfish

Unlike the freshwater biota, POPs in local marine fish and shellfish were relatively well studied. Data were retrieved primarily from two toxic substances consultancy studies (EPD, 2003a,b), the EPD ad hoc baseline survey (EPD, 2003c), and the 2004 CEDD Environmental Monitoring and Audit for Contaminated Mud Pit IV at East Sha Chau (CEDD, 2005). Ad hoc studies by local academia also contributed significantly to the data pool (Lam and Lam, 2004; So et al., 2005; Wong et al., 2005).

Common local marine fish investigated included the pony fish (*Leiognathus brevirostris*), burrowing goby (*Trypauchen vagina*), ovate sole (*Solea ovata*), gizzard shad (*Clupanodon punctatus*), flathead mullet (*Mugil cephalus*), Indian mackerel (*Rastrelliger kanagurta*), rabbit fish (*Siganus oramin*) and tilapia (*Tilapia spp.*). Common local marine shellfish investigated included shrimps (*Palaeomonetes spp.*, *Metapenaeus spp.*, *Oratosquilla spp.*), crabs (*Varuna litterata*), bivalves (*Perna viridis*) and molluscs (*Bucardium fimbriatum*, *Anadara ferruginea*). Most POPs pesticides were detected in a variety of marine fish and shellfish sampled at multiple sites throughout Hong Kong. DDT, endrin and heptachlor were found to be the major POPs pesticide contaminants of both marine fish

Table 7.8. Mean levels of POPs contamination in aquatic biota of Hong Kong in 2000–2004

Chemical	Freshwater fish ($\mu g\ kg^{-1}$ ww)			Marine fish ($\mu g\ kg^{-1}$ ww)			Marine shellfish ($\mu g\ kg^{-1}$ ww)			Water bird eggs ($\mu g\ kg^{-1}$ ww)			Marine cetaceans ($\mu g\ kg^{-1}$ ww)		
	No. of sites	No. of genus	Mean[b] (min–max)	No. of sites	No. of genus	Mean[b] (min–max)	No. of sites	No. of genus	Mean[b] (min–max)	No. of sites	No. of genus	Mean (min–max)	No. of sites	No. of genus	Mean (min–max)
Aldrin	1	4	0	3	7	28.9 (0.08–<100)	11	7	0						
Chlordane				3	7	3.8 (0.39–16.4)	10	6	1.12 (0.11–5.02)	2	2	156 (31.0–280)			
DDT	3	4	6.78 (3.32–10.9)	13	14	27.6 (0.83–99.0)	21	14	7.73 (0.16–28.6)	2	2	900 (600–1200)	NR	1	32,763
Dieldrin	1	4	0	9	8	2.18 (<0.08–15.8)	17	9	0.21 (<0.01–0.40)						
Endrin	1	4	0	9	8	28.1 (0.14–<100)	17	9	5.86 (<0.01–25.2)						
Heptachlor	1	4	0	9	8	25.3 (0.18–<100)	17	9	5.99 (<0.01–25.1)						
HCB				11	8	5.8 (<0.20–18.1)	18	7	0.8 (0.13–3.43)						
Mirex				2	4	0	2	2	0				NR	2	178 (70.5–286)
Toxaphene				2	4	1.33 (0.25–2.36)	2	2	0				NR	2	32 (19.7–44.2)
PCBs	2	1	57.8	16	13	22.6 (<2.00–153)	23	11	13.8 (<1.00–55.0)	2	2	595 (230–960)	NR	1	8190
Dioxins/ furans[a]				2	4	0.33 (0.09–0.57)	2	2	0.53 (0.21–0.85)						

Note: NR = multiple sites, exact number not recorded.

[a] Unit of dioxins/furans = ng I-TEQ kg^{-1} ww.

[b] "0" indicates values were <DL; DL of pesticides in freshwater fish = 0.01 $\mu g\ kg^{-1}$ ww; DL of aldrin/mirex and toxaphene in marine fish/shellfish = 100 and 0.2 $\mu g\ kg^{-1}$ ww, respectively; if mixed values of >DL and <DL were recorded in a sample pool, mean value was calculated by assuming "0.5DL" for samples <DL.

and shellfish, while aldrin was prominent only in the marine fish. The mean concentration of PCBs in local marine fish and shellfish was 22.6 and 13.8 $\mu g\ kg^{-1}$ ww, respectively. Dioxins/furans were detected in all fish and shellfish genera examined. The mean level of dioxin/furan contamination of marine fish was 0.33 ng I-TEQ kg^{-1} ww and that of marine shellfish was 0.53 ng I-TEQ kg^{-1} ww. With the exception of dioxins/furans, the level of POPs contamination was found to be generally higher in marine fish than shellfish.

Table 7.9 compares the level of POPs contamination of marine fish in Hong Kong and other countries/regions. On the whole, the level of POPs contamination of local fish was comparable to that found in fish of most other coastal locations around the world. The concentration of HCB in local marine fish appeared high compared to the extremely low range reported in many Asian countries (Monirith et al., 1999; Ueno et al., 2003), Brazil, the Mediterranean (Stefanelli et al., 2002) and North Pacific regions (Ueno et al., 2003). The mean concentration of DDT in marine fish of Hong Kong was similar to that of the Mainland coast, the Japanese Sea (Ueno et al., 2003) and the Mediterranean coast (Stefanelli et al., 2002), but slightly higher than the range reported in most South East Asia locations (Monirith et al., 1999; Ueno et al., 2003). The mean concentration of PCBs in local marine fish was generally comparable to that reported in the Mainland coast, the Brazilian coast and the North Pacific (Ueno et al., 2003), and fell at the lower end of the range recorded in the Mediterranean coast (Stefanelli et al., 2002) and the Japanese Sea (Ueno et al., 2003). The dioxin/furan concentration in marine fish of Hong Kong was in the same range as that of the Adriatic Sea (Bayarri et al., 2001) and the San Francisco Bay (Fairey et al., 1997), above that found in Australia (Australian Government, 2004b) and the Finnish coast (UNEP Chemicals, 2002), but below the range reported in the Baltic Sea (Kiviranta et al., 2003), Tokyo Bay (Tsutsumi et al., 2003), New York Harbour (Litten et al., 2003) and Southern Norway (Knutzen et al., 2003).

Similarly, a comparison was made on the level of POPs contamination of marine shellfish in Hong Kong and other countries/regions and the results are presented in Table 7.10. The concentration of POPs pesticides and PCBs in local marine shellfish was found to be generally comparable to that reported in most Asian countries (Tanabe et al., 2000; Monirith et al., 2000, 2003; Bayen et al., 2004) and Australia (Australian Government, 2004b). Exceptions were the level of DDT contamination which was significantly lower than that in the Mainland coast (Monirith et al., 2003) and the concentration of PCBs which fell at the very low end of the range reported in the Mediterranean coast of Egypt (El Nemr et al., 2003). The mean dioxin/furan concentration in local marine shellfish was similar

Table 7.9. Comparison of the level of POPs contamination in marine fish of Hong Kong and other coastal locations

Location	Period	Chlordane[b]	DDT[b]	HCB[b]	PCBs[b]	PCDD/Fs[c]	Reference
Hong Kong, China	2000–2004	3.80 (0.39–16.4)	27.6 (0.83–99.0)	5.80 (<0.20–18.1)	22.6 (<2.00–153)	0.33 (0.09–0.57)	EPD, 2005b
Australia	2004[a]					0.0054–0.095	Australian Government, 2004b
Baltic Sea	2003[a]					15.0 (1.77–74.0)	Kiviranta et al., 2003
Brazil	1997–2001	3.40 (1.73–4.75)	4.97 (2.43–8.10)	0.13 (0.097–0.162)	24.8 (18.4–31.9)		Ueno et al., 2003
Cambodia	1997	<0.01–0.23	0.30–4.00	<0.01–0.18	0.07–1.20		Monirith et al., 1999
China							
East China Sea	1997–2001	3.65–4.76	18.6–35.3	0.078–0.173	34.7–37.1		Ueno et al., 2003
South China Sea	1997–2001	3.08	54.3	0.178	11.3		Ueno et al., 2003
Finnish Coast	2002[a]					0.0029–0.024	UNEP Chemicals, 2002
Germany, Baltic Sea	2002[a]					1.90	Karl et al., 2002
Indonesia	1997–2001	0.53 (0.51–0.56)	2.11 (1.77–2.38)	0.09 (0.09–0.09)	3.40 (2.86–3.94)		Ueno et al., 2003
Italy, Adriatic Sea	2001[a]					0.23–1.07	Bayarri et al., 2001
Japan	1997–2001	10.5 (6.08–13.3)	48.5 (41.8–54.2)	0.49 (0.40–0.60)	85.5 (77.9–114)		Ueno et al., 2003
Tokyo Bay	2003[a]					0.05–23.1	Tsutsumi et al., 2003
Mediterranean, Sicilian coast	1999	1.37 (0.30–4.70)	52.0 (0.95–300)	0.22 (<0.01–0.92)	74.9 (21.4–325)		Stefanelli et al., 2002
North Pacific	1997–2001	0.90–3.05	2.13–4.13	0.14–0.67	7.81–19.1		Ueno et al., 2003
Norway	2003[a]					1.90–26.2	Knutzen et al., 2003
Pakistan	1999 -2000		6.97		1.26		Sanpera et al., 2003
Philippines	1997–2001	0.49 (0.41–0.70)	2.84 (1.62–3.77)	0.049 (<0.04–0.09)	5.51 (4.06–7.54)		Ueno et al., 2003
USA							
New York Harbour	2003[a]					1.90–29.0	Litten et al., 2003
San Francisco Bay	1997[a]					0.12–1.75	Fairey et al., 1997

Note: ND = not detected.

[a] Year of data reporting.

[b] Expressed as mean (min–max); unit = μg kg^{-1} ww.

[c] Expressed as mean (min–max); unit = ng I-TEQ kg^{-1} ww.

Table 7.10. Comparison of the level of POPs contamination in marine shellfish of Hong Kong and other coastal locations

Location	Period	Chlordane[b]	DDT[b]	HCB[b]	PCBs[b]	PCDD/Fs[c]	Reference
Hong Kong, China	2000–2004	1.12 (0.11–5.02)	7.73 (0.16–28.6)	0.80 (0.13–3.43)	13.8 (<1.00–55.0)	0.53 (0.21–0.85)	EPD, 2005b
Australia	2004[a]					0.012–0.9	Australian Government, 2004b
Corio Bay, Victoria	1992	0.038–0.18		0.005–0.012	0.65–4.55		Prest et al., 1995
Cambodia	2000[a]	0.12±0.03	0.50±0.50	0.02±0.01			Tanabe et al., 2000
China (Mainland)	1999, 2001	3.0 (0.20–10.0)	240 (15.0–640)	1.30 (<0.01–13.0)	2.50 (0.30–13.0)		Monirith et al., 2003
Egypt, Mediterranean Coast	2000				7.70–436		El Nemr et al., 2003
India	2000[a]	0.50±0.50	11.0±10.0	0.06±0.11			Tanabe et al., 2000
Indonesia	2000[a]	0.30±0.10	1.10±0.90	0.01±0.01			Monirith et al., 2000
Italy, Adriatic Sea	2001[a]					0.07–0.24	Bayarri et al., 2001
Japan	1994	6.0 (1.70–17.0)	3.50 (0.80–12.0)	0.08 (<0.01–0.30)	30.0 (7.40–84.0)		Monirith et al., 2003
	2003[a]					0.07–1.10	Tsutsumi et al., 2003
Korea	2001[a]					0.001–1.20	Choi et al., 2001
Malaysia	2000[a]	2.20±3.20	1.40±1.50	0.01±0.01			Monirith et al., 2000
Mediterranean, Baltic Sea	2001[a]	0.06–0.09					Falandysz et al., 2001
New Zealand	1999[a]					0.015–0.26	Scobie et al., 1999
Norway	2002[a]					1.60–3.0	Karl et al., 2002
Philippines	2000[a]	3.70±3.70	1.70±1.20	0.01±0.01			Tanabe et al., 2000
Singapore	2002	1.40 (0.43–3.30)	3.40 (0.51–12.0)	<0.01			Bayen et al., 2004
South Korea	1998	0.55 (0.20–1.20)	3.50 (0.70–7.50)	0.05 (<0.01–0.20)	3.70 (0.80–7.20)		Monirith et al., 2003
Thailand	1997[a]	1.20±1.40	5.60±8.10	0.05±0.04			Kan-atireklan et al., 1997
USA							
Acata Bay	2003[a]					0.22(0.16–0.25)	Wenning et al., 2003
New York Harbour	2003[a]					1.50–38.0	Litten et al., 2003
Vietnam	2000[a]	0.30±0.40	44.0±111	0.01±0.02			Tanabe et al., 2000

Note: ND = not detected.

[a] Year of data reporting.

[b] Expressed as mean (min–max), min–max or mean ± SD; unit = μg kg^{-1} ww.

[c] Expressed as mean (min–max) or min–max; unit = ng I-TEQ kg^{-1} ww.

to the low range reported in Japan (Tsutsumi et al., 2003), Korea (Choi et al., 2001), Australia (Australian Government, 2004b), New Zealand (Scobie et al., 1999) and a number of European countries (Bayarri et al., 2001; Karl et al., 2002), and well below that of New York Harbour (Litten et al., 2003).

7.4.2.3. Water bird eggs

Data on POPs contamination in local water birds were limited. Results of one ad hoc study conducted by the local academia on persistent organic contaminants in Ardeids contributed to the inventory on POPs in local water birds, using the bird egg as a body burden indicator. The eggs of two Ardeid species, the Little Egret (*Egretta garzetta*) and the Black-crown Night Heron (*Nycticorax nycticorax*), were collected from two egretries located in the woodlands of the New Territories (Mai Po Marshes in the west and A Chau in the east) and analyzed for chlordane, DDT and PCBs (Connell et al., 2003; Lam and Lam, 2004). A relatively high level of all three POPs was detected in the Ardeid eggs, with average concentration of 156, 900 and 595 μg kg^{-1} ww for chlordane, DDT and PCBs, respectively.

7.4.2.4. Marine mammals

Levels of POPs in two local marine mammals, the Indo-Pacific humpback dolphin (*Sousa chinensis*) and finless porpoise (*Neophocaena phocaenoides*), were measured in two ad hoc studies of stranded cetaceans in 1995–2000 and 2000–2001, respectively (Jefferson et al., 2002; Imanishi et al., 2004). Cetacean tissue samples were collected from stranded animals found in Hong Kong and analyzed for DDT, mirex, toxaphene and PCBs. High mean blubber concentrations of DDT (32.8 mg kg^{-1} ww) and PCBs (8.19 mg kg^{-1} ww) were reported.

Table 7.11 summarizes the level of POPs contamination in cetaceans of Hong Kong and other countries/regions. The mean DDT concentration in local cetaceans was similar to the range reported in the South China Sea (Parsons et al., 1999) and the California coast (Kajiwara et al., 2001), and was among the highest found in marine habitats around the world. The mean PCBs concentration fell in the general range reported in the South China Sea (Parsons et al., 1999), the Philippines, India (Minh et al., 2000), Australia, Costa Rica, Caribbean Sea and the Arctic (UNEP Chemicals, 2003d); higher than that found in the Alboran Sea (Borrell and Aguilar, 2005) and Bering Sea (Deagars and Garlich-Miller, 2001), and substantially lower than the range recorded in Japan (Minh et al., 2000), the California coast (Kajiwara et al., 2001), the coast of

Table 7.11. Comparison of the level of POPs contamination in cetaceans of Hong Kong and other marine habitats

Location	Period	DDT[a]	Mirex[a]	Toxaphene[a]	PCBs[a]	Reference
Hong Kong, China	2000–2004	0.03	0.18 (0.07–0.29)	0.03 (0.02–0.04)	8.19	EPD, 2005b
Arctic	2003	0.23–3.60			0.24–2.87	UNEP Chemicals, 2003d
Australia	2003	0.98–3.34			1.20–3.30	UNEP Chemicals, 2003d
Brazil	1998–1999		0.05–0.20	0.02–0.12		Imanishi et al., 2004
Costa Rica	2003	2.70–6.50			1.50–6.40	UNEP Chemicals, 2003d
India	1990–1992		0.010	0.86		Imanishi et al., 2004
Bay of Bengal	1990				1.60–3.0	Minh et al., 2000
Japan	1998–2001		0.005–0.06	0.17–2.67		Imanishi et al., 2004
	1989–1993				4.10–57.0	Minh et al., 2000
Mediterranean						
Alboran Sea	1992–1994	1.71–115			2.85–83.5	Borrell and Aguilar, 2005
Black Sea	1993		0.009	1.50		Imanishi et al., 2004
Caribbean Sea	2003	1.40–7.40			2.0–5.0	UNEP Chemicals, 2003d
The Irish & the Aegean Sea	1987–1991				1.39–25.8	Troisi et al., 1998
Philippines	1996		0.02	0.66		Imanishi et al., 2004
	1996				2.40–8.60	Minh et al., 2000
Russia, Pacific Coast	2003			0.93–1.30		UNEP Chemicals, 2003d
South China Sea	1994	33.0	0.01		1.79	Parsons et al., 1999
USA						
Bering Sea, Alaska	1991				0.09–0.45	Deagars and Garlich-Miller, 2001
California Coast	1991–1997	7.55–104			4.55–247	Kajiwara et al., 2001
Coast of Massachusetts	1986, 1990	7.0 ± 0.93			15.0 ± 2.2	Tilbury et al., 1999

[a] Expressed as mean, min–max, mean (min–max) or mean ± SD; unit = mg kg^{-1} ww.

Massachusetts (Tilbury et al., 1999), the Irish Sea and the Aegean Sea (Troisi et al., 1998).

7.5. Dietary exposure to POPs

7.5.1. Contamination levels of POPs in locally consumed foods

The level of contamination of POPs in locally consumed foods is monitored year-round by the Food and Environmental Hygiene Department (FEHD) of the HKSAR Government under a routine food surveillance programme (FEHD, 2003). Food items (mainly imports from the Mainland and other countries) are sampled on a regular basis from local market stalls, supermarkets, fresh provision shops, food wholesalers and at the points of entry into Hong Kong (e.g., border checkpoint at Man Kam To and the International Airport). Analysis of toxic chemical contamination is carried out by the Government Laboratory (GL) of the HKSAR Government.

Table 7.12 summarizes the level of POPs contamination in eight main locally consumed food groups in 2003. With the exception of DDT and HCB, POPs pesticides were not detected in most food groups. DDT was found in cereals, fruits, dairy products and seafoods, while HCB was detected in cereals only. PCBs was not detected in fruits, dairy products, meats or poultry, but found in seafood items at a mean concentration of 4.07 $\mu g\ g^{-1}$ food. Measurable levels of dioxins/furans were found in cereals, dairy products, eggs, seafoods, meats and poultry, with mean dioxin/furan levels ranging from 0.001 (meats) to 0.285 (seafoods) pg TEQ g^{-1} food. Dioxins/furans were not analyzed in vegetable and fruit items sampled in 2003.

7.5.2. Estimate of daily dietary exposure to POPs

Human exposure to POPs through dietary intake was estimated based on measurement of the level of POPs contamination in various foods and information on daily food consumption pattern of the local population. Since comprehensive local food consumption data at the population level was not available, the food consumption patterns of Far East countries (including China) published by WHO in 2003 (GEMS/Food Regional Diets 2003) were adopted for estimation of human exposure to POPs through the dietary intake pathway. Dietary exposure of Hong Kong residents to DDT, HCB, PCBs and dioxins/furans was estimated to be 29.3 ng, 1.11 ng, 8.31 ng and 0.91 pg-TEQ kg^{-1} bw d^{-1}, respectively

(Table 7.12). The major food groups contributing to POPs exposure were cereals, seafoods and dairy products.

The dietary exposure of the local population to DDT was comparable to the range reported in many European countries and the US (Herrera et al., 1996); higher than that in Australia (Kannan et al., 1994; Miller et al., 2002) and New Zealand (Pesticide Action Network UK, 1998), but substantially lower (by 1–3 orders of magnitude) than that in Mainland China (Chen and Gao, 1993), Vietnam, India (Kannan et al., 1992) and Egypt (Pesticide Action Network UK, 1998) (Table 7.13). The estimated dietary intake of HCB was found to be generally similar among residents of Hong Kong, other Asian countries/regions (Kannan et al., 1992), Australia (Kannan et al., 1994; Miller et al., 2002), the US (Herrera et al., 1996), the Netherlands (Brussard et al., 1996) and Slovakia (Prachar et al., 1996), but lower than the value reported in Spain or Switzerland (Herrera et al., 1996). Based on the few published data available for comparison, the level of local dietary PCBs exposure was found to be much lower than in other Asian countries (Kannan et al., 1992). The estimated dietary exposure of Hong Kong residents to dioxins/furans was generally comparable to the level reported in most European countries (Malisch, 1998), Canada (Codex Alimentarius Commission, 2003) and the US (USEPA, 2001); slightly higher than the values recorded in Australia (Australian Government, 2004c), New Zealand (Buckland et al., 1998b) or the UK (Food Standards Agency, 2003), but appreciably lower than that found in Norway and Spain (Jimenez et al., 1996).

7.6. Human body burden of POPs

POPs in the environment can enter the food chain, bio-accumulate and bio-magnify as they move up the trophic levels and ultimately end up in the human body. It is expected that POPs will continue to accumulate in the body fat and their average concentrations will increase with age. The level of POPs contamination in human blood/serum and breast milk can serve as a good indicator of their body burden.

Local data on the level of POPs in breast milk of lactating mothers were reported in two ad hoc studies of Hong Kong residents, including a study conducted by local academia as part of the 3rd Round WHO/EURO Exposure Study 2002–2003 (Wong et al., 2002; Hedley et al., 2004). Table 7.14 presents the level of POPs contamination in breast milk of lactating mothers in Hong Kong in 2000–2003. In total, 115 local lactating mothers (aged 22–46, during their weeks 3–5 postpartum) participated in the milk sampling for analysis of DDT and PCBs and 316

Table 7.12. Estimates of dietary exposure to POPs contamination in foods of Hong Kong in 2003

	Cereals	Vegetables	Fruits	Dairy products	Eggs	Seafoods	Meats	Poultry	Daily consumption/exposure
Food consumption (g per capita d^{-1})[b]	445.7	340.3	186.3	66.3	22.2	122.5	33.3	26.3	1242.9
Contamination level ($\mu g\ kg^{-1}$ food)									
Aldrin	0[a]	0	0	0	–		0	–	
Chlordane	0	0	0	0	–	0	0	0	
DDT	0.85	0	0.14	1.00	–	10.5	0	0	
Dieldrin	0	0	0	0	–	–	0	–	
Endrin	–	0	0	–	–	–	–	–	
Heptachlor	0	0	0	0	–	0	0	0	
HCB	0.15	0	0	0	–	0	0	0	
Mirex	–	0	0	–	–	–	–		
PCBs	–	–	0	0	–	4.07	0	0	
Dioxins/furans (pg TEQ g^{-1} food)	0.015	–	–	0.100	0.137	0.285	0.001	0.131	
Estimated daily exposure ($ng\ kg^{-1}$ bw d^{-1})[c]									
Aldrin	0	0	0	0	–	–	0	–	0
Chlordane	0	0	0	0	–	0	0	0	0
DDT	6.31	0	0.43	1.11	–	21.4	0	0	29.3
Dieldrin	0	0	0	0	–	–	0	–	0
Endrin	–	0	0	–	–	–	–	–	0
Heptachlor	0	0	0	0	–	0	0	0	0
HCB	1.11	0	0	0	–	0	0	0	1.11
Mirex	–	0	0	–	–	–	–	–	0
PCBs	–	–	0	0	–	8.31	0	0	8.31
Dioxins/furans (pg TEQ kg^{-1} bw d^{-1})	0.110	–	–	0.111	0.051	0.582	0.001	0.057	0.91

[a] "0" indicates values were <DL; DL of pesticides and PCB = 0.005 mg kg^{-1}; DL of dioxins/furans = 0.02/0.05/0.10 ng kg^{-1} for individual congeners.

[b] Due to the lack of local data, food consumption patterns of Far East Countries (including China) published by WHO (2003) in "GEMS/Food Regional Diets" were adopted for estimation of daily dietary exposure, except in the case of the Seafoods Group where local Hong Kong data were available.

[c] Estimate was based on an average adult body weight of 60 kg.

Table 7.13. Comparison of dietary intake of POPs by the residents of Hong Kong and other urban locations

Location	Dietary intake (ng kg^{-1} bw d^{-1})				Reference
	DDT	HCB	PCBs	PCDD/Fs[a]	
Hong Kong, China	29.3	1.1	8.3	0.91	EPD, 2005b
Australia	7	4.67		0.03–0.34	Kannan et al., 1994; Miller et al., 2002; Australian Government, 2004b
Canada				0.8	Codex Alimentarius Commission, 2003
China, Mainland	341				Chen and Gao, 1993
Egypt	13,700				Pesticide Action Network UK, 1998
Finland	26				Pesticide Action Network UK, 1998
France				1.45	Miller et al., 2002
Germany				0.88	Malisch, 1998
India	800	2.17			Kannan et al., 1992
Italy				0.25–2.13	Zanotto et al., 1999
New Zealand	3			0.22	Pesticide Action Network UK, 1998; Buckland et al., 1998b
Norway				2.28–3.16	Becher et al., 1998
Slovakia	95.8	3.75			Prachar et al., 1996
Spain	20.3	17.2		2.4	Herrera et al., 1996; Jimenez et al., 1996
Switzerland	28.3	18.3			Herrera et al., 1996
Sweden				1.06	Miller et al., 2002
Thailand	70	1.3	25		Kannan et al., 1992
The Netherlands	16.7	3.33		0.67	Brussard et al., 1996; Freijer et al., 2001
UK	50			0.3	Pesticide Action Network UK, 1998; Food Standards Agency, 2003
USA	26	0.5		0.56	Herrera et al., 1996; USEPA, 2001
Vietnam	320	1.7	62		Kannan et al., 1992

[a] Unit = pg TEQ kg^{-1} bw d^{-1}.

Table 7.14. The level of POPs contamination in breast milk of lactating mothers in Hong Kong in 2000–2002

Chemical	Human breast milk concentration			
	No. of participants	Mean	Min	Max
DDT (μg g^{-1} lipid wt)	115	2.68	0.66	5.61
PCBs (μg g^{-1} lipid wt)	115	0.04	0.01	0.07
Dioxin-like PCBs (pg TEQ g^{-1} lipid wt)	316	4.67	2.80	6.58
Dioxins/furans (pg TEQ g^{-1} lipid wt)	316	8.25	5.80	10.1

local lactating mothers (aged 18–42, during their weeks 2–6 postpartum) contributed milk samples for analysis of dioxin-like PCBs and dioxins/furans. The mean breast milk concentration of DDT and indicator PCBs in Hong Kong mothers was 2.68 and 0.04 μg g^{-1} lipid wt, respectively, and that of dioxin-like PCBs and dioxins/furans was 4.67 and 8.25 pg TEQ g^{-1} lipid wt, respectively. No information on the level of POPs contamination in the blood/serum of local residents was available.

A WHO study was conducted to compare the level of POPs contamination in breast milk of lactating mothers from different countries/regions worldwide (Malisch and van Leeuwen, 2002, 2004). Figure 7.4 summarizes the study results. The level of DDT contamination in breast milk of Hong Kong mothers ranked the highest among 16 countries/regions which participated in the study. In contrast, the contamination level of indicator PCBs, dioxin-like PCBs and dioxins/furans in breast milk of Hong Kong mothers was the 8th, 10th and 13th lowest, respectively, among the 26 participating countries/regions.

7.7. Ecological risk assessment

7.7.1. Approach and methodology

The ecological risk assessment was conducted in accordance with the USEPA guidance document "*Guidelines for Ecological Risk Assessment* (USEPA, 1998)". A four-step assessment process was adopted: problem formulation, exposure characterization, characterization of ecological effects and risk evaluation.

The receptors of interest included pelagic organisms, benthic organisms and marine mammals (dolphins/porpoises). For the pelagic and benthic organisms, ecological risk assessment was conducted at the population level. For the dolphins and porpoises, risk assessment was conducted at the organism level.

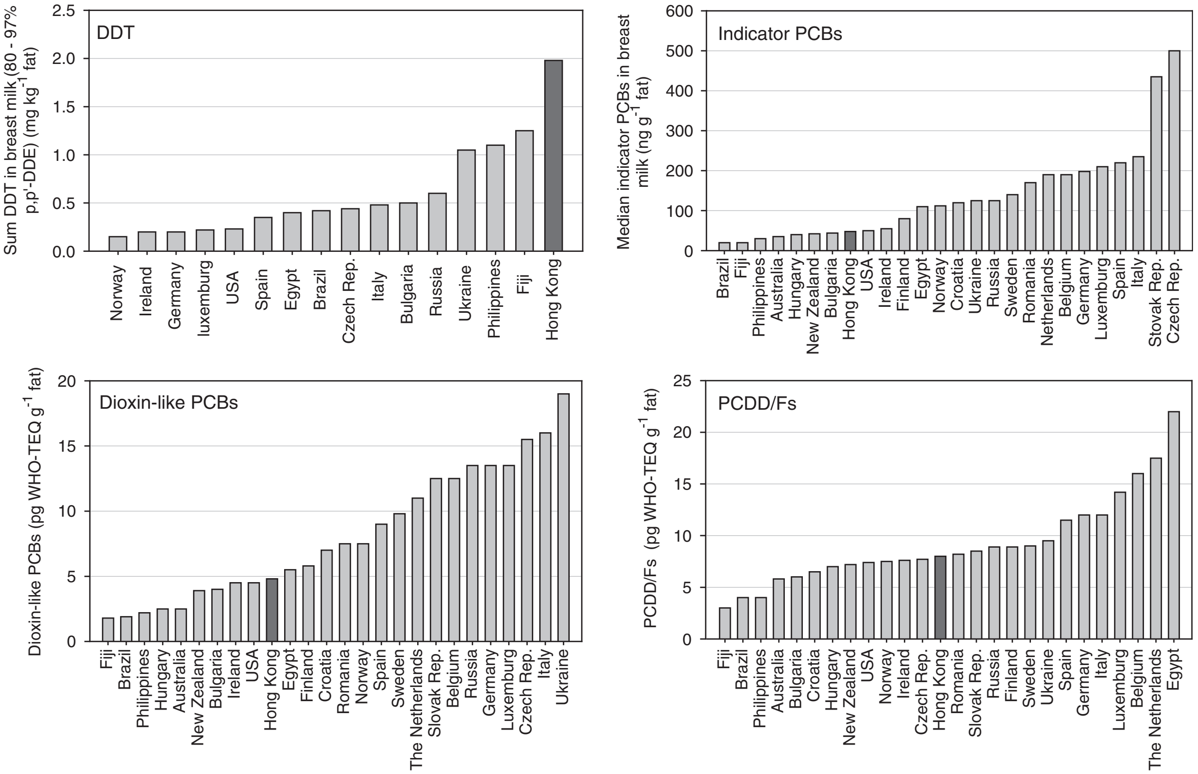

Figure 7.4. Comparison of the level of POPs contamination in breast milk of lactating mothers in Hong Kong and other countries (from Malisch and van Leeuwen, 2004).

7.7.1.1. Pelagic organisms risk assessment

A two-tiered approach was adopted for the population level ecological risk assessment for pelagic organisms. The Tier 1 assessment process involved calculation of a simple deterministic Hazard quotient (HQ) of individual POPs. The HQ was defined as the ratio of mean POPs concentration in the local marine water to its chronic toxicity value. Relevant existing water quality guidelines/criteria established by regulatory authorities, including the United States Environmental Protection Agency (USEPA) (USEPA, 2002), the Australian and New Zealand Environmental and Conservation Council (ANZECC) (ANZECC, 2000) and the Canadian Council of Ministers of the Environment (CCME) (CCME, 1999), were used as chronic toxicity values. For the POPs that did not have appropriate existing guideline/criteria values available, conservative chronic toxicity values were estimated by using an ''acute-to-chronic'' ratio of 50.

POPs with a calculated HQ less than unity were judged to be unlikely to pose ecological risk of toxicological concern to the local pelagic organisms and therefore were not considered further in the Tier 2 risk assessment. POPs with a HQ greater than unity were identified as chemicals of potential toxicological concern and were subject to further, in-depth Tier 2 Probabilistic Risk Assessment (PRA) using the procedures described by Solomon and Takacs (2002).

Tier 2 PRA process involved developing environmental exposure data and chronic toxicity data distributions for individual POPs. The mean concentrations of POPs in local marine water measured at various locations were used as exposure data in the construction of the exposure distribution. The chronic toxicity data distribution was established based on published international acute toxicity data (LC_{50}, EC_{50}) on a variety of aquatic organisms tested in many jurisdictions, drawn primarily from the USEPA ECOTOX database (2002) (available at http://www.epa.gov/ecotox). If the upper 5th centile of the measured chemical exposure data distribution did not exceed the lower 5th centile of its estimated chronic toxicity distribution, the potential ecological risk posed by the chemical was judged to be tolerable (Hall and Giddings, 2000).

7.7.1.2. Benthic organisms risk assessment

The ecological risk to local benthic organisms from potential exposure to POPs through direct contact with marine sediment was also assessed. Direct contact with the contaminated sediment was the most significant pathway of exposure for benthic organisms. The use of chemical specific toxicity data on aquatic organisms as surrogate was in accordance with the Fugacity theory (Mackay, 1991) which predicts that benthic organisms would accumulate organic chemicals proportionally to the concentration of these chemicals in the sediment pore water.

A two-tiered approach similar to that for pelagic organisms was adopted for the population level ecological risk assessment for benthic organisms. In the Tier 1 assessment process, simple deterministic HQ of individual POPs were calculated by comparing mean concentrations of POPs in the local marine sediment to the range of published Screening Sediment Quality Criteria (SQC)/Guidelines by other regulatory authorities including the US National Oceanic and Atmospheric Administration (NOAA), Environment Canada, Ontario Ministry of Environment, Canada and ANZECC.

POPs with a calculated HQ less than unity were judged to be unlikely to pose ecological risk of toxicological concern to the local benthic organisms and therefore were not considered further in the Tier 2 risk assessment. POPs with a HQ greater than unity were identified as chemicals of potential toxicological concern and were subject to further, in-depth Tier 2 PRA using site-specific SQC, taking into account the local sediment properties (i.e., organic carbon content, partitioning coefficient for sediment organic carbon, etc.) (Long et al., 1995).

7.7.1.3. Marine mammals risk assessment

Contrary to that for the pelagic and benthic organisms, ecological risk assessment for the marine mammal (dolphins and porpoises) evaluated the potential adverse health effects of exposure to POPs in the marine environment at the organism level. Two species of local cetaceans, the Indo-Pacific hump-backed dolphins (*S. chinensis*) and the finless porpoises (*N. phocaenoides*), had been studied (Jefferson et al., 2002; Imanishi et al., 2004). Ecological risk assessment of POPs was conducted following an individual-based methodology analogous to the human health risk assessment process and using chronic toxicity values derived from terrestrial mammalian studies as surrogates.

Consumption of fish and shellfish was identified as the significant pathway for potential exposure of dolphins/porpoises to the POPs. Little information existed on the feeding habits of local dolphins/porpoises in Hong Kong waters. Based on the limited data available (Parsons, 1997; Jefferson, 2001), it was assumed that the dolphin diet consisted of 90% fish and 10% shellfish (mainly crustaceans and cephalopods), while the ratio of fish and shellfish in the porpoises diet was 50:50. Dietary exposure to individual POPs was calculated based on the concentration of POPs measured in local marine biota (i.e., the local marine fish and shellfish data), assuming a typical dolphin weight of 225 kg and porpoise weight of 55 kg, and adopting a conservatively estimated consumption rate of 0.065 and 0.075 kg food kg^{-1} bw d^{-1} for the dolphins and porpoises, respectively (Montgomery Watson, 1998; Parsons, 1998). Exposure to POPs from water ingestion was not accounted for in the absence of corresponding water sampling data, but contribution from this exposure pathway was expected to be relatively insignificant.

The simple deterministic HQ of individual POPs were calculated by comparing the estimated dietary exposure to the adopted surrogate chronic toxicity values published by other national authorities and international organizations (USDoE, 1996; USEPA Integrated Risk Information System (IRIS) database (available at http://www.epa.gov/iris); US Agency for Toxic Substances and Disease Registry (ATSDR) database ToxFAQs$^{\text{TM}}$ (available at http://www.atsdr.cdc.gov/toxfaq.html); WHO, 1998). POPs with a calculated HQ less than unity were judged to be unlikely to pose ecological risk of toxicological concern to the local dolphins/porpoises residing in the Hong Kong waters. POPs with a calculated HQ greater than unity would suggest that the current exposure level of local cetaceans to the POPs concerned might be of toxicological relevance and warranted further, in-depth investigation.

7.7.2. Assessment results

7.7.2.1. Pelagic organisms risk assessment

The calculated HQs for POPs, except DDT, were all below unity, indicating that there was no unacceptable risk of toxicological significance associated with exposure of local pelagic organisms to these POPs (Table 7.15). DDT was subject to further evaluation by the in-depth Tier 2 PRA. The results of the PRA, as illustrated by Fig. 7.5, indicated that the lower 5th centile of the estimated chronic DDT toxicity distribution was not exceeded by the upper 5th centile of aquatic DDT exposure distribution, suggesting the potential ecological risk posed by exposure of local pelagic organisms to DDT was within a tolerable range.

7.7.2.2. Benthic organisms risk assessment

The calculated HQs for all POPs in the marine sediment, against the range of published SQC/Guidelines, were <1 (Table 7.16). The mean contamination level of POPs in the marine sediment of Hong Kong generally fell at the lower end of the range of screening concentrations

Table 7.15. Tier 1 ecological risk assessment of POPs to pelagic organisms in Hong Kong in 2000–2004

Chemical	Mean concentration in Hong Kong's marine water (ng L^{-1})	Conservative screening chronic toxicity value	Hazard quotient[g]
Aldrin	<10	21.3[d]	<1
Chlordane	<10	88.0[d]	<1
DDT	<15	1.4[d]	>1
Dieldrin	<10	22.0[d]	<1
Endrin	<10	44.0[d]	<1
Heptachlor	<10	68.0[d]	<1
HCB	<10	600[d]	<1
Mirex	<10	400[e]	<1
Toxaphene	<10	43.2[d]	<1
PCBs	<100	7800[d]	<1
Dioxins/furans[a]	0.55[b], 5.21[c]	10[f]	<1

[a] Unit of dioxins/furans = pg I-TEQ L^{-1}; 2,3,7,8-TCDD $<$DL in all 104 samples.

[b] The value was calculated assuming zero for individual congener level $<$DL.

[c] The value was calculated assuming 0.5 DL for individual congener level $<$DL.

[d] The value represents LC_{50} divided by 50; LC_{50} = lethal concentration that kills 50% of the organisms under a specified time duration.

[e] Value from ANZECC—Australian and New Zealand Guidelines for Marine Water Quality 2000.

[f] Value from Human Health and Ecological Risk Assessment Work Plan (USEPA, 2004) and from Development of Aquatic Quality Standards for Dioxins (Final Report to the Department for Environment, Food and Rural Affairs, UK, 2003).

[g] Hazard quotient = ratio of mean concentration in marine water to screening chronic toxicity value.

published in the SQC/Guidelines of the US, Canada and Australia/New Zealand. The results indicated that there would be unlikely to be any risk of toxicological significance associated with exposure of local benthic organisms to the current level of POPs in the marine sediment.

7.7.2.3. Marine mammals risk assessment

Results of the ecological risk assessment of POPs in the marine environment to local cetaceans (the hump-backed dolphins and the finless porpoises) showed the HQs for eight POPs studied (chlordane, DDT, dieldrin, heptachlor, HCB, toxaphene, PCBs and dioxins/furans) were all less than unity, suggesting that there was no unacceptable risk of toxicological significance associated with exposure of local cetaceans to the current contamination level of these POPs in the marine environment (Table 7.17).

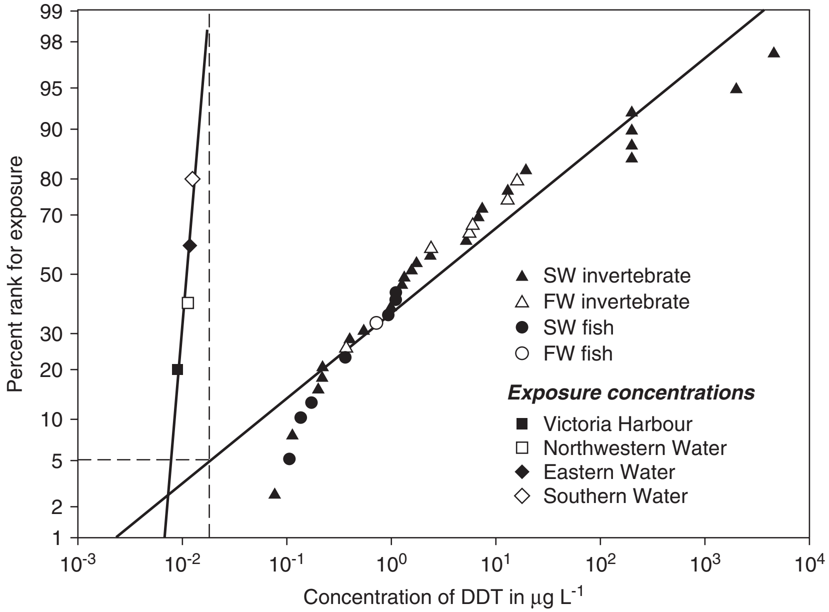

Figure 7.5. Tier 2 probabilistic risk assessment on pelagic organisms exposed to DDT.

7.8. Human health risk assessment

7.8.1. Approach and methodology

The human health risk assessment was conducted based on exposure estimates from two most relevant exposure pathways, namely dietary intake of POPs from food consumption and inhalation intake of airborne POPs contaminants. The potential intake of POPs from drinking water (considered to be a relatively minor exposure pathway) was not taken into account due to lack of relevant local data necessary for their estimation.

7.8.1.1. Human non-carcinogenic risk assessment

The potential for non-carcinogenic health effects associated with exposure of local residents to POPs in locally consumed food items and the ambient air was evaluated by calculating the relevant HQ for individual POPs. The HQ was defined as the ratio of the estimated lifetime average daily dose (LADD) of POPs from dietary (Table 7.6) and inhalation

Table 7.16. Tire 1 ecological risk assessment of POPs to benthic organisms in Hong Kong in 2000–2004

Chemical	Mean concentration in Hong Kong's marine sediment (μg kg^{-1} dw)[b]	Screening sediment quality criteria	Reference
Aldrin	4.70	9.5	NOAA, SQuiRTs^{TM}, AET[c]
		2–80	Ontario Guideline, Low to severe[d]
Chlordane	4.20	4.50–8.87	Canadian Sediment Quality Guideline, ISQG to PEL[e]
		0.5–6	NOAA, SQuiRTs^{TM}, ERL to ERM[c]
		0.5–6	ANZECC ISQG, Low to high[f]
		7–60	Ontario Guideline, Low to severe[d]
DDT	6.81	1.58–46.1	NOAA, SQuiRTs^{TM}, ERL to ERM[c]
		1.58–46.1	ANZECC ISQG, Low to high[f]
		7–120	Ontario Guideline, Low to severe[d]
		6.15–20.03	Canadian Sediment Quality Guideline, ISQG to PEL[e]
		20.4	Sediment Quality Criteria[g]
Dieldrin	5.19	0.02–8	NOAA, SQuiRTs^{TM}, ERL to ERM[c]
		0.02–8	ANZECC ISQG, Low to high[f]
		2.85–6.67	Canadian Sediment Quality Guideline, ISQG to PEL[e]
		2–910	Ontario Guideline, Low to severe[d]
		76.6	Sediment Quality Criteria[g]
Endrin	3.86	2.67–62.4	Canadian Sediment Quality Guideline, ISQG to PEL[e]
		0.02–8	ANZECC ISQG, Low to high[f]
		3–1300	Ontario Guideline, Low to severe[d]
Heptachlor	4.48	298	Sediment Quality Criteria[g]
HCB	5.98	6	NOAA, SQuiRTs^{TM}, AET[c]
		380	Washington State Sediment Criteria[h]
Mirex	<10.0	7–1300	Ontario Guideline, Low to severe[d]
		96.0	Sediment Quality Criteria[g]
Toxaphene	<10.0	0.1	Canadian Sediment Quality Guideline, ISQG[e]
		43.2	Sediment Quality Criteria[g]
PCBs	24.1	22.7–180	NOAA, SQuiRTs^{TM}, ERL to ERM[c]
		21.5–189	Canadian Sediment Quality Guideline, ISQG to PEL[e]
		70–5300	Ontario Guideline, Low to severe[d]
		237	Sediment Quality Criteria[g]

Table 7.16. (*Continued*)

Chemical	Mean concentration in Hong Kong's marine sediment ($\mu g\ kg^{-1}$ dw)[b]	Screening sediment quality criteria	Reference
Dioxins/furans[a]	9.10	0.85–21.5	Canadian Sediment Quality Guideline, ISQG to PEL[e]
		16.6	Sediment Quality Criteria[g]

[a] Unit for dioxins/furans = ng I-TEQ kg^{-1} dw.

[b] The average organic carbon content in Hong Kong marine sediments is approximately 0.8% (2004 data); 1% is assumed for ease of calculation and comparison in this table.

[c] US National Oceanic and Atmospheric Administration (NOAA) Sediment Guidelines, Screening Quick Reference Table for Organics (SQuiRT^{TM}), 1999; AET = Apparent Effects Threshold; ERL = Effect Range Low; ERM = Effect Range Medium.

[d] Ontario Ministry of Environment Screening Level Guideline (normalized to 1% organic carbon), 1993; a low level is the lowest concentration that toxic effects become apparent; a severe level represents concentrations that could effectively eliminate most of the benthic organisms.

[e] Canadian Sediment Quality Guideline for Protection of Aquatic Life, 2002; ISQG = Interim Sediment Quality Guideline; PEL = Probable Effect Level.

[f] ANZECC recommended interim sediment quality guideline (ISQG) (normalized to 1% organic carbon), 2000; the ISQG low and high values correspond to the ERL and ERM used in the NOAA listing.

[g] Sediment quality criteria adopted in EPD's consultancy study "A Study of Toxic Substances Pollution in Hong Kong, Agreement No. CE 22/99 (Environmental)"; unit for dioxins/furans = ng I-TEQ kg^{-1}.

[h] Washington State Sediment Quality Chemical Criteria, WAC 173-204-320 (a).

Table 7.17. Ecological risk assessment of POPs to cetaceans in Hong Kong in 2001–2002

Chemical	Overall exposure dose [a] ($\mu g\ kg^{-1}$ bw d^{-1})		Adopted toxicity value ($\mu g\ kg^{-1}$ bw d^{-1})	Hazard quotient (exposure dose/ toxicity value)	
	Dolphin	Porpoise		Dolphin	Porpoise
Chlordane	1.21×10^{-1}	8.55×10^{-2}	1.88×10^{1}	<1	<1
DDT	6.68×10^{-1}	4.71×10^{-1}	1.00×10^{2}	<1	<1
Dieldrin	1.26×10^{-2}	1.06×10^{-2}	6.25×10^{-1}	<1	<1
Heptachlor	1.60×10^{-2}	1.14×10^{-2}	1.25×10^{0}	<1	<1
HCB	3.07×10^{-2}	2.30×10^{-2}	1.00×10^{1}	<1	<1
Toxaphene	7.56×10^{-2}	5.51×10^{-2}	4.38×10^{1}	<1	<1
PCBs	7.12×10^{-1}	5.88×10^{-1}	6.25×10^{0}	<1	<1
Dioxins/furans	2.28×10^{-5}	2.66×10^{-5}	1.25×10^{-4}	<1	<1

[a] Exposure dose = estimated chemical intake from local marine fish and shellfish consumption; data extracted from EPD's consultancy study "A Study of Toxic Substances Pollution in Hong Kong, Agreement No. CE 22/99".

(Table 7.4) pathways to the reference dose (RfD) (USEPA) or tolerable daily intake (TDI) (WHO). Exposure levels below the RfD or TDI (i.e., HQs < 1) would be considered unlikely to elicit adverse health effects.

7.8.1.2. Human carcinogenic risk assessment

The potential for carcinogenic health effects associated with exposure of local residents to POPs, being known/probable/possible human carcinogens, was evaluated by the total excess lifetime cancer risk of exposure to individual POPs in the ambient air (inhalation cancer risk) and in locally consumed food items (dietary cancer risk). The excess lifetime inhalation cancer risk of POPs was estimated based on the measured concentration of POPs in the ambient air (for 2000–2004) and using unit risk factors published by USEPA (USEPA IRIS database). The excess lifetime dietary cancer risk of POPs was calculated by multiplying the LADD of chemical exposure from consumption of local food items by its carcinogenic slope factor (USEPA IRIS database). Since the carcinogenic slope factor often represented an upper 95th centile confidence limit of the probability of response based on experimental animal data in a multistage model, the calculated excess lifetime cancer risk would generally be an upper-bound estimate, i.e., the actual excess risk was likely be lowered. Excess lifetime cancer risk of a POPs chemical in the range of 1×10^{-4}–1×10^{-6}, commonly considered acceptable for regulatory purposes in protecting human health in various USEPA programmes, was adopted as the limit of acceptable carcinogenic risk of toxicological concern associated with a lifetime exposure to the chemical.

7.8.1.3. Health risk assessment of POPs in the local marine environment

The health risk to local residents associated specifically with exposure to POPs contamination in the local marine environment was assessed by (a) comparing the levels of POPs contamination in marine fish and shellfish sampled in the local waters with relevant Food Safety Standards/Action Levels; and (b) evaluating the non-carcinogenic and carcinogenic risks of individual POPs intake via consumption of locally caught seafood and incidental ingestion of seawater during recreational activities.

The potential for non-carcinogenic risk associated specifically with exposure to POPs contamination in the local marine environment was evaluated by calculating the HQ which was defined as the ratio of the LADD from consumption of locally-caught seafood (marine fish and shellfish) and incidental ingestion of marine water (during recreational activities) to the RfD (USEPA) or TDI (WHO) appropriately apportioned for exposure attributed to locally caught seafood only (taking into full account background exposure due to local consumption of all other non-seafood food items). Exposure levels below the apportioned RfD or TDI (i.e., $HQ < 1$) would be considered unlikely to elicit any adverse systemic health effects.

The potential for carcinogenic risk associated specifically with exposure to POPs contamination in the local marine environment was evaluated by the excess lifetime cancer risk calculated by multiplying the LADD of individual POPs exposure from consumption of locally caught seafood (marine fish and shellfish) and incidental ingestion of marine water (during recreational activities) by its carcinogenic slope factor (USEPA IRIS database). Excess lifetime cancer risk of a POPs chemical in the range of 1×10^{-4}–1×10^{-6} was adopted as the limit of acceptable carcinogenic risk of toxicological concern.

7.8.2. Assessment results

7.8.2.1. Human non-carcinogenic risk assessment

Results of assessment of non-carcinogenic risk associated with exposure of local residents to POPs in the locally consumed food items and the ambient air are presented in Table 7.18. The calculated HQs of all 12 POPs under the Stockholm Convention were well below unity, indicating that there was no unacceptable non-carcinogenic risk of toxicological significance associated with a lifetime exposure of local residents to the current levels of POPs contamination in locally consumed food items and the ambient air. The estimated level of exposure of local residents to dioxins/furans (0.93 pg TEQ kg^{-1} bw d^{-1}, assuming negligible intake via the drinking water route) fell at the lower end of the range (1–4 pg TEQ kg^{-1} bw d^{-1}) of TDI of dioxins/furans set by WHO (1998). Dietary exposure was the major route, accounting for 98.2% of total exposure to dioxins/furans, while inhalation exposure accounted for only 1.8%. The finding was in good agreement with internationally reported data.

7.8.2.2. Human carcinogenic risk assessment

Results of assessment of dietary and inhalation carcinogenic risks associated with exposure of local residents to POPs in the locally consumed food items and the ambient air are presented in Table 7.19. The calculated dietary or inhalation or total excess lifetime cancer risks of POPs all fell at the lower end of the 1×10^{-4}–1×10^{-6} range, indicating there was no unacceptable dietary or inhalation or total cancer risk of toxicological

Table 7.18. Non-carcinogenic risk assessment of POPs to the residents of Hong Kong in 2003

Chemical	Daily intake (mg kg^{-1} bw d^{-1})			Reference dose (RfD)/tolerable daily intake (TDI) (mg kg^{-1} bw d^{-1})[d]	Hazard quotient (total daily intake/RfD or TDI)
	Dietary[b]	Inhalation[c]	Total		
Aldrin	0	0	0	3.00×10^{-5}	<1
Chlordane	0	–	0	5.00×10^{-4}	<1
DDT	2.93×10^{-5}	1.44×10^{-8}	2.93×10^{-5}	5.00×10^{-4}	<1
Dieldrin	0	0	0	5.00×10^{-5}	<1
Endrin	0	0	0	3.00×10^{-4}	<1
Heptachlor	0	8.64×10^{-9}	8.64×10^{-9}	5.00×10^{-4}	<1
HCB	1.10×10^{-6}	4.61×10^{-8}	1.15×10^{-6}	8.00×10^{-4}	<1
Mirex	0	–	0	2.00×10^{-4}	<1
Toxaphene	–	–	–	–	–
PCBs	8.31×10^{-6}	1.38×10^{-7}	8.45×10^{-6}	2.00×10^{-5}	<1
Dioxins/furans[a]	0.91	0.02	0.93	1–4	<1

[a] Unit for daily intake of dioxins/furans = pg TEQ kg^{-1} bw d^{-1}.

[b] Dietary intake estimated by adopting the oriental food consumption pattern published in WHO GEMS 2003.

[c] Assuming a respiratory rate of 20 min^{-1} and a tidal volume of 600 ml, for an average adult of 60 kg bw.

[d] Data from USEPA Integrated Risk Information System (IRIS) database, except for dioxins/furans (TDI from WHO 1998).

concern associated with a lifetime exposure of local residents to the current levels of POPs contamination in the locally consumed foods and the ambient air.

7.8.2.3. Health risk assessment of POPs in the local marine environment

In the absence of Food Safety Standards on POPs specific to Hong Kong, the level of POPs contamination in marine fish and shellfish sampled in the local waters was examined against Food Safety Standards/Action Levels published by other regulatory authorities (Table 7.20). The level of POPs contamination in marine fish and shellfish from Hong Kong waters was well below (by 1–2 orders of magnitude) the Food Safety Standards/Action Levels set by the US, Mainland China and/or the European Community.

Furthermore, the estimated level of exposure of local residents to all 12 POPs under the Stockholm Convention was found to be well below

Table 7.19. Carcinogenic risk assessment of POPs to the residents of Hong Kong in 2003

Chemical	USEPA Cancer Classification[a]	Dietary			Inhalation			Total Excess Lifetime Cancer Risk	Acceptable Range of Excess Lifetime Cancer Risk (USEPA)
		Daily Intake† (mg kg^{-1} bw d^{-1})	Slope Factor[c]	Excess Lifetime Cancer Risk	Daily Intake‡ (mg kg^{-1} bw d^{-1})	Unit risk[c]	Excess Lifetime Cancer Risk		
Aldrin	B2	0	1.70×10^{1}	0	0	4.90×10^{-3}	0	0	1×10^{-4}–1×10^{-6}
Chlordane	B2	0	3.50×10^{-1}	0	–	3.70×10^{-4}	–	0	1×10^{-4}–1×10^{-6}
DDT	B2	2.93×10^{-5}	3.40×10^{-1}	9.96×10^{-6}	1.44×10^{-8}	9.70×10^{-5}	4.9×10^{-9}	9.97×10^{-6}	1×10^{-4}–1×10^{-6}
Dieldrin	B2	0	1.60×10^{1}	0	0	4.60×10^{-3}	0	0	1×10^{-4}–1×10^{-6}
Endrin	D	0	–	–	0	–	–	–	–
Heptachlor	B2	0	4.50×10^{0}	0	8.64×10^{-9}	1.30×10^{-3}	3.90×10^{-8}	3.90×10^{-8}	1×10^{-4}–1×10^{-6}
Hexachlorobenzene	B2	1.10×10^{-6}	1.60×10^{0}	1.76×10^{-8}	4.61×10^{-8}	4.60×10^{-4}	7.40×10^{-8}	9.16×10^{-8}	1×10^{-4}–1×10^{-6}
Mirex	2B[b]	0	–	–	–	–	–	–	–
Toxaphene	B2	–	1.10×10^{0}	–	–	3.20×10^{-4}	–	–	–
PCBs	B2	8.31×10^{-6}	4.00×10^{-1}	3.32×10^{-9}	1.38×10^{-7}	9.30×10^{-5}	4.50×10^{-8}	4.83×10^{-8}	1×10^{-4}–1×10^{-6}
Dioxins/furans*	B2	9.11×10^{-10}	1.00×10^{5}	9.11×10^{-5}	1.73×10^{-11}	3.30×10^{1}	2.00×10^{-6}	9.33×10^{-5}	1×10^{-4}–1×10^{-6}

*Unit for daily intake of dioxins/furans = mg TEQ kg^{-1} bw d^{-1}.

†Dietary intake estimated by adopting the oriental food consumption pattern published in WHO GEMS 2003.

‡Assuming a respiratory rate of 20 min^{-1} and a tidal volume of 600 ml, for an average adult of 60 kg bw.

[a] USEPA Weight-of-Evidence Cancer Classification System (B2 = probable human carcinogen; D = not classifiable).

[b] International Agency for Research on Cancer (IARC) Cancer Classification (2B = possible human carcinogen).

[c] USEPA Integrated Risk Information System (IRIS) database.

Table 7.20. Comparison of the level of POPs contamination in marine fish and shellfish sampled in Hong Kong waters (2000–2004)

Chemical	Mean concentration (μg kg^{-1} ww)		Food safety standards/action levels
	Marine fish	Marine shellfish	
Aldrin	28.9	10.9	300 (USFDA[b])
Chlordane	3.8	1.12	300 (USFDA[b])
DDT	27.6	7.73	5000 (USFDA[b]) 1000 (PRC[c])
Dieldrin	2.18	0.21	300 (USFDA[b])
Endrin	28.1	5.86	
Heptachlor	25.3	5.99	300 (USFDA[b])
HCB	5.80	0.80	
Mirex	0	0	100 (USFDA[b])
Toxaphene	1.33	0	
PCBs	22.6	13.8	2000 (USFDA[b])
		0	200 (PRC[c])
Dioxins/furans[a]	0.33	0.53	4 (EC[d])

[a] Unit for dioxins/furans = pg I-TEQ g^{-1} ww.

[b] USFDA Chemical Contaminant and Pesticide Action Levels, and Guidance Levels; unit = μg kg^{-1} ww.

[c] PRC Seafood Standard; unit = μg kg^{-1} ww.

[d] European Community Seafood Standard for fish and fish products; unit = pg WHO-TEQ g^{-1} ww.

the apportioned RfD or TDI and all calculated HQs were below unity (Table 7.21). The results indicated that there was no unacceptable non-carcinogenic risk of toxicological concern associated specifically with a lifetime exposure of local residents to the current level of POPs contamination in the local marine environment via dietary intake of locally caught seafood (marine fish and shellfish) and incidental ingestion of seawater during recreational activities, taking into full account background dietary exposure to POPs from consumption of all other local, non-seafood food items.

Results of assessment of carcinogenic risks associated with exposure of local residents to POPs contamination in the local marine environment are presented in Table 7.22. The calculated cancer risks of POPs all fell well within the 1×10^{-4}–1×10^{-6} range, indicating there was no unacceptable cancer risk of toxicological concern associated specifically with a lifetime exposure of local residents to the current level of POPs contamination in the local marine environment via dietary intake of locally caught seafood (marine fish and shellfish) and incidental ingestion of seawater during recreational activities.

Table 7.21. Human non-carcinogenic risk assessment of POPs pollution in the marine environment of Hong Kong in 2000–2004

Chemical	Background exposure[a] (mg kg^{-1} bw day^{-1})	Lifetime average daily exposure[b] (mg kg^{-1} bw day^{-1})	RfD[c] or TDI[c] (mg kg^{-1} bw day^{-1})	Hazard quotient (LADD/RfD[c] or TDI[c])
Aldrin	0	5.78×10^{-6}	3.00×10^{-5}	<1
Chlordane	0	8.01×10^{-7}	5.00×10^{-4}	<1
DDT	7.85×10^{-6}	5.80×10^{-6}	2.12×10^{-4}	<1
Dieldrin	0	4.44×10^{-7}	5.00×10^{-5}	<1
Endrin	0	5.83×10^{-6}	3.00×10^{-4}	<1
Heptachlor	0	5.28×10^{-6}	5.00×10^{-4}	<1
HCB	1.11×10^{-6}	1.19×10^{-6}	4.14×10^{-4}	<1
Mirex	0	0.00×10^{0}	2.00×10^{-4}	<1
Toxaphene	–	2.66×10^{-7}	–	–
PCBs	0	5.03×10^{-6}	2.00×10^{-5}	<1
Dioxins/furans (mg TEQ kg^{-1} w day^{-1})	3.3×10^{-10}	8.92×10^{-11}	$(2.13\text{–}8.51) \times 10^{-10}$	<1

[a] Background exposure = exposure attributed to consumption of all non-seafood food items calculated based on estimates of daily dietary exposure (Table 7.12).

[b] Lifetime average daily exposure = exposure attributed to consumption of locally caught fish and shellfish (Table 7.8) and incidental ingestion of seawater during recreational activities (Table 7.4).

[c] RfD or TDI apportioned for seafood only, taking into account background contribution from all non-seafood food items.

7.9. Assessment of current POPs situation in Hong Kong

Overall, the current level of POPs contamination was found to pose no unacceptable risk of potential toxicological concern to the local environment or human health. Key assessment findings are summarized below:

1. None of the nine intentional POPs pesticides (i.e., aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, HCB, mirex and toxaphene) were registered pesticides for use in Hong Kong. The 2004 data in the inventory indicated that there was only a very small quantity of PCBs in PCB-containing equipment in local use/stockpile compared with those reported for other industrialized areas around the world. Indeed, results of an initial questionnaire survey conducted by the EPD in early 2005 suggested that there was little current trading, domestic production and/or use of any of these Convention POPs chemicals in Hong Kong.

Table 7.22. Human carcinogenic risk assessment of POPs pollution in the marine environment of Hong Kong in 2000–2004

Chemical	USEPA Cancer Classification[b]	LADD (total, mg kg^{-1} bw d^{-1})[d]	Slope factor[e]	Excess lifetime cancer risk	Acceptable range of excess lifetime cancer risk (USEPA)
Aldrin	B2	5.78×10^{-6}	1.70×10^{1}	9.83×10^{-5}	1×10^{-4}–1×10^{-6}
Chlordane	B2	8.01×10^{-7}	3.50×10^{-1}	2.80×10^{-7}	1×10^{-4}–1×10^{-6}
DDT	B2	5.80×10^{-6}	3.40×10^{-1}	1.97×10^{-6}	1×10^{-4}–1×10^{-6}
Dieldrin	B2	4.44×10^{-7}	1.60×10^{1}	7.10×10^{-6}	1×10^{-4}–1×10^{-6}
Endrin	D	5.83×10^{-6}	–	–	
Heptachlor	B2	5.28×10^{-6}	4.50×10^{0}	2.38×10^{-5}	1×10^{-4}–1×10^{-6}
Hexachlorobenzene	B2	1.19×10^{-6}	1.60×10^{0}	1.90×10^{-6}	1×10^{-4}–1×10^{-6}
Mirex	2B[c]	0.00×10^{-0}	–	–	
Toxaphene	B2	2.66×10^{-7}	1.10×10^{0}	2.93×10^{-7}	1×10^{-4}–1×10^{-6}
PCBs	B2	5.03×10^{-6}	4.00×10^{-1}	2.01×10^{-6}	1×10^{-4}–1×10^{-6}
Dioxins/furans[a]	B2	8.92×10^{-11}	1.00×10^{5}	8.92×10^{-6}	1×10^{-4}–1×10^{-6}

[a] Unit for dioxins/furans = mg TEQ kg^{-1} bw d^{-1}.

[b] USEPA Weight-of-Evidence Cancer Classification System (B2 = probable human carcinogen; D = not classifiable).

[c] International Agency for Research on Cancer (IARC) Cancer Classification (2B- possible human carcinogen).

[d] Lifetime average daily exposure = exposure attributed to consumption of locally caught fish and shellfish (Table 7.8) and incidental ingestion of seawater during recreational activities (Table 7.4).

[e] USEPA Integrated Risk Information System (IRIS) database.

2. On a "per capita" basis, the current (2003) annual dioxin/furan release in Hong Kong was generally similar to those in Asian regions, Canada, the US and Australia, and was the 2nd lowest in air emission.
3. The level of POPs contamination in the local environment (ambient air, marine water, marine sediment, marine fish and shellfish) was generally comparable to the range reported in most urban locations in Asia Pacific, Europe, the US and Australia.
4. Assessment based on best available data indicated that overall, there was unlikely to be any unacceptable ecological risk of toxicological significance associated with exposure of local marine life to the current level of POPs contamination in the marine environment of Hong Kong.
5. The daily exposure of local residents to DDT, heptachlor, HCB and PCBs was well below (by 1–5 orders of magnitude) the RfD set by USEPA. The estimated total exposure (inhalation and dietary) to dioxins/furans was 0.93 pg TEQ kg^{-1} bw d^{-1}, falling at the lower end of the TDI of 1–4 pg TEQ kg^{-1} bw d^{-1} set by the WHO (1998). Dietary intake was the major route, accounting for 98.2% of total exposure to dioxins/furans.
6. Results of human health risk assessment indicated that there was no unacceptable inhalation nor dietary chronic/carcinogenic risk of toxicological concern associated with a lifetime exposure of Hong Kong residents to the current level of POPs contamination in the local environment and locally consumed foods.
7. The level of POPs contamination in the marine fish and shellfish from Hong Kong waters was found to be well below (by 1–2 orders of magnitude) the Food Safety Standards/Action Levels set by Mainland China, the US and/or the European Community.

7.10. POPs management and implementation strategy in Hong Kong under the Stockholm Convention

The HKSARIP for the Stockholm Convention has identified legislative and inventory data gaps, as well as action items in order for the HKSAR to fully comply with the Convention. On strengthening the institutional and regulatory systems, we need to develop an integrated and transparent legislative framework to effectively control, minimize and prevent the potentially harmful impact of POPs on human health and the environment. On the data gaps identified in the local emission sources, environmental levels, dietary exposure and human body burden of POPs, we need to put in place structured and comprehensive monitoring and auditing to validate and refine the POPs inventory. On measures to reduce production and release of unintentional POPs, i.e., dioxins/furans, we have been and shall continue pursuing the various reduction measures as part of the HKSAR Government's environmental portfolio in accordance with the established timetable. These measures address emission of dioxins/furans to air and to the aquatic environment as well as integrated environmental waste management. We should uphold the principle of environmental sustainability in pursuing community development and endeavour to apply Best Available Techniques (BAT) and Best Environmental Practices (BEP) to achieve the goal of further reducing and, where feasible, ultimately eliminating POPs from our environment.

Raising public awareness of the POPs-related issues and encouraging public participation are also important elements of the Stockholm Convention. On the public awareness campaign, the HKSAR Government has launched, as a priority action item of the HKSARIP, a dedicated EPD thematic website on POPs (available at http://www.epd.gov.hk/epd/english/international_conventions/pops/pops_main.html) and integrated the topic into the overall environmental protection education programme.

Hong Kong is geographically located at the Pearl River Estuary. Sound and effective environmental management of POPs has a regional dimension to encompass the PRD Region as a whole. On capacity building and strengthening regional collaboration with the PRD, we need to enhance technical information exchange and data sharing, involving not only the state and regional authorities, but also the academia at large. Harmonization of monitoring protocol and risk assessment methodology underpins the successful planning of future joint regional POPs monitoring and inventory development.

7.11. Conclusions

This chapter focuses on the 12 most toxic POPs subject to control of the Stockholm Convention. It is recognized that there are other POPs which have been demonstrated to elicit adverse effects of toxicological significance on human health and the environment, for which international agreement has yet to be reached on their inclusion in the Convention list. Indeed, five new POPs candidates (hexabromobiphenyl (6-PBB), pentabromodiphenyl ether (PBDE), perfluorooctane sulfonate (PFOS), chlordecone and lindane) were proposed and considered at the First Meeting of the POPs Review Committee of the Stockholm Convention in November 2005 (UNEP, 2005). The challenge is for the local scientific community and regulatory authorities to keep abreast of development in the international POPs arena and join force on the local/regional/global fronts in combating the POPs problem and working towards a POPs free environment for our future generations.

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Chapter 8

Persistent Organic Pollutants in Waterbirds with Special Reference to Hong Kong and Mainland China

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Abstract

Persistent organic pollutants (POPs) have been widely used as pesticides and/or industrial chemicals. Because most POPs are persistent, toxic and bioaccumulative, the United Nations Environment Programme (UNEP) has implemented an approach to reduce/eliminate these substances. A set of 12 POPs have been targeted for global restriction of production/use under Stockholm Convention. The 12 POPs are: aldrin, endrin, dieldrin, dichlorodiphenyltrichoroethanes, polychlorinated biphenyls, polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, chlordane, toxaphene, heptachlor, hexachlorobenzene, and mirex. Predatory waterbirds are susceptible to bioaccumulation of POPs through the ingestion of contaminated food sources. They are long-lived and top trophic-level animals in the food web, consequently they are able to integrate pollutant levels over a broad area by bioaccumulation. Thus, they can serve as useful bioindicators for environmental monitoring. This report reviews the relevant literature on the environmental levels and biological effects of the 12 priority POPs, listed under the Stockholm Convention, to waterbirds. Particular attention will be given to the pollution status of POPs in Hong Kong, their threats to waterbirds.

8.1. Background

Hong Kong, located at the mouth of the Pearl River in south China, receives persistent toxic contaminants into marine habitats from a variety of sources including shipping activity, wastewater, industrial wastes and agricultural runoff. Long-term, and often indiscriminate discharges of such contaminants as petroleum hydrocarbons, polycyclic aromatic hydrocarbons, and organochlorine pesticides have compromised water

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and sediment quality, with potentially detrimental implications for environmental integrity, and human and wildlife health. The rapid development of industrial and urban areas in the hinterland of the Pearl River Delta is also an increasingly important source of contaminants to Hong Kong, especially via riverine and aerial inputs. The main purpose of this report is to provide a comprehensive review of the relevant literature to collate and analyze information and data on the environmental levels and biological effects of 12 specific persistent organic pollutants (POPs), listed under the Stockholm Convention, to waterbirds. Particular attention will be given to the pollution status of POPs in Hong Kong, their threats to waterbirds.

Since the Second World War the manufacture and use of organic and inorganic chemicals have increased in both agricultural and industrial areas, and many of these chemicals are released into the environment. There is a considerable concern amongst governments, scientists and nongovernmental organizations over the adverse effects on the environment, wildlife and humans from exposure to chemicals, such as organochlorines. These chemicals are persistent and accumulate along food chains and are often found in natural environments (Barrett et al., 1985). The long life span and the potential for long-range transport of certain chemicals require government intervention to control such chemicals.

It has been widely reported that the decline of bird populations is associated with an increase in the use of organochlorine pesticides, such as DDTs, for insect control in urban and agricultural environments (Blus et al., 1979; Cade et al., 1971; Peakall, 1974). It is also known that some chemicals, in particular organochlorines, interfere with the functioning of reproductive, endocrine, immune, and nervous systems (Yamashita et al., 1993; Jiménez, 1997).

In 1997, the United Nations Environment Programme (UNEP) Governing Council decided that immediate international action should be taken to protect human health and the environment. International negotiations to reduce and eliminate the emission and discharges of an initial set of 12 POPs were initiated at the Stockholm Convention on POPs in May 2001. The 12 substances that were addressed at the Stockholm Convention were: aldrin, endrin, dieldrin, dichlorodiphenyltrichoroethanes (DDTs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), chlordane, toxaphene, heptachlor, hexachlorobenzene (HCB) and mirex. Basic information and status of major organochlorine pesticides in China are summarized in Table 8.1.

Waterbirds are valuable and useful for environmental monitoring. They are particularly susceptible to environmental contaminants because they live long and are top trophic-level animals in the food web.

Table 8.1. Basic information and status of organochlorine pesticides in China

Organochlorine pesticides	CAS no.	Start of use	Ban of use	Total production	Specific exemption	Ban of use in Hong Kong	References
Aldrin	309–00–2	Not used	1983	–	–	1988	Wong et al. (2005) and the references therein
Dieldrin	60–57–1	Not used	1983	–	–	1988	Same as above
Endrin	72–20–8	Not used	–	–	–	Not registered	Same as above
Chlordane	57–74–9	1945	1999	–	Termite control: 95% for structures of houses, 1% for dams and the rest for cable boxes.	1991	
DDT	50–29–3	–	1983	0.27 million tons (1951–1983)	–	1988	Li et al. (2001)
Heptachlor	76–44–8	1948	1982	–	–	Not registered	Wong et al. (2005) and the references therein
HCB	118–74–1	1945	–	–	–	Not registered	Same as above
Mirex	2385–85–5	1958	–	–	20–30% of mirex for termite control in structures of houses, dams and underground cable boxes.	1997	Same as above
Toxaphene	8001–35–2	1948	1982	–	–	1984	Same as above

Consequently, they are able to integrate pollutant levels over a broad area by bioaccumulation (Furness, 1993). A bird egg, unlike a mammalian fetus, is an isolated and independent metabolic system. In addition, persistent, bioaccumulative and lipophilic pollutants (e.g. PCBs, polychlorinated dibenzodioxins and furans) are known to biomagnify in the egg yolk and result in concentrations of orders of magnitude higher than the ambient concentrations in the diet of the female bird (Kleinow et al., 1999). The contaminant levels in waterbird eggs, therefore, provide important and useful information for monitoring changes in environmental quality.

Although there are many peer-reviewed publications about organochlorine pesticides, PCBs and PCDDs/PCDFs, on or in water, sediments and mussels, information about these compounds on or in waterbirds in China is limited. In the present review, most of the data that were presented from China were from limited peer-reviewed publications (Connell et al., 2003; De Luca-Abbott et al., 2001; Dong et al., 2004; Nakata et al., 2005; Wan et al., 2006). Furthermore, it should be noted that the concentrations of various POPs reported were measured in different tissues of separate species, and expressed in different units. Thus, caution should be taken when the information is used or interpreted.

8.1.1. Hexachlorobenzene (HCB)

HCB is an organochlorine product. It was first introduced in 1933 as a fungicide for seed treatment of onion, sorghum and crops, such as wheat, barley, oats and rye, and was used to make fireworks, ammunition and synthetic rubber (Barber et al., 2005; UNEP Chemicals, 2002). It is currently speculated that HCB originates in the environment as a by-product or is the result of impurity in the production of certain chlorinated pesticides, particularly lower chlorinated benzenes and industrial chemicals; the manufacture and application of HCB-contaminated pesticides; and the combustion of waste (Barber et al., 2005; UNEP, 2003; Voldner & Smith, 1989).

The peak of HCB production was between the late 1970s and the early 1980s worldwide (Barber et al., 2005). HCB was introduced in China in 1945, but it was not used as a pesticide (Wong et al., 2005). Rather, it was used as an intermediary in the production of other chlorinated substances, such as sodium-pentachlorophenol (Na-PCP). No information is available on HCB levels in seabirds in China.

Predatory birds, such as cormorants, eagles and guillemots have been used as biomonitoring tools. In the Arctic, the cold annual temperatures and the cold condensation at the higher latitudes may facilitate the deposition and accumulation of HCB (Wania & Mackay, 1993). This hypothesis was further supported by Braune et al. (2001) that the concentration of HCB was higher, for example, in thick-billed murre eggs at higher latitudes. Rocque & Winker (2004) provided evidence for the long-range transport of HCB in cormorants on the Aleutian Islands. The level of HCB declined from west to east in the North Pacific, which suggested that the distribution patterns of HCB might be attributed to industries in Asia, from where it had been transported.

In Antarctica, several studies have reported the concentration of HCB in the eggs of penguins (Corsolini et al., 2002, 2006). A recent study that was conducted by Corsolini and co-workers reported a relatively high concentration of HCB in penguin eggs (Corsolini et al., 2006). However, it was lower than those of the European Arctic and Canadian Arctic seabirds (Table 8.2) (Borgå et al., 2001). The HCB concentration that was found in migratory birds has provided more information about the HCB contamination of their overwintering grounds, though the real situation may be more complex (Muir et al., 1999). Very high concentrations of HCB (up to 10,700 ng g^{-1} dry wt.) were found in birds (e.g. the shoveler) that wintered in China, whereas much lower mean concentrations (10 ng g^{-1} dry wt.) were found in resident birds (e.g. the mallard and the Slavonian grebe). This suggested that significant sources of HCB existed in China (Lebedev et al., 1998). The concentrations of HCB in resident birds collected in the Philippines, India, Vietnam, South India and Japan were compared (Table 8.2) (Kunisue et al., 2003; Minh et al., 2002; Tanabe et al., 1998). Japan had the greatest concentrations of HCB, whereas the Philippines had the lowest concentrations.

In Alaska, HCB concentrations remained relatively stable in Bogoslof and St. George common murre eggs from 1973 to 1976, whereas concentrations of other organochlorines declined (Vander Pol et al., 2004). This phenomenon reflected the continuous production of HCB as a by-product in the manufacture of some industrial chemicals and incineration of waste (Vander Pol et al., 2004). In the Great Lakes, the levels of HCB in the eggs of herring gulls declined significantly by over 90% between 1974 and 2001 (Barber et al., 2005). The reductions of HCB by 70, 90 and 98%, respectively, were observed in the St. Lawrence, Niagara and Detroit Rivers (Barber et al., 2005). The levels of HCB in the bird eggs of black-legged kittiwakes and thick-billed murres in the Canadian Arctic decreased by 64% and 55%, respectively, between 1975 and 1998 (Braune et al., 2001). In the Barents Sea north of Norway, the levels of HCB in the eggs of herring gulls decreased by 37% between 1983 and 1993 (Barrett et al., 1985, 1996). The HCB levels decreased slowly in black guillemots in Iceland

Table 8.2. Hexachlorobenzene (HCB) concentrations in bird samples from different countries

Location	Species	Year	*n*	Tissue	Concentration (ng g^{-1} lipid wt. corrected)	References
Ross Sea, Antarctica	Adelie penguin (*Pygoscelis adeliae*)	1995–1996	6	Egg	197	Corsolini et al. (2006)
Edmonson Point, Antarctica		1996	5	Egg	< 100	Corsolini et al. (2002)
Canadian Arctic	Black-legged kittiwake (*Rissa tridactyla*)	1993–1998	30	Egg	281	Braune et al. (2001)
	Northern fulmur (*Fulmarus glacialis*)	1993–1998	30	Egg	363	
	Thick-billed murre (*Uria lomvia*)	1993–1998	30	Egg	389	
European Arctic	Black guillemot (*Cephyus grylle*)	1995	10	Liver	340	Borgå et al. (2001)
	Brunnich's guillemot (*U. lomvia*)	1995	10	Liver	580	
	Black-legged kittiwake (*R. tridactyla*)	1995	11	Liver	870	
	Glaucous gull (*Larus hyperboreus*)	1995	15	Liver	4100	
Philippines	Painted snipe (*Rostratula benghalensis*)	1994	6	Whole body	1.7	Kunisue et al. (2003)
	Chinese little bittern (*Ixobrychus sinesis*)	1994	3	Whole body	3.0	
	Schrenck's little bittern (*Ixobrychus eurhythmus*)	1994	2	Whole body	4.4	
	Green backed heron (*Butrides striatus*)	1994	3	Whole body	4.9	
India	House crow (*Corvus splendens*)	1995	2	Whole body	4.2	Tanabe et al. (1998)
	Little egret (*Egretta garzetta*)	1995	1	Whole body	10	
	Pond heron (*Ardeola grayii*)	1995	2	Whole body	8.3	
	White-breasted kingfisher (*Halcyon smymensis*)	1995	1	Whole body	3	

	Black-winged stilt (*Himantopus himantopus*)	1995	1	Whole body	13	
	Kentish plover (*Charadrius alexandrinus*)	1995	5	Whole body	8.5	
	Little ringed plover (*Charadris dubius*)	1995	5	Whole body	5.5	
	Kentish plover (*C. alexandrinus*)	1998	2	Whole body	3.3	Kunisue et al. (2003)
Vietnam	Black-capped kingfisher (*Halcyon pileata*)	1997	2	Whole body	26	Minh et al. (2002)
	Common kingfisher (*Alcedo atthis*)	1997	7	Whole body	28	
	White-throated kingfisher (*Halcyon smyrnensis*)	1997	1	Whole body	11	
Vietnam	Common moorhen (*Gallinula chloropus*)	1997	1	Whole body	110	Minh et al. (2002)
	Cinnamon bittern (*Ixobrychus cinnamomeus*)	1997	1	Whole body	25	
	White-breasted waterhen (*Amaurornis phoenicurus*)	1997	3	Whole body	6.9	
Japan						
Shinobazu pond	Common cormorant (*Phalacrocorax carbo*)	1993	8	Liver	4300	Guruge et al. (1997)
Lake Biwa	Common cormorant (*P. carbo*)	1993	9	Liver	360	
Japan	Golden eagle (*Aquila chrysaetos*)	1993–1995	3	Breast muscle	220	Kunisue et al. (2003)
Japan	Golden eagle (*A. chrysaetos*)	1996–1998	8	Liver	1200	
Hokkaido	White-tailed sea-eagle (*Haliaeetus albicilla*)	1997	2	Liver	200	
Hokkaido	White-tailed sea-eagle (*H. albicilla*)	1998	1	Breast muscle	220	

between 1976 and 1996, with a half-time of 16.1 years (Ólafsdóttir et al., 2005).

8.1.2. Heptachlor and chlordane

8.1.2.1. Heptachlor

Heptachlor was isolated from technical chlordane in 1946 and was introduced as an insecticide in the United States in 1952 (USEPA, 1986a; WHO, 1984a). Technical-grade heptachlor contains ~70% heptachlor and 30% related compounds that include 20% chlordane (WHO, 1995). It is a nonsystemic stomach and contact insecticide, which is primarily used against soil insects and termites (WHO, 1984a). It has also been used against cotton insects, grasshoppers, crop pests and to combat malaria (Smith, 1991; WHO, 1995). Heptachlor epoxide is an oxidation product of heptachlor and chlordane (WHO, 1995). The toxicities of heptachlor and heptachlor epoxide are similar and they bioaccumulate in the fat of organisms.

It is difficult to determine the actual amount of heptachlor that is used; however, the total use of heptachlor in the United States was estimated to be 16,000 tons between 1971 and 1976 (Fendick et al., 1990). Due to the adverse effects of heptachlor, most commercial, agricultural and domestic uses of heptachlor in the United States were phased out between 1974 and 1988, and all uses of heptachlor products were banned by the United States Environmental Protection Agency (USEPA) in 1988 (USEPA, 1990a). The only current use of heptachlor is in the treatment of fire ants in power plants (ATSDR, 2005). Heptachlor was used in 1948 in China and it was banned in 1982 (Wong et al., 2005).

In the 1970s, heptachlor was extensively used, and caused serious problems in wild birds. The applications of granular heptachlor in Georgia and heptachlor in Mississippi caused the long-term decline in the population of northern bobwhite quail (*Colinus virinanus*) and a short-term abrupt decline in the population of several passerines (Ferguson, 1964; Rosene, 1965). Several wild bird populations, including Canada geese and American kestrels in the Columbia Basin in the United States, declined due to heptachlor (Blus et al., 1984; Henny et al., 1983). Heptachlor epoxide residues that were found in the brains of dead Canada geese at the Umatilla National Wildlife Refuge in Oregon in 1978 and 1979 were equal to or exceeded the lethal hazard zone level (8–9 μg g^{-1} wet wt.). Moreover, the residues that were found in eggs were greater than 10 μg g^{-1} wet wt., which was related to low nest success (Blus et al., 1984). The source of exposure was thought to be heptachlor treated seeds that were consumed by the geese. After a substitution of lindane with heptachlor, the reproductive success of geese increased and adult mortality decreased. The nesting population increased from 102 pairs in 1979 to 170 pairs in 1983 (Blus et al., 1984). The reproductive success of American kestrels in the same area decreased (Henny et al., 1983). Heptachlor epoxide residues that were found in the eggs were greater than 1.5 μg g^{-1} wet wt. and such concentrations were associated with the reduced productivity. As kestrels were not seed eaters, heptachlor epoxide bioaccumulates along the food chain through eating geese (Blus et al., 1984). Dong et al. (2004) reported that the heptachlor and heptachlor epoxide levels of heron eggs from Lake Tai in China were up to 126 ng g^{-1} dry wt. but the occurrence of these compounds was low.

8.1.2.2. Chlordane

Chlordane is a mixture of at least 120 compounds and technical chlordane typically contains 64–67% chlorine (Dearth & Hites, 1991a,b; WHO, 1995). Of these 120 compounds, 60–75% are chlordane isomers (*cis*- and *trans*-) and the remainder is related to endo-compounds that include heptachlor, nonachlor, diels-alder adduct of cyclopentadiene and penta/hexa/octachlorocyclopentadienes (UNEP Chemicals, 2002). Heptachlor contributes up to 10% of technical chlordane and it is also a pesticide formulation.

Chlordane was introduced as an insecticide in 1945 and was the first cyclodiene insecticide that was used in agriculture (Eisler, 1990). It was the second most important organochlorine pesticide after toxaphene from 1976 to 1977 (Stansley & Roscoe, 1999). It has been used on agricultural crops and extensively in the control of termites (Smith, 1991). Chlordane and heptachlor can be metabolized into two persistent (oxygenated) epoxides—oxychlordane and heptachlor epoxide—in mammals (Nomeir & Hajjar, 1987) such that the two compounds are always measured together with chlordane and heptachlor.

The production of chlordane was reduced from ~3.5 to 4.0 million pounds in 1986 to 100,000 to 1 million pounds in 1991 (ATSDR, 1994a). More than 63 million kg of chlordane were produced and used in the United States, mostly after 1960 before sales and its use were suspended in 1988 (Dearth & Hites, 1991a,b). Restrictions were imposed on the use of chlordane in 1979 because of its potential human carcinogenicity. After this time chlordane was used mainly for underground termite control and in building construction (Dearth & Hites, 1991a,b). In Japan, chlordane was only permitted for the control of termites and powder post beetles (Miyazaki et al., 1980). USEPA cancelled its registration for commercial production, delivery, sale, and use in 1988 (USEPA, 1988). The use of chlordane was introduced in China in 1945 but it was banned in 1999 (Wong et al., 2005). With special exemption, it is still produced in China and is used locally for termite control—95% for structures of houses, 1% for dams and the remainder for cable boxes.

The first chlordane-related mortality was of three wild birds and was recorded between 1978 and 1981 (Blus et al., 1983). The levels of chlordanes and heptachlor epoxide from the two adult male red-shouldered hawks (*Buteo lineatus*) and an adult female great horned owl (*Bubo virginianus*) were within the critical lethal range that has been defined by experimental studies (heptachlor epoxide in brain tissue: 3.4–8.3 $\mu g\ g^{-1}$ wet wt.; oxychlordane in brain tissue: 1.1–5.0 $\mu g\ g^{-1}$ wet wt.). The chlordane poisoning of birds has been reported in several studies in the United States (Blus et al., 1983, 1985; Post, 1951; Stansley & Roscoe, 1999). From 1986 to 1990, 122 cases of avian mortality due to chlordane and/or dieldrin were documented in New York, Maryland and New Jersey (Okoniewski & Novesky, 1993). High pesticide concentrations were found in cyclodiene-resistant insect populations. These pesticide-tainted insects, when eaten by birds, caused mortalities in the avian populations (Okoniewski & Novesky, 1993).

Comparisons of data are difficult as different studies have reported total chlordanes with different compositions (e.g. sum of oxychlordane, heptachlor epoxide, *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor, MC5 and MC7 vs. sum of oxychlordane, heptachlor epoxide, *trans*-nonachlor) and with different tissue samples. Attention should be paid to the definition of total chlordanes because it has different meanings. In the following paragraphs, the concentrations of the sum of chlordane and its metabolites, heptachlor and heptachlor epoxide, are both discussed. Oxychlordane, *trans*-nonachlor and *cis*-nonachlor contributed to the major components of total chlordane in bird samples (Table 8.3) (Fisk et al., 2001; Stansley & Roscoe, 1999). The levels of oxychlordane in the livers and eggs of the bird samples that were collected in the Canadian high Arctic between 1975 and 1976 were similar and lower, respectively, than those of the samples that were collected in the high Arctic of Northwater Polynya, in 1998 (Fisk et al., 2001). Another study showed that there was a significant decrease of total chlordanes (the sum of oxychlordane, heptachlor epoxide, *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor, and *cis*-nonachlor) in the eggs of black-legged kittiwakes from 1975 to 1998 (Braune et al., 2001). Total chlordanes (the sum of oxychlordane, trans-nonachlor and heptachlor epoxide) that were found in the livers of glaucous gulls that were collected in the southern Barents Sea in 1991 were similar to those that were found in

Table 8.3. Total chlordane concentrations in bird samples from different countries

	Location	Species	Year	*n*	Tissue	Concentration (ng g^{-1} lipid wt. corrected)	References
1975–1998	Canadian Arctic	Black-legged kittiwake (*Rissa tridactyla*)	1975	12	Egg	490	Braune et al. (2001)
			1976	6	Egg	1400	
			1993	15	Egg	390	
			1998	15	Egg	360	
1990s–now	Southern Barents Sea, Arctic	Black-legged kittiwake (*R. tridactyla*)	1991	19	Liver	780	Savinova et al. (1995)
		Black-legged kittiwake (*R. tridactyla*)	1998	10	Liver	660	Fisk et al. (2001)
	Northwater Polynya, Arctic	Glaucous gull (*Larus hyperboreus*)	1991	10	Liver	2300	Savinova et al. (1995)
	Southern Barents Sea, Arctic	Glaucous gull (*L. hyperboreus*)	1998	11	Liver	2200	Fisk et al. (2001)
	Ross Sea, Antarctica	Adelie penguin (*Pygoscelis adeliae*)	1995–1996	6	Egg	19	Corsolini et al. (2006)
	Canadian Arctic	Black-legged kittiwake (*R. tridactyla*)	1993–1998	30	Egg	370	Braune et al. (2001)
		Northern fulmur (*Fulmarus glacialis*)	1993–1998	30	Egg	660	
		Thick-billed murre (*Uria lomvia*)	1993–1998	30	Egg	220	
	Philippines	Green backed heron (*Butrides striatus*)	1994	3	Whole body	78 (44–110)	Kunisue et al. (2003)
	India	Long-billed Mongolian plover (*Chradrius mongolus*)	1995	6	Whole body	170	Tanabe et al. (1998)

Table 8.3. (*Continued*)

Location	Species	Year	*n*	Tissue	Concentration (ng g^{-1} lipid wt. corrected)	References
India	Little tern (*Sterna albifrons*)	1995	2	Whole body	27	Tanabe et al. (1998)
	Short-billed Mongolian plover (*Chradrius mongolus*)	1995	6	Whole body	29	
Lake Baikal, Russia	Grey heron (*Ardea cinerea*)	1996	2	Breast muscle	27	Kunisue et al. (2002)
Japan						
Shinobazu pond	Common cormorant (*Phalacrocorax carbo*)	1993	8	Liver	9600	Guruge et al. (1997)
Lake Biwa	Common cormorant (*P. carbo*)	1993	9	Liver	1300	
Japan	Golden eagle (*Aquila chrysaetos*)	1993–1995	3	Breast muscle	3300	Kunisue et al. (2003)
	Golden eagle (*A. chrysaetos*)	1996–1998	8	Liver	14,000	
Hokkaido	White-tailed sea-eagle (*Haliaeetus albicilla*)	1997	2	Liver	2700	
	White-tailed sea-eagle (*H. albicilla*)	1998	1	Breast muscle	3000	
Hong Kong	Little egret (*Egretta garetta*)	2000	9	Egg	4300 (1230–7100)	Connell et al. (2003)
	Black-crowned night heron (*Nycticorax nycticorax*)	2000	9	Egg	460 (77–1300)	

Northwater Polynya in 1998 (Fisk et al., 2001; Savinova et al., 1995). For the penguin eggs that were collected in Antarctica between 1995 and 1996, total chlordanes (sum of oxychlordane, *trans*-chlordane, *cis*-chlordane, and *trans*-nonachlor) were much lower than those of the bird eggs from the Arctic (Braune et al., 2001; Corsolini et al., 2006). The levels of chlordanes in resident bird tissue samples from the Philippines, India, Russia and Vietnam were similar, whereas those of Japan and Hong Kong had high levels of chlordanes (Table 8.3) (Connell et al., 2003; Guruge et al., 1997; Kunisue et al., 2002; Minh et al., 2002; Tanabe et al., 1998). In conclusion, Japan and Hong Kong had the highest concentrations and were followed by the Artic region, which was higher than that of the Philippines, India, Vietnam and Russia, while the Antarctic region had the lowest concentration.

8.1.3. Mirex

Mirex was first synthesized in 1946 but it was not introduced as a pesticide against hymenopterous insects, especially ants, until 1959 (Smith, 1991). Technical grade mirex consists of approximately 95% mirex and less than 2.5% chlordecone, mostly kepone (Eisler, 1985). Mirex is a stomach insecticide with little contact activity. The main use of mirex was against the imported fire ants in the south-eastern United States (WHO, 1984b). It has also been used to control leaf cutters in South America, harvester termites in South Africa, Western harvester ants in the United States, the pineapple mealy bug in Hawaii and it was proposed to have been used against yellow jacket wasps in the United States (WHO, 1995). Under the trade name of Dechlorane, mirex was used as a fire retardant in electronic components, fabrics, rubber, plastics and electrical goods (Eisler, 1985; WHO, 1995).

The total sales of mirex by Hooker Chemicals and Plastics Corporation, in the United States between 1959 and 1975, were around 1,528,000 kg (Kaiser, 1978). Among the total sales of mirex, 26% was for insecticidal use and 76% was for other uses, such as the incorporation of mirex into plastics to improve flame- and fire-retardant properties (Kaiser, 1978). Between 1961 and 1975, ~400,000 kg of mirex were used as pesticides, of which approximately 250,000 kg were sold in the south eastern United States for the control of native and imported fire ants (*Solenopsis* spp.) and most of the remainder was exported to Brazil for use in fire ant control (Eisler, 1985).

The concern about mirex became of international importance after its discovery in fish from Lake Ontario (Kaiser, 1978). The mirex contamination in fish from the Bay of Quinte, approximately 50 km upstream from the mouth of this “tributary” to Lake Ontario and the nearest producer and processor of the compound, Hooker Chemicals and Plastics Corporation, was located in New York State on the Niagara River, approximately 250 km from the site of the observed fish contamination. This raised the question of whether these findings were due to local contamination or of widespread occurrence (Kaiser, 1978). A herring gull egg was destroyed after pipping the eggshell, and deformation of the beak of a Lake Ontario bird’s chick due to mirex was observed (Kaiser, 1978). Photomirex (8-monhydromirex) was formed during degradation and was found in herring gull eggs (Hallett et al., 1976). This derivative has similar chemical and physical properties, and also similar biological potency to mirex (Hallett et al., 1976). In 1978, the United States Environmental Protection Agency banned all uses of mirex as a pesticide (USEPA, 2001). Mirex has been used in China since 1958 and it is still produced and used locally for termite control (Wong et al., 2005).

Limited data are available on mirex worldwide except in the United States. The levels of mirex found in birds that were collected in the United States, except of those from the southeastern United States and the Great Lakes, were low and were considered nonhazardous in the 1970s (Cain & Bunck, 1983). White (1979) investigated the wings of mallards and American black ducks (*Anas rubripes*) that were collected from four major flight pathways between 1976 and 1977 (Eisler, 1985 and the references therein). The results showed that Atlantic mallards had the highest detection frequencies of occurrence at 50% and the highest concentration of mirex (0.14 $\mu g\ g^{-1}$ wet wt.). They were followed by Mississippi mallards at 29% and 0.03 $\mu g\ g^{-1}$ wet wt., Central mallards at 14% and 0.06 $\mu g\ g^{-1}$ wet wt., and Pacific mallards at 4% and 0.03 $\mu g\ g^{-1}$ wet wt. (Eisler, 1985).

Between 1972 and 1973, Ohlendorf and co-workers measured the levels of mirex and other organochlorine compounds in eggs of anhingas (*Anhinga anhinga*), herons, egrets, bitterns, ibises and storks in various locations throughout the eastern United States (Eisler, 1985). The highest mean mirex concentration of 0.74 $\mu g\ g^{-1}$ wet wt. that ranged from 0.19 to 2.5 $\mu g\ g^{-1}$ wet wt., was found in the eggs of green herons (*Butorides striatus*) from the Savannah National Wildlife Refuge in South Carolina and in a single egg of the cattle egret (*Bubulcus ibis*) with a mirex level of 2.9 $\mu g\ g^{-1}$ wet wt. However, the Great Lakes region had the highest overall frequency of mirex occurrence (24%) in eggs among the study areas: the south Atlantic coastal region (15.6%), inland areas (10.7%), the Gulf Coast (4.4%) and the North Atlantic region (3.2%) (Eisler, 1985).

Mirex residues were detected in migratory birds that were collected from various locations and included areas that were far from known sources or applications of mirex (Eisler, 1985). For example, 22% of the eggs from 19 species of Alaskan seabirds that were collected between 1973 and 1976 contained mirex. The highest concentration was 0.044 μg g^{-1} wet wt. in eggs of a fork-tailed storm petrel (*Oceanodroma furcata*) from the Barren Islands. Mirex residues were low compared with those of other organochlorine compounds. The eggs from clapper rails (*Rallus longirostris*) that were collected in New Jersey from 1972 to 1974 contained 0.16 to 0.45 μg g^{-1} wet wt. of mirex (Klaas et al., 1980). The eggs of greater black-backed gulls (*Larus marinus*) that were collected from Appledore Island, in Maine, in 1977 contained up to 0.26 μg g^{-1} wet wt., but no mirex was detected in the eggs of common eiders (*Somateria mollissima*) or herring gulls from the same area. The greater black-backed gull is an active carnivore and the higher mirex levels in black-backed gulls might be attributed to its predatory feeding habits on small birds and mammals (Szaro et al., 1979). The eggs of pigeon hawks (*Falco columbarius*) and peregrine falcons (*Falco peregrinus*) had very high concentrations of mirex (0.25 μg g^{-1} wet wt. and 0.43 μg g^{-1} wet wt., respectively) in the higher latitudes of the Arctic (eastern and northern Canada). These two species feed on migratory birds or may migrate to mirex-affected areas (Kaiser, 1978).

Mirex was also found in the eggs of cormorants (*Phalacrocorax* sp.) from the Bay of Fundy on the Atlantic coast of Canada. The residue levels from 1975 (0.113 μg g^{-1} wet wt.) were double that of earlier levels from 1973 (0.058 μg g^{-1} wet wt.) and 1974 (0.059 μg g^{-1} wet wt.) (Kaiser, 1978). The source of contamination was suspected to be the southern wintering range in Florida and the Gulf of Mexico (Kaiser, 1978).

Few studies were available to evaluate the temporal change of mirex in bird samples. The only studies of mirex in seabird eggs were conducted by Braune et al. (2001) on the temporal trends from 1975 to 1998 in the Canadian Arctic. A decreased trend of mirex levels was only observed in eggs of black-legged kittiwakes but not in northern fulmars and thick-billed murres. The levels of mirex that were measured in the eggs of the studied animals ranged from 0.003 to 0.013 μg g^{-1} wet wt. in 1998. There did not appear to be any consistent change in the proportions over the study period (Braune et al., 2001). No information is available on the level of mirex in waterbirds in China.

Bird et al. (1983) found that when captive American kestrels (*Falco sparverius*) were fed 8 mg kg^{-1} of mirex for 69 days, there was a decline in sperm concentration and a slight increase in semen volume. An overall net decrease of 70% in sperm number was observed. The investigators believed that lower semen quality in the breeding season, coupled with altered courtship, could reduce the fertility of eggs and the reproductive fitness of individuals (Bird et al., 1983). Studies showed that eggshells of mallards that were fed 100 mg kg^{-1} of mirex, thinned and duckling survival was reduced (Waters et al., 1977).

8.1.4. Aldrin and dieldrin

Dieldrin and aldrin were first synthesized in 1948 and they were commercially manufactured as pesticides in 1950 (WHO, 1989). Technical grade aldrin contains 90% 1,2,3,4,10,10-hexachloro-1,4,4α,5,8,8α-hexahydro-1,4-endo,exo-5,8-dimethanonaphthalene (HHDN). Technical-grade dieldrin contains 85% 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4α,5,6,7,8,8α-octahydro-1,4-endo,exo-5,8-dimethanonaphthalene (HEOD). Dieldrin can be synthesized from aldrin (WHO, 1989). As aldrin is readily metabolized into dieldrin by both plants and animals, aldrin residues are only found in trace amounts in plants and animals, if at all (WHO, 1989).

The peak period for the use of aldrin and dieldrin was between the late 1960s and the early 1970s throughout various parts of the world (WHO, 1989). The use pattern of aldrin and dieldrin are quite similar. They act as effective contact and stomach poisons for insects. They are used to control soil insects (e.g. grasshoppers and corn rootworm), and protect crops and wooden structures from termites (WHO, 1989). The production of aldrin and dieldrin has decreased since the early 1960s. In the United States, the peak use of aldrin from 19 million pounds in 1966 decreased to 10.5 million pounds in 1970 (USEPA, 1980). During this same period (1966–1970), annual dieldrin use dropped from 1 million to 670,000 pounds. These decreases were primarily due to increased insect resistance to the aldrin and dieldrin, and to the development and availability of more effective and environmentally friendly pesticides (USEPA, 1980).

The global production of aldrin and dieldrin decreased from 20,000 tons in 1971 to less than 2500 tons in 1984 (WHO, 1989). In 1972, USEPA discontinued all but three specific uses of these compounds for subsurface termite control, "dipping of nonfood plant roots and tops, and moth-proofing in manufacturing processes in closed systems" (USEPA, 2003). In China, aldrin and dieldrin were produced on a small scale for research purposes and were regarded as "not used" (Wong et al., 2005). They were banned in China in 1983.

Between 1963 and 1975, HEOD (dieldrin) accounted for ~50% and 39% of all recorded sparrow hawk and kestrel deaths, respectively, in Britain (Newton et al., 1992). There was a recovery of the populations in between 1987 and 1990 after a marked reduction in aldrin–dieldrin use (Newton et al., 1992). The decline of the bird populations was due to the fact that these chemicals were highly toxic and poisoned birds immediately, which increased the mortality above the natural level (Newton et al., 1992). During the period between 1967 and 1971, a total of 192 bird casualties were recorded along the Texas Gulf Coast. The main cause of the deaths was intoxication due to the intake of aldrin treated rice (WHO, 1989).

Several studies of aldrin and dieldrin on the effect of normal fertility and hatchability on chickens and pheasants have been conducted (WHO, 1995). Normal fertility and hatchability slightly decreased when the chickens were fed a 10 mg dieldrin kg^{-1} diet, whereas when pheasants were fed a 50 mg dieldrin kg^{-1} diet, it caused a significant effect on fertility and hatchability (WHO, 1995). Based on these findings, the WHO (1989) concluded that reproductive success was not consistently affected in the absence of maternal toxicity.

There are declining trends of dieldrin that have been measured from bird samples. Residue levels of dieldrin in unhatched bald eagle eggs that were collected from 1974 to 1980 along Lake Erie, decreased from 1.28 to 0.49 μg g^{-1} wet wt. as compared with those that were collected from 1989 to 1994 (ATSDR, 2002a). A similar decreasing trend was also observed of the eggs of murres at Bogoslof Island and St. George Island in Alaska between 1973 and 2000 (Table 8.4a) (Vander Pol et al., 2004). In another study of the Canadian Arctic, Braune's group found that there was a decreasing trend of dieldrin in black-legged kittiwakes but there was no decreasing trend in northern fulmurs and thick-billed murres in the same area (Braune et al., 2001).

The levels of dieldrin and aldrin are also studied in the United States, the Canadian Arctic, Greece and Alaska (Table 8.4a). The bird samples from New Jersey from 1996 to 1997 had the highest levels of dieldrin and aldrin (Stansley & Roscoe, 1999), whereas the Canadian Arctic had the lowest levels of dieldrin and aldrin (Braune et al., 2001). A recent study from Greece reported that the concentrations of dieldrin and aldrin from the liver samples of birds were much lower than that of the United States but were similar to those of the Arctic (Sakellarides et al., 2006). Dong et al. (2004) showed that the occurrence of aldrin and dieldrin in herons in China were low as compared with Italy (50–73%) (Table 8.4b) (Fasola et al., 1998) and dieldrin was absent in little egrets and cattle egrets. The authors suggested that aldrin and dieldrin are not used as frequently in China as in Europe.

8.1.5. Endrin

Endrin was introduced in the United States as an insecticide, rodenticide and avicide in 1951 (ATSDR, 1996a). It was also used as an

Table 8.4a. Dieldrin concentrations in bird samples from different countries

Location	Species	Year	*n*	Tissue	Concentration (ng g^{-1} wet wt.)	References
Bogoslof, Alaska	Murre (*Uria aalge*)	1973–1976	7	Egg	34	Vander Pol et al. (2004) and the references therein
St George, Alaska	Murre (*U. aalge*)	2000	9	Egg	2.3	Vander Pol et al. (2004)
Bogoslof, Alaska	Murre (*U. aalge*)	1973–1976	11	Egg	9	Vander Pol et al. (2004) and the references therein
St George, Alaska	Murre (*U. aalge*)	1999	11	Egg	4.2	Vander Pol et al. (2004)
Canadian Arctic	Black-legged kittiwake (*Rissa tridactyla*)	1975	12	Egg	14	Braune et al. (2001)
		1998	15	Egg	9	
	Northern fulmur (*Fulmarus glacialis*)	1975	15	Egg	13	
		1998	15	Egg	14	
	Thick-billed murre (*Uria lomvia*)	1975	9	Egg	14	
		1998	15	Egg	15	
New Jersey, USA	Red tailed hawk (*Buteo jamaicensis*)	1997	2	Brain	1600–3100	Stansley and Roscoe (1999)

	Cooper's hawk (*Accipiter cooperi*)	1996–1997	9	Brain	Up to 2600	
Greece	White stork (*Ciconia ciconia*)	2003	6	Liver	0.086	Sakellarides et al. (2006)
	Greater flamingo (*Phoenicopterus ruber*)	2003	2	Liver	3.9	
	Dalmatian pelican (*Pelecanus crispus*)	2003	1	Liver	28	
	Little bittern (*Ixobrychus minutus*)	2003	10	Liver	1.2	
	Bittern (*Botaurus stellaris*)	2003	1	Liver	7.1	
	Little egret (*Egretta garetta*)	2003	5	Liver	1.1	
Lake Tai, China	Black-crowned night heron (*Nycticorax nycticorax*)	2000	65	Egg	1.13	Dong et al. (2004)
	Little egret (*E. garetta*)	2000	36	Egg	n.d.[a]	
	Cattle egret (*Bubulus ibis*)	2000	13	Egg	n.d.	
	Chinese pond heron (*Ardeola bacchus*)	2000	17	Egg	0.072	

[a] n.d.: Not detected.

Table 8.4b. Percentage occurrence of aldrin, dieldrin and endrin in bird samples

Location	Species	Year	*n*	Tissue	Occurrence (%)			References
					Aldrin	Dieldrin	Endrin	
Lake Tai, China	Black-crowned night heron (*Nycticorax nyticorax*)	2000	65	Egg	4.6	22	9.2	Dong et al. (2004)
	Little egret (*Egretta garetta*)	2000	36	Egg	47	0	0	
	Cattle egret (*Bubulus ibis*)	2000	13	Egg	0	0	7.7	
	Chinese pond heron (*Ardeola bacchus*)	2000	17	Egg	24	35	12	
Northern Italy	Little egret (*E. garetta*)	1993–1994	22	Egg	73	50	27	Fasola et al. (1998)
	Black-crowned night heron (*N. nyticorax*)	1993–1994	7	Egg	100	100	29	
		1982–1983	20	Egg	55	15	30	

insecticide agent on bird perches. Although the chemical properties of endrin (*endo*, *endo* stereoisomer of dieldrin) are very similar to those of aldrin or dieldrin, it had never been used extensively for termite or other applications in urban areas (Blus et al., 1989). Endrin had been one of the major chemicals used for controlling voles (*Microtus* spp.) in orchards (Petrella et al., 1975). Endrin aldehyde and endrin ketone are the impurities or degradation products of endrin, and trace amounts of impurities, such as aldrin and dieldrin, could also be found (ATSDR, 1996a; USEPA, 1985).

Because of the environmental concern and the development of resistance in certain pests, the use of endrin was greatly reduced in the United States and elsewhere (USEPA, 1985). The total sale of endrin in the United States was estimated to be 2.3 million kg in 1962, whereas the total production of endrin was decreased to 450,000 kg in the United States in 1971 (ATSDR, 1996a). The extreme toxicity of endrin affected the nontarget populations of raptors, such as California quail and chukars, and migratory birds in Washington State fruit orchards, and was a major reason for its discontinuation as a pesticide agent (ATSDR, 1996a; Blus et al., 1989). All uses of endrin in the United States were voluntarily discontinued by the manufacturer in 1986, and its use as a toxicant on bird perches was also discontinued in 1991 (ATSDR, 1996a; USEPA, 1983).

There was a disastrous die-off of the transplanted pelicans in Louisiana in 1975 (Blus et al., 1979). Endrin was the major factor for the die-offs, as the residues in the brains of several pelicans were similar to those that were found in the brains of experimental birds that were dying from doses of endrin (Blus et al., 1989). Stickel and co-workers reported that all of the experimental passerines died between 2 and 9 days after they were fed with 10 $\mu g\ g^{-1}$ wet wt. of endrin and the endrin residues in the brains were found to be lethal ($\geqslant 0.8\ \mu g\ g^{-1}$ wet wt.) or in the danger zone (0.6–0.79 $\mu g\ g^{-1}$ wet wt.) of experimental birds. Fat and pectoral musculature was greatly reduced or absent in all birds or in some, respectively. Between 1979 and 1983, among the 194 birds that were found dead in or near Central Washington Orchards, 6 and 46 of them had 0.6–0.79 $\mu g\ g^{-1}$ wet wt. (danger zone) and greater than 0.8 $\mu g\ g^{-1}$ wet wt. (lethal) endrin residues, respectively, in the brains of the birds (Blus et al., 1989). The applications of endrin in the orchard garden attributed to these casualties. It was also suggested that endrin might have induced serious physiological problems and caused the mortalities from other factors, such as the effect of vehicles or other objects due to effects on vision, predation or disease. However, there was no evidence to demonstrate that endrin depressed reproductive success.

There are limited data available to understand the geographical distribution of endrin residues in bird. Goutner et al. (2001) reported that the levels of endrin residues in the eggs of Audouin's gulls in the north-eastern Mediterranean between 1997 and 1998 was much lower than those of the birds of Blus et al. (1989) between 1981 and 1983 (Table 8.55). In a more recent study that measured the level of endrin residues in the livers and muscles of birds in Greenland, however, the total drin (sum of dieldrin, aldrin and endrin) was given and it was difficult to obtain the level of endrin residues from Greenland biota (Vorkamp et al., 2004). Dong et al. (2004) measured the levels of endrin in herons from Lake Tai in China. The occurrence and levels of endrin in heron eggs were low compared with those of Italy (Fasola et al., 1998).

8.1.6. Toxaphene

Toxaphene has been in use since 1949. It is a complex mixture that consists of at least 670 chlorinated terpenes (Jansson & Wideqvist, 1983). It was used as a nonsystemic stomach and contact insecticide. As it is nontoxic to plants (except to cucurbius), it was used to control many insects that inhabited cotton, corn, fruit, vegetables and small grains, and to control the *Cussia obtusifola* soybean pest. Toxaphene solutions were usually mixed with other pesticides because it can help to solubilise other insecticides with lower water solubility (e.g. DDT, lindane, etc.) (ATSDR, 1996b).

During the early 1970s, toxaphene or mixtures of toxaphene with rotenone were applied in lakes and streams by game fish agencies as a piscicide to remove undesirable fish for sport fishing, however, it was found to cause damage to nontarget organisms (ATSDR, 1996b). The peak consumption of toxaphene occurred in 1972 after DDT was banned. The use of toxaphene declined in the United States drastically after 1975 and it was reported to be the most heavily used pesticide (ATSDR, 1996b). In 1974, ~20 million kg of toxaphene was used in the United States, whereas in 1980, the total use of toxaphene was estimated at around 8.5 million kg and 4.9 million kg in 1982 (WHO, 1984c). In 1990, all registered uses of toxaphene and its mixtures were discontinued in the United States (USEPA, 1990b). China began to use toxaphene in 1958 and the total production of toxaphene from 1964 to 1980 was estimated to be 24,000 tons (Wong et al., 2005). There is no current use and stockpiling of toxaphene after it was banned in 1987.

Generally, the levels of toxaphene and the frequency of occurrence in birds are low or nondetected as compared with other organochlorine

Table 8.5. Endrin concentrations in bird samples from different countries

Location	Species	Year	*n*	Tissue	Concentration (ng g^{-1} wet wt.)	References
Lake Tai, China	Black-crowned night heron (*Nycticorax nyticorax*)	2000	65	Egg	0.42	Dong et al. (2004)
	Little egret (*Egretta garetta*)	2000	36	Egg	n.d.[a]	
	Cattle egret (*Bubulus ibis*)	2000	13	Egg	0.075	
	Chinese pond heron (*Ardeola bacchus*)	2000	17	Egg	0.084	
Northern Italy	Little egret (*E. garetta*)	1993–1994	22	Egg	13	Fasola et al. (1998)
	Black-crowned night heron (*N. nyticorax*)	1993–1994	7	Egg	10	
	Black-crowned night heron (*N. nyticorax*)	1982–1983	20	Egg	110	
North-Eastern Mediterranean	Audouin's gull (*Larus audouinni*)	1997–1998	59	Egg	0.73 (up to 3.3)	Goutner et al. (2001)
Washington, USA	California quail (*Callipepla californica*)	1981–1982	17	Liver	220 (n.d.–5300)	Blus et al. (1989)
	Mallard (*Anas platyrhynchos*)	1981–1982	10	Liver	n.d.–20	
	Canada geese (*Branta canadensis*)	1982	3	Liver	250 (190–380)	

[a] n.d.: Not detected.

pesticides and those in fish (Eisler & Jacknow, 1985). However, there are some extensive reports on toxaphene occurrence. Fifty-five male wild turkeys (*Meleagris gallopavo*) that were collected during the hunting season in southern Illinois in 1974 had up to 0.9 μg g^{-1} wet wt. toxaphene (Eisler & Jacknow, 1985). Toxaphene poisoning was reported from the deaths of two birds in California (Pollock & Kilgore, 1978). The causes of the deaths were due to the results of the biomagnification of toxaphene through food consumption and the direct exposure of toxaphene during a spray for the control of grasshoppers. Bird carcasses contained 0.1–9.6 μg of toxaphene g^{-1} wet wt. 2–3 weeks after the spray. Fetotoxic effects were reported on ring-necked pheasants (Pollock & Kilgore, 1978). Reduced hatchability in eggs was recorded in this bird after it was fed 100 mg toxaphene kg^{-1}. Reduced growth and backbone impairment were observed when ducklings were fed 10 or 50 mg toxaphene kg^{-1} for 90 days (Mehrle et al., 1979).

There is limited information of the levels of toxaphene on avian species, particularly seabirds. From a study in the Baltic region, the level of toxaphenes of the breast muscles of guillemots from 1970 to 1981 did not show any temporal trend (Andersson et al., 1988). The level of toxaphene in another study from the same sampling areas showed that the levels of toxaphene in eggs of guillemot had decreased from 1976 to 1989 (Table 8.6) (Wideqvist et al., 1993). The authors suggested that the negative results of the previous study for a temporal trend might be due to the large variation in the accumulation of contaminants from different sex and age (Wideqvist et al., 1993).

With limited information, generally, the levels of toxaphene were lower in the Polar Regions as compared with those in the north Pacific (Table 8.6). The eggs of skuas (*Catharacta* sp.) and penguins (*Pygoscelis* sp.) that were collected from Antarctica between 1993 and 1994, and the livers of glaucous gulls that were collected from Bear Island and the Arctic of Norway between 1995 and 1999 all contained low levels of toxaphene (Herzke et al., 2003; Muir et al., 2002). In contrast, the eggs of blackfooted albatross that were collected between 1994 and 1995 contained higher toxaphene levels (Muir et al., 2002). Witte et al. (2000) reported a decreasing trend of toxaphene in eggs of common terns in Trischen, northern Germany between 1981 and 1997. In another study, although reduced levels of toxaphenes were observed in the livers of glaucous gulls from Bear Island, no significant decreasing trend was observed (Herzke et al., 2003). Limited materials, large differences in age, different migratory patterns and metabolic processes or choice of food items contributed to the large variation in toxaphene levels, which could have masked any decreasing trends. There is no information available for toxaphene on waterbirds in China.

Table 8.6. Toxaphene concentrations in bird samples from different countries

	Location	Species	Year	*n*	Tissue	Concentration (μg g^{-1} wet wt.)	References
1974–1989	Baltic	Guillemot (*Uria aalge*)	1974	10	Egg	68[a]	Wideqvist et al. (1993)
			1976	2	Egg	130[a]	
			1978	10	Egg	30[a]	
			1982	10	Egg	25[a]	
			1987	10	Egg	7.7[a]	
			1989	2	Egg	21[a]	
1980s–now	Bear Island, Arctic	Glaucous gull (*Larus hyperboreus*)	1995	3	Liver	<LOD-0.12	Herzke et al. (2003)
			1999	15	Liver	<LOD-0.054	
	Svalbard, Arctic	Glaucous gull (*L. hyperboreus*)	1995	4	Liver	<LOD-0.04	
		Skuas (*Catharacta* sp.)	1993–1994	10	Egg	0.025	Muir et al. (2002) and the references therein
		Penguin (*Pygoscelis* sp.)	1993–1994	10	Egg	0.0011	
	Midway Atoll, Pacific Ocean	Blackfooted albatross (*Diomedea nigripes*)	1994–1995	2	Egg	0.53	Muir et al. (2002)
	Trischen, northern Germany		1981	10	Egg	0.057	Witte et al. (2000)
			1989	10	Egg	0.023	
			1997	10	Egg	0.009	

[a] Concentrations reported on lipid weight basis.

8.1.7. DDT

DDT (1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane) was first synthesized by Othmar Zeidle in Germany in 1874. Its insecticidal properties were not discovered until 1939 by the Swiss chemist Paul Müller. It was widely used in the Second World War to protect the troops against malaria, typhus and other vector borne diseases (Smith, 1991). After the war, DDT was widely used on agricultural crops and in disease vector control (Van Metre et al., 1997).

Technical-grade DDT is a mixture that consists of *p,p′*-DDT (85%) as an active ingredient, *o,p′*-DDT (15%), and *o,o′*-DDT (trace amounts). It also contains DDE (1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene)/*p,p′*-DDE and DDD (1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane)/*p,p′*-DDD as impurities. DDT breaks down into DDE and DDD. The peak production and use of DDT was around 82 million kg in 1962 and at the time DDT was registered for use on 334 agricultural commodities (ATSDR, 2002b). Because of the growing concern about the adverse effects on the environment, especially on wild birds, its production declined abruptly at ~2000 tons in the early 1970s (ATSDR, 2002b). In 1973, all uses of DDT were discontinued in the United States except for emergency public health uses and special cases (ATSDR, 2002b). Before the ban of DDT, more than 80% of DDT was used for agricultural purposes mainly on cotton and followed by peanuts and soybean. *p,p′*-DDD was also used as an insecticide and *o,p′*-DDD is used medically in the treatment of cancer of the adrenal gland, while DDE has no commercial use (ATSDR, 2002b; WHO, 1995). DDT was widely used in China after it was introduced in the 1950s (Li et al., 1999). From 1951 to 1983, the production of DDT was estimated to be 0.27 million tons. Although DDT was banned in 1983, its production for export continues, as does that for dicofol production. DDT is present as an impurity in an acaricide (mitecide) known as Dicofol, which is currently being used widely in China. Dicofol may contain from 1.8% to 2.4% of DDT in the formulation sold in south China (Leung et al., 2005). In China, ~250 metric tons of DDT is currently used annually as an additive in the production of antifouling paint. It is estimated that the accumulative total of DDT used for this purpose since 1950s has reached 10,000 metric tons. This use of DDT is not permitted under the Stockholm Convention, and the Chinese government is taking steps to address this problem.

DDT is not highly toxic to birds when compared with fish. It is best known for the adverse effects on reproduction that is associated with the effects on eggshell thinning, especially DDE. Ratcliffe established the relationship between eggshell thickness and the widespread use of toxic substances (De Luca-Abbott et al., 2001). The decline of the double-crested cormorant population on the Great Lakes of North America in the 1960s and the reduction of the population on Lake Ontario to three pairs were attributed to the breakage of eggs, with 95% breaking before hatching (Weseloh et al., 1983). Cooke et al. (1976) demonstrated a clear linear relationship between the proportion of pair breaking eggs and DDE. However, there is a large discrepancy between the concentrations of DDE that is required to induce critical eggshell thinning, even though in the same species (Fitzner et al., 1988; Henny et al., 1984; Thomas & Anthony, 1999).

In Britain, the levels of *p,p′*-DDE that were found in the eggs of shags between 1963 and 1971, and in those from Ireland in 1964 are shown in Table 8.7. It is considered to be much lower than the levels that were found in the eggs of terrestrial predators during the same period (Walker, 1990). There was no decline in the levels of DDE in shag eggs between 1963 and 1971. The DDE levels of sandwich terns from the Netherlands ($<1\,\mu g\ g^{-1}$ wet wt.) were lower than those that were found in Great Britain in the 1960s. In contrast, very high levels of *p,p*-DDE were found in gannet eggs from Bonaventure Island, Canada between 1968 and 1970. In other studies of the Mediterranean and the Black Sea between 1980 and 1984, high levels of *p,p*-DDE were found in some locations, such as the Danube delta, Majorca and the Po delta (Walker, 1990).

The levels of total DDT in certain bird species were available in Asia between 1993 and 2000 (Table 8.7). The highest levels of total DDT were found in common cormorants in Shinobuza, Japan in 1993 (Guruge et al., 1997) and very high total DDT levels were found in white-tailed sea-eagles in Hokkaido, Japan in 1997 (Kunisue et al., 2003). Little ringed plovers and pond herons from India in 1995, and white-breasted water hen that were collected in Vietnam in 1997 also had high levels of total DDT (Minh et al., 2002; Tanabe et al., 1998). Somewhat lower levels of total DDT were found in little egrets and black-crowned night herons in Hong Kong in 2000 (Connell et al., 2003). In contrast, the egg collected from Lake Tai, China in 2000, of black-crowned night herons, little egrets and thick-billed reed warblers had higher total DDT levels than those of Hong Kong. However, the total DDT levels were lower in Bombay ducks in Jinshan, China between 2000 and 2001 (Nakata et al., 2005). The lowest levels of DDT were found in green back herons and gray herons that were collected in the Philippines in 1994 and in Lake Baikal, in Russia in 1996 and 1997, respectively (Kunisue et al., 2002, 2003).

In Antarctica, low levels of total DDT were found in the eggs of penguins in 1995 and 1996 (Corsolini et al., 2006). In contrast, the levels of total DDT or *p,p′*-DDE that were found in murre eggs in the Arctic region were higher (Braune et al., 2001; Vander Pol et al., 2004).

Table 8.7. DDT concentrations in bird samples from different countries

	Location	Species	Year	*n*	Tissue	Concentration (μg g^{-1} wet wt.)	References
1960s–1980s	Britain	Shag (*Phalacrocorax aristolles*)	1963–1971	n.s[a].	Egg	0.55–3.1	Walker (1990) and the references therein
		Sandwich tern (*S. sandvicensis*)	1963–1965	n.s.	Egg	0.2–1.1	
	Ireland	Shag (*P. aristolles*)	1964	n.s.	Egg	0.3–0.7	
	Netherlands	Sandwich tern (*S. sandvicensis*)	1965–1966	n.s.	Egg	0.61	
	Bonaventure Island, Canada	Gannet (*Sula bassana*)	1968	n.s.	Egg	28 (17–50)	
			1969	n.s.	Egg	31 (19–50)	
			1970	n.s.	Egg	34 (22–57)	
	Mediterranean and the Black Sea						
	Danube delta	Common cormorant (*P. carbo*)	n.s.	n.s.	Egg	19–57	Walker (1990) and the references therein
	Majorca	Corys shearwater (*Calomectris diomedea*)	1984	n.s.	Egg	13–19	
	Po delta	Little tern (*Sterna albifrons*)	1980–1982	n.s.	Egg	5.8–11	
		Gull-billed tern (*S. nilotica*)	1980–1982	n.s.	Egg	4.7–12	

	Japan						
1990–now	Shinobuza	Common cormorant (*P. carbo*)	1993	8	Liver	13	Guruge et al. (1997)
	Hokkaido	White-tailed sea-eagle (*Haliaeetus albicilla*)	1997	2	Liver	1.5	Kunisue et al. (2003)
	India	Little ringed plover (*Chladrius dubius*)	1995	5	Whole body	4.3	Tanabe et al. (1998)
		Pond heron (*Ardeola grayii*)	1995	2	Whole body	3.5	
	Vietnam	White-breasted waterhen (*Amaurornis phoenicurus*)	1997	3	Whole body	3.8	Minh et al. (2002)
	China						
	Hong Kong	Little egret (*E. garztta*)	2000	9	Egg	1.2	Connell et al. (2003)
		Night heron (*Nycticorax nyticorax*)	2000	9	Egg	0.6	
	Lake Tai	Little egret (*E. garztta*)	2000	36	Egg	0.41	Dong et al. (2004)
		Night heron (*N. nyticorax*)	2000	65	Egg	1.1	

Table 8.7. (*Continued*)

Location	Species	Year	n	Tissue	Concentration ($\mu g\ g^{-1}$ wet wt.)	References
Lake Tai	Thick-billed reed warbler (*Acrocephalus aedon*)	2001	3	Whole body	5.1	Nakata et al. (2005)
Jinshan	Bombay duck	2001	2	Whole body	1.6	
Philippines	Green backed heron (*Butrides striatus*)	1994	3	Whole body	0.058	Kunisue et al. (2003)
Lake Baikal, Russia	Grey heron (*Ardea cinerea*)	1996	2	Breast muscle	0.027	Kunisue et al. (2002)
Alaska	Murre (*Uria aalge*)	1999–2000	67	Egg	0.12	Vander Pol et al. (2004)
Ross sea, Antarctica	Adelie penguin (*Pygoscelis adeliae*)	1995–1996	6	Egg	0.023	Corsolini et al. (2006)
Canadian Arctic	Black-legged kittiwake (*Rissa tridactyla*)	1998	15	Egg	0.06	Braune et al. (2001)
	Thick-billed murre (*U. lomvia*)	1998	15	Egg	0.1	
	Northern fulmur (*Fulmarus glacialis*)	1998	15	Egg	0.21	

1975–1998	Canadian Arctic	Northern fulmur (*F. glacialis*)	1975	15 (pooled samples)	Egg	0.67	Braune et al. (2001)
			1976	12 (pooled samples)	Egg	0.86	
			1977	15 (pooled samples)	Egg	0.43	
			1987	6 (pooled samples)	Egg	0.22	
			1993	15 (pooled samples)	Egg	0.4	
			1998	15 (pooled samples)	Egg	0.21	
1975–1998	Canadian Arctic	Black-legged kittiwake (*Rissa tridactyla*)	1975	12 (pooled samples)	Egg	0.24	Braune et al. (2001)
			1976	6 (pooled samples)	Egg	0.42	
			1987	3 (pooled samples)	Egg	0.11	
			1993	15 (pooled samples)	Egg	0.071	
			1998	15 (pooled samples)	Egg	0.06	
1975–1998	Canadian Arctic	Thick-billed murre (*U. lomvia*)	1975	9 (pooled samples)	Egg	0.20	Braune et al. (2001)
			1976	9 (pooled samples)	Egg	0.23	

Table 8.7. (*Continued*)

Location	Species	Year	*n*	Tissue	Concentration (μg g^{-1} wet wt.)	References
		1977	9 (pooled samples)	Egg	0.23	
		1987	9 (pooled samples)	Egg	0.16	
		1988	9 (pooled samples)	Egg	0.1	
		1993	15 (pooled samples)	Egg	0.14	
		1998	15 (pooled samples)	Egg	0.1	

[a] n.s.: Not stated.

There were declining trends of the total DDT/*p,p′*-DDE residues in seabird eggs in the Canadian Arctic and the Alaskan Arctic. The levels of total DDT in the eggs of black-legged kittiwakes, northern fulmars and thick-billed murres that were collected in the Canadian Arctic reduced from 1975 to 1998 (Braune et al., 2001).

8.1.8. Polychlorinated biphenyls (PCBs) and Polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDDs/PCDFs)

8.1.8.1. PCBs

PCBs are mixtures of chlorinated hydrocarbons. Regarding the source of contamination, they can be divided into two main groups: intentional (commercial products) and unintentional (by-products of combustion, such as an incinerator; trace amounts of PCBs have been reported in agricultural chemicals or chemical products as impurities) (UNEP Chemicals, 2002). PCBs were produced commercially in the United States from 1929 to 1977. Due to their chemical inertness, heat resistance, a high dielectric constant and nonflammable properties, they have been used extensively for a variety of industrial purposes, such as dielectrics in transformers and large capacitors as heat exchange fluids and in plastics (WHO, 1993).

They are produced under different trade names, such as Aroclor, Askarel, and Thermino. They are commercially produced as complex mixtures that contain multiple isomers at different degrees of chlorination that are named with a four-digit number. The first two digits refer to the number of carbon atoms in the biphenyl ring (12 for PCBs) and the second two digits indicate the percentage of chlorine by mass in the mixture. The peak production of Aroclor in the United States was in 1970 with a total volume of 85 million pounds (39 million kg) (WHO, 1995). Due to their widespread environmental problems and detrimental health effects, the first set of effluent standards for PCBs was issued by USEPA in 1977 and manufacturing and import limitations of PCBs were issued in 1979. In China, the production of PCBs from 1965 to 1975 was estimated to be 10,000 tons and they were known as PCB3 and PCB5 (Fu et al., 2003). The major uses of PCBs in China were in the electrical industry, such as dielectric fluid in capacitors and transformers, and they were also used in carbon-free copy papers and in paint additives. The uses of PCBs were banned in the 1980s in China.

There are 209 possible PCBs from three monochlorinated isomers to the fully chlorinated decachlorobiphenyl isomer. The toxicology of PCBs depends on the number and position of chlorine atoms. Coplanar PCBs refer to the PCBs without *ortho* substitution, whereas noncoplanar PCBs refer to others (WHO, 1993). Coplanar PCBs have similar effects as dioxins on Ah-receptors in that they bind to the receptor and thus they are usually regarded as dioxin-like compounds (see below). There is much information on the effects of PCB mixtures or congeners on human or laboratory animals and wildlife; however, it is difficult to compare the levels because different studies may report different PCB mixtures or individual congener groups. Similarly, it is not always possible to compare analytical data for PCBs in different studies because different laboratories use different PCB standards or methods of quantification.

Although there are 209 possible PCBs, there are common effects of PCBs on laboratory animals or wildlife. Coplanar PCBs can bind to Ah-receptor that affects defense mechanisms against foreign compounds. PCB residues in eggs were found to be associated with reproductive effects; however, the levels of PCBs that cause this phenomenon varies greatly from species to species. For example, an oral dosage of 1 mg $kg^{-1}day^{-1}$ was linked to lower hatching rates in chickens (*Gallus gallus*), whereas 105 mg $kg^{-1}day^{-1}$were reported to have no effect on the hatching success of mallards (*Anas platrhychos*) (Haseltine & Prouty, 1980). Many studies have concentrated on PCBs and reproductive success, such as hatching success and eggshell thickness. Custer et al. (1999) performed a logistic regression of hatching success with organochlorine levels in double-crested cormorants. They showed that DDE was identified as the major risk factor, not dieldrin and PCBs, and pointed out that many studies focused on PCBs and neglected other more important compounds, such as DDE.

8.1.8.2. Polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDDs/PCDFs)

The PCDDs and PCDFs are two groups of tricyclic planar aromatic compounds. PCDDs and PCDFs are not manufactured commercially except on a small scale for chemical and toxicological research, but they are known to occur naturally, such as in the incomplete combustion of organic material due to forest fires or volcanic activity (ATSDR, 1994b, 1998). PCDDs and PCDFs are produced unintentionally during uncontrolled chemical reactions that involve the use of chlorine, undesired by-products in various chemical formulations, and combustion or incineration processes (ATSDR, 1994b, 1998; WHO 1985). As there can be one to eight chlorine atoms that attach to the benzene rings, they can be categorized into eight families that depend on the degree of chlorination. Hart et al. (1991) investigated the relationship between the concentrations of PCDDs and PCDFs in great blue heron eggs and the effects on chicks. They showed that 10, 135 and 211 ng kg^{-1} wet wt. 2,3,7,8-tetrachlorodibenzo-*p*-

dioxin (or 2,3,7,8-TCDD) in eggs did not cause any effect on the survival of chicks. However, the increased TCDD levels decreased the growth, depressed skeletal growth and increased subcutaneous edema of chicks. Shortened beaks and a scarcity of down follicles in the chicks were also observed from more PCDD- and PCDF-contaminated sites.

To facilitate the evaluation of the toxicity of PCDDs and PCDFs, and also certain PCB congeners, international toxicity equivalency factors (TEFs) are assigned to individual PCDDs or PCDFs and some congeners of PCBs. 2,3,7,8-TCDD is regarded as the most toxic substance among PCDDs, PCDFs and PCBs and it can bind to the Ah-receptor strongly. This receptor is responsible for the control of the mixed function oxidase system, which is an important defense mechanism against foreign compounds. TEFs are assigned to each of the individual dioxins, furans, and coplanar PCBs based on their toxicity relative to 2,3,7,8-TCDD (estimated in terms of their binding affinities to the Ah-receptor). The strength of this binding is used to calculate the TEFs for different dioxins, furans, and PCB congeners with TEF of 2,3,7,8-TCDD set at 1. For each compound, this number is then multiplied by the corresponding concentration to obtain the toxic equivalent (TEQ). This approach can be used in the reverse; the degree of induction of the enzyme is measured and then converted into dioxin equivalents (Safe, 1992).

The TEFs of individual PCDDs, PCDFs and PCB congeners can be obtained from Van den Berg et al. (1998). Usually, the TEQ is calculated from PCDDs, PCDFs and Co-planar PCBs to evaluate whether there is a risk for the tested samples against the value that is obtained from relevant animal tests.

There is a decreasing trend of total PCBs from 1975 to 1998 in Alaska (Table 8.8). Vander Pol et al. (2004) conducted a study on the temporal change of POPs in Alaskan murre (*Uria* spp.) eggs. The total PCBs in thick-billed (*Uria lomvia*) murre eggs that were collected from Prince Leopold Island, in eastern Canada, showed a decreasing trend from 1975 to 1998 (Vander Pol et al., 2004). A decreasing trend of the total PCBs in the livers of adult northern fulmars (*Fulmarus glacialis*) from Prince Leopold Island was observed from 1975 to 1993 (Muir et al., 1999). The decreasing trend of PCBs was also observed in black guillemots in Iceland from 1976 to 1996 (Ólafsdóttir et al., 2005).

The level of total PCBs of common murre eggs in the Arctic regions was higher than those of penguin eggs in Antarctica (Table 8.8) (Corsolini et al., 2006; Vander Pol et al., 2004). Cormorants in Japan had the highest total PCBs and were followed by herons that were collected in Hong Kong (Connell et al., 2003; Guruge et al., 1997; Kunisue et al., 2003). Cormorants that were collected in Romania had lower levels of total

Table 8.8. PCBs concentrations in bird samples from different countries

	Location	Species	Year	*n*	Tissue	PCB method[a]	Concentration (ng g^{-1} wet wt.)	References
1975–1998	Prince Leopold Island, Eastern Canada	Thick-billed murre (*Uria lomvia*)	1975–1977	55	Egg	A	820	Vander Pol et al. (2004) and the references therein
			1987–1988	18	Egg	67	190	Braune et al. (2001)
			1993–1998	30	Egg	67	140	
1975–1993	Prince Leopold Island, Eastern Canada	Northern fulmur (*Fulmarus glacialis*)	1975	7	Liver	A	1100	Muir et al. (1999)
			1976	7	Liver	A	2000	
			1987	8	Liver	A	560	
			1993	10	Liver	A	340	
1990s–now	Canadian Arctic	Common murre (*U.* spp)	1999–2000	67	Egg	46	110	Vander Pol et al. (2004)
	Ross sea, Antarctica	Adelie penguin (*Pygoscelis adeliae*)	1995–1996	6	Egg	46	25	Corsolini et al. (2006)
	Japan							
	Shinobazu pond	Common cormorant (*Phalacrocorax carbo*)	1993	8	Liver	K 300, 400, 500	40,000	Guruge et al. (1997)
	Lake Biwa	Common cormorant (*P. carbo*)	1993	9	Liver	K 300, 400, 500	7900	

Hong Kong	Little egret (*Egretta garztta*)	2000	9	Egg	K 300, 400, 500, 600	960	Connell et al. (2003)
	Night heron (*Nycticorax nyticorax*)	2000	9	Egg	K 300, 400, 500, 600	230	
Romania	Common cormorant (*P. carbo*)	2001	2	Liver	23	110	Covaci et al. (2006)
Philippines	Green backed heron (*Butrides striatus*)	1994	5	Whole body	K 300, 400, 500, 600	85	Kunisue et al. (2003)
Vietnam	Common moorhen (*Gallinula chloropus*)	1997	1	Whole body	K 300, 400, 500, 600	40	Kunisue et al. (2003)
	Cinnamon bittern (*Ixobrychus cinnamomeus*)	1997	1	Whole body	K 300, 400, 500, 600	210	
India	Little egret (*Egretta garzetta*)	1995	1	Whole body	K 300, 400, 500, 600	34	Tanabe et al. (1998)
	Pond heron (*Ardeola grayii*)	1995	2	Whole body	K 300, 400, 500, 600	42	
Russia	Grey heron (*Ardea cinerea*)	1996–1997	2	Breast muscle	K 300, 400, 500, 600	7.7	Kunisue et al. (2002)

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[a] Methods used to analyse PCBs were based on Aroclor 1254 standard (A), total number of PCB congeners used and Kanechlor preparations.

PCBs than those from Hong Kong, but were higher than those from the Philippines and Vietnam (Covaci et al., 2006). Green backed herons in the Philippines and common moorhen and cinnamon bitterns in Vietnam had similar levels of total PCBs but the herons in India had lower PCBs levels (Kunisue et al., 2003; Minh et al., 2002; Tanabe et al., 1998). The gray herons in Russia had the lowest level of total PCBs (Kunisue et al., 2002).

The levels of PCDDs and PCDFs in waterbirds that were collected at different periods from different countries were compared (Table 8.9) (Choi et al., 2001; Harris et al., 2003; Kannan et al., 2003; Kubota et al., 2004; Senthilkumar et al., 2002; Wan et al., 2006). Bald eagle muscles that were collected from the Upper Peninsula of Michigan, in 2000, had relatively high levels of PCDDs and PCDFs, whereas the livers of white tailed sea eagles from eastern Germany from 1990 to 1998, the eggs of double-crested cormorants that were collected from Canada between 1990 and 1998, and the livers of various species of birds that were collected in Japan from 1997 to 2001 had relatively low levels of PCDDs and PCDFs. The livers of herring gulls that were collected from China in 2002, the subcutaneous fat of black-tailed gulls that was collected from Korea between 1992 and 1994, and the livers of white-tailed sea eagles from west Poland showed lower levels of PCDDs and PCDFs.

Total PCDDs and PCDFs were usually used for comparison, however, it should be noted that different studies used different standards to calculate total PCDDs/PCDFs. The eggs of double-crested cormorants that were collected from Mandarte Island, and Crofton and Mitlenatch Islands, in the Strait of Georgia, in British Columbia, Canada, between 1973 and 1998 have been analyzed for PCDDs and PCDFs (Harris et al., 2003). The study showed that the levels of total PCDDs and PCDFs in 1998 were lower than those from 1973 to 1989 (Table 8.9). In another study, the PCDDs/PCDFs levels in white-tailed sea eagle livers were analyzed (Kannan et al., 2003). It showed that no significant difference in the total PCDDs/PCDFs in adult females that were collected from 1985 to 1995 was observed. However, this observation was confounded by small sample sizes and associated inherent biological variations.

8.2. Biological effects

Organochlorine pesticides, PCBs and PCDDs/PCDFs caused the decline of several avian populations in the late 1960s, such as sparrow hawks and kestrels in Europe and North America (Newton, 1992). The effects of these compounds on birds were linked with direct mortality due to pollutants and reproductive performance, such as eggshell thinning and

Table 8.9. Polychlorinated dibenzo-*p*-dioxins/ dibenzo-*p*-furans (PCDDs/PCDFs) concentrations in bird samples from different countries

	Location	Species	Year	*n*	Tissue	TEQ (pg of TEQ g^{-1}, lipid wt.)	Concentration (pg g^{-1}, lipid wt. corrected)	References
1990s–now	Upper Peninsula of Michigan	Bald eagle	2000	6	Muscle	21,000	34,000	Senthilkumar et al. (2002)
	Eastern Germany	White-tailed sea-eagle (*Haliaeetus albicilla*)	1990–1998	19	Liver	–	2500	Kannan et al. (2003)
	Strait of Georgia, BC, Canada	Double-crested cormorant (*Phalacrocorax auritus*)	1990–1998	70	Egg	42	1200	Harris et al. (2003)
	Lake Biwa, Japan	Common cormorant (*P. carbo*)	2001	26	Liver	1200	2800	
	Chiba, Tokyo, Japan	Gray heron (*Ardea cinerea*)	1997–1998	2	Liver	1800	11,000	Senthilkumar et al. (2002)
		Spot-billed duck (*Anas poecilorhyncha*)	1997–1998	2	Liver	1500	1500	
		Whimbrel (*Numenius phaeopus*)	1998	1	Liver	400	2200	
		Short-tailed shearwater (*Puffinus tenuirostris*)	1998	1	Liver	18	33	
		Cattle egret (*Bubulcus ibis*)	1999	1	Liver	1800	2700	
		Great egret (*Ardea alba*)	1999	1	Liver	3500	4900	
	Tianjin, China	Herring gull (*Larus argentatus*)	2002	20	Liver	–	860	Wan et al. (2006)

Table 8.9. (*Continued*)

	Location	Species	Year	*n*	Tissue	TEQ (pg of TEQ g^{-1}, lipid wt.)	Concentration (pg g^{-1}, lipid wt. corrected)	References
	Nakdong River estuary, Korea	Black-tailed gull (*L. crassirostris*)	1992–1994	10	Fat	230	390	Choi et al. (2001)
	Western Poland	White-tailed sea-eagle (*Haliaeetus albicilla*)	1996–1998	4	Liver	–	440	
1973–1998	Mandarte Island, Canada	Double-crested cormorant (*Phalacrocorax auritus*)	1973	14 (pooled samples)	Egg	1500	2000	Harris et al. (2003)
			1979	5 (pooled samples)	Egg	1800	3500	
			1985	5 (pooled samples)	Egg	2600	7100	
			1989	20 (pooled samples)	Egg	1800	2800	
			1990	11 (pooled samples)	Egg	1300	2000	
			1991	10 (pooled samples)	Egg	690	880	
			1992	10 (pooled samples)	Egg	1200	1700	
			1994	15 (pooled samples)	Egg	660	870	
			1995	10 (pooled samples)	Egg	1100	1200	
			1998	14 (pooled samples)	Egg	500	730	

decreased reproduction success (Table 8.10, see also De Luca-abbott et al., 2001). In addition, body condition, such as body mass controlled for body size, including head and bill, showed a significant negative relationship with these contaminants, and all organochlorines (e.g. HCB, DDE, PCBs), except oxychlordane in females but not in the males of great black-backed gulls (Helberg et al., 2005) may also affect immune status and function (Bustnes et al., 2004). Significant or near significant positive relationships ($0.1 > p > 0.001$) were found between most persistent organochlorines and the levels of heterophils in the blood for both sexes and the lymphocytes of male gulls (Bustnes et al., 2004). There is evidence that organochlorines affect immune systems, which may decrease their efficiency and make birds more susceptible to parasites and diseases.

Some studies have suggested there is interaction among organochlorine pesticides, PCBs and PCDDs/PCDFs with other compounds (Blus et al., 1983). For example, a toxic interaction between dieldrin and chlordane has been suggested that caused mortality in wild birds (Blus et al., 1983; Okoniewski & Novesky, 1993). Different cyclodienes may have bound to a common target site—a gamma-aminobutyric acid-regulated chloride ion channel in a nerve membrane—that resulted in convulsions (Cole & Casida, 1986). The additive effects of chlordane and dieldrin have been demonstrated in rats (Keplinger & Deichmann, 1967). Other interactive effects among organochlorine pesticides and PCBs have been discussed elsewhere (Stansley & Roscoe, 1999; Walker, 1990).

8.3. Limitations

There are important limitations in understanding the spatial and temporal trend of the pollutant levels of waterbirds, which is particularly true in China. Many studies that have been conducted in China have focused on water and sediment. There is limited information of pollutant levels in waterbirds available in China. In addition, a number of studies have investigated target pollutants with different tissue samples of different species. It has been determined that different tissue samples of species of birds can accumulate varying degrees of pollutants. It would be more instructive to compare tissue samples within species. Moreover, it is difficult to adequately compare current results with previous ones (i.e. 1940s–1970s) because of the advanced capability and improved sensitivity of instruments, and the application of different extraction methods and standards for quantification.

Standard protocol that uses the same tissue of birds is useful to evaluate the global level of contaminants, spatially and temporally. The egg is

Table 8.10. Adverse effects caused by organochlorine pesticides, PCBs and TCDD

Compounds	Species	Means of dosage/tissue measured	Mean concentration in tissue measured/dosage	Adverse effect	References	Remarks
Heptachlor epoxide	American Kestrel (*Falco sparverius*)	Dietary fed	$\geqslant 1.5\,\mu\text{g g}^{-1}\text{ day}^{-1}$	Reproductive impairment	Henny et al. (1983)	
	Canada geese (*Branta canadensis*)	Dietary fed	$\geqslant 10\,\mu\text{g g}^{-1}\text{ day}^{-1}$	Reproductive impairment	Blus et al. (1984)	
	Canada geese (*B. canadensis*)	–	$\geqslant 10\,\mu\text{g g}^{-1}\text{ day}^{-1}$	Nest success lower		
Dieldrin	Japanese quail (*Coturnix coturnix japonica*)	Dietary fed	$20\,\text{mg kg}^{-1}\text{day}^{-1}$	Reduced survival of parent, reduced egg/hen	WHO (1989) and the references therein	9 weeks
		Dietary fed	$30\,\text{mg kg}^{-1}\text{day}^{-1}$	Reduced survival of parent, reduced egg/hen, reduced hatchability, reduced survival of chick		7 weeks
		Dietary fed	$40\,\text{mg kg}^{-1}\text{day}^{-1}$	Reduced survival of parent, reduced egg/hen, reduced survival of chick		6 weeks
	Bobwhite quail (*Colinus virginianus*)	Dietary fed	$10\,\text{mg kg}^{-1}\text{day}^{-1}$	Reduced survival of parent		34 weeks
		Dietary fed	$20\,\text{mg kg}^{-1}\text{day}^{-1}$	Reduced survival of parent, reduced egg/hen		34 weeks

		Dietary fed	$40\,\mathrm{mg\,kg^{-1}day^{-1}}$	Reduced survival of parent, reduced egg/hen		34 weeks
HCB	Japanese quail (*C. coturnix japonica*)	Dietary fed	$100\,\mu\mathrm{g\,g^{-1}\,day^{-1}}$	Increased mortality	WHO (1995) and the references therein	90 days
			$20\,\mu\mathrm{g\,g^{-1}\,day^{-1}}$	Reduced hatchability		
TCDD	Three-day-old chickens	Dietary fed	1 or $10\,\mu\mathrm{g\,g^{-1}\,day^{-1}}$	Suffered from subcutaneous and pulmonary edema, distended abdomens and increased peritoneal and pericardial fluid	Hart et al. (1991) and the references therein	3 weeks
Mirex	Chicken	Dietary fed	$300\,\mathrm{mg\,kg^{-1}day^{-1}}$	Reduced survival of hatchlings	Davison et al. (1975) and the references therein	12 weeks
		Dietary fed	$600\,\mathrm{mg\,kg^{-1}}$	Reduced survival of hatchlings and hatchling survival		6 weeks
	Mallard (*Anas platyrhynchos*)	Dietary fed	$100\,\mathrm{mg\,kg^{-1}}$	Egg shell thinning and reduced duckling survival	Waters et al. (1977)	
	American Kestrel (*F. sparverius*)	Dietary fed	$8\,\mathrm{mg\,kg^{-1}}$	Reduced sperm concentration and increased semen volume	Bird et al. (1983)	69 days
Toxaphene	Duckling	Dietary fed	10 or $50\,\mathrm{mg\,kg^{-1}day^{-1}}$	Reduced growth and backbone impairment	Mehrle et al. (1979)	90 days

Table 8.10. (*Continued*)

Compounds	Species	Means of dosage/tissue measured	Mean concentration in tissue measured/ dosage	Adverse effect	References	Remarks
p,p′-DDE	Black-crowned night heron (*Nycticorax nycticorax*)	Eggs	8200*	Decreased fledging success	Henny et al. (1984)	
p,p′-DDE	Common cormorant (*Phalacrocorax carbo*)	Eggs	4000	Eggshell thinning	Dirksen et al. (1995)	
p,p′-DDE	Little egret (*Egretta garzetta*)	Eggs	1000	Young survival	Connell et al. (2003)	
p,p′-DDE	Double-crested cormorant (*Phalacrocorax auritus*)	Eggs	960–11,000	Decreased reproduction	Custer et al. (1999)	
p,p′-DDE	Dalmatian Pelican (*Pelecanus crispus*)	Eggs	14,000–22,000	Eggshell thinning	Crivelli et al. (1989)	
			Mean concentration of dosage/in tissue measured			
p,p′-DDE	Great Egret (*Ardea alba*)	Liver	124,300	Shell breakage	Pratt (1972)	
p,p′-DDE	Great Blue Heron (*A. herodias*)	Eggs	>10,000	Reproductive impairment	Custer et al. (1998)	
p,p′-DDE	Great Blue Heron (*A. herodias*)	Eggs	3000	Reduced hatching	Blus (1996)	

p,p'-DDE	Great Blue Heron (*A. herodias*)	Liver	569,740	Lethal effects	Call et al. (1976)
$\sum$PCBs	Common cormorant (*P. carbo*)	Liver	40,000	Sublethal effects	Guruge et al. (2000)
$\sum$PCBs	Common cormorant (*P. carbo*)	Liver	319,000	Adult mortality	Koeman et al. (1973)
$\sum$PCBs	Common cormorant (*P. carbo*)	Eggs	7300–8200	Unhatched eggs, Deformed bill	Larson et al. (1996)
$\sum$PCBs	Double-crested cormorant (*P. auritus*)	Eggs	3500	Reproductive success	Tillitt et al. (1992)
$\sum$PCBs	Double-crested cormorant (*P. auritus*)	Eggs	6600–7300	Chick deformities	Yamashita et al. (1993)
$\sum$PCBs	Double-crested cormorant (*P. auritus*)	Eggs	30,000	Embryo mortality	Barron et al. (1995)
$\sum$PCBs	Black-crowned night heron (*N. nycticorax*)	Eggs	10,000–63,000	Decreased hatching and fledging success	Sakellarides et al. (2006) and the references therein

a better option for the biomonitoring of pollutants, and its advantages and limitations in biomonitoring have been discussed (De Luca-abbott et al., 2001; Peakall, 1994). Basically, pollutants can be transferred from a female to her eggs, hence, the measurement of pollutant levels in eggs can provide an idea of the level of pollutants in the environment that are bioavailable to birds. It can also reduce confounding factors from birds, such as sex, age and feeding habits. However, the availability and accessibility of the eggs of some birds make it difficult for routine use in biomonitoring under certain circumstances.

8.4. Study on persistent organic pollutants in local waterbirds in Hong Kong

Among the wildlife in Hong Kong, waterbirds are one of the conspicuous groups of animals in our coastal environment, and they have high conservation value in the Hong Kong marine ecosystem. In Hong Kong, waterbirds are mainly found in two estuaries, namely Deep Bay and Starling Inlet (Carey, 1998; Young & Cha, 1995). In recent years, there is increasing evidence that the western waters are under threat from a wide range of environmental contaminants as compared to the eastern part of Hong Kong. A complete evaluation of the environmental impacts of these pollutants to the Hong Kong coastal environment would be instructive to provide a scientific basis for risk characterization and management.

Waterbirds are valuable/useful for environmental monitoring. Waterbirds are particularly susceptible to environmental contaminants because they are long-lived and are top trophic-level animals in the food web. Consequently, they are able to integrate pollutant levels over a broad area by bioaccumulation (Furness, 1993). Contaminant levels in waterbird eggs, therefore, provide important and useful information for monitoring changes in the environmental quality of the Hong Kong coastal areas. This is particularly relevant in the Northwestern part of Hong Kong, which is heavily influenced by increased activities arising from the rapid industrialization of the PRD region. In Hong Kong, Ardeids (Herons and Egrets) represent the dominant and the most conspicuous groups of resident waterbirds. Local Ardeid species include Chinese Pond Heron (*Ardeola bacchus*), Cattle Egret (*Bubulcus ibis*), Little Egret (*Egretta garzetta*), Great Egret (*Egretta alba*) and Black-crowned Night Heron (*Nycticorax nycticorax*).

A study commissioned by the Agriculture, Fisheries and Conservation Department (AFCD) of Hong Kong, "Study on the effect of water pollution on the breeding success of Ardeids" completed in 2001, detected organochlorines in the eggs of Little Egrets (*Egretta garzetta*) and Black-crowned

Night Herons (*Nycticorax nycticorax*) collected from Mai Po and A Chau, respectively (Lam et al., 2001). The results indicated that Little Egret and Black-crowned Night Heron eggs had concentrations of DDE (a metabolite of DDT) sufficient to initiate adverse effects on the breeding success of these species (Connell et al., 2003). In addition, total PCBs present in eggs were at threshold levels where adverse effects could be initiated with the Little Egret, but not Black-crowned Night Herons.

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Chapter 9

Persistent Toxic Substances in India

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Abstract

Over the past few decades there has been a steady increase in the use of many pesticides for agricultural and disease control purposes in developing countries including India. Apart from this, India is now becoming an industrially developed nation, compelling it to use several other man-made chemicals for its ongoing industrial development. In spite of the fact that India has promulgated several laws for the control of such chemicals, in practice, there has been little control over their production and usage. As a result, there has been widespread contamination of the Indian environment and biota, including human, by all these chemicals. Most recent studies have shown that, in contrary to the popular belief that the developed nations are the prime sources of the highly toxic chemicals such as PCDDs/DFs, India is also contributing such chemicals to the global environment in considerable quantities. Many popular articles and scientific publications have shown a grim situation in several sectors of human life in India with regard to xenobiotic chemical contamination. Our group at the Center for Marine Environmental Studies (CMES), Ehime University has been carrying-out monitoring and toxicological studies of many of those chemicals in India for the past three decades. Apart from our works, sizable literature is available on the status of contamination of persistent toxic substances (PTS) such as DDTs, PCBs, PCDDs/DFs, PBDEs, HBCDs, OTs, etc. Viewing from a global pollution point of view, a detailed review of the available information on PTS pollution in India is necessary for planning and executing control measures to restrain their expansion on a wide scale. With this view in mind, this review provides information on the history of usage of PTS in India, their occurrence in the aquatic and terrestrial environment and in the flora and fauna. Finally the review provides a brief account of the laws

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governing the manufacture and usage and the management practices of those chemicals.

9.1. Introduction

In the Asian region India plays a prominent role in the context of global distribution of persistent toxic pollutants. India is the highest populated (1.04 billion—as per 2004 statistics) nation in the world—next only to China (1.29 billion), industrially developing, has a transforming economy, but still depends heavily on agriculture. India still fights with large numbers of seasonal vector borne diseases. Above all, India is a generic giant (Dave, 1996; Gupta, 2004), manufacturing and using large quantities of pesticides. Now India is in a stage of examining the problems of pesticides and industrial chemicals and potential solutions in the aftermath of the Green Revolution and the ongoing industrial development. In the light of such a situation and also in the present era of implementation of Stockholm Convention which has come into as a legally binding document on May 17, 2004, a detailed review on the present status of available information on these chemicals in India will provide valuable information from the global pollution perspective.

In the year 2003, a furor erupted in India on the issue raised by a prominent nongovernmental organization (NGO) that many popular soft drink brands had high levels of pesticides. Later, after many expert sittings and debates, a high level committee reported unequivocally to the Parliament that soft drinks do have pesticides (India Today, February 16, 2004). This seems to be only the tip of a massive iceberg. Not much has been done after this either by the Indian government or by the multitude of industries in India on such problems, as ever in the past. The multitude of scientific publications and popular articles which have appeared during the last three decades on the existence of several persistent toxic substances in India did not attract much attention of the public and policy makers in the country.

The detection of remarkably high concentrations of DDTs and HCHs in the air off the western coast of India by Tanabe and Tatsukawa (1980) and the continuous downward fluxes of HCHs from air to water in Bay of Bengal and Arabian Sea by Iwata et al. (1993a,b, 1994) suggest higher amount of transport of organic chemicals from India via atmosphere. Tanabe et al. (1982a,b) showed that, apart from the amount of usage and volatilization characteristics of the chemicals concerned, the meridianal circulation of the atmosphere, particularly the mass flows in the troposphere also contributes to the atmospheric transport and global distribution of organic compounds worldwide. The authors also suggested that the reason for the considerable levels of HCH and DDT compounds in the Antarctic Ocean may be their transport from countries like India, situated in lower latitudes, which are still using persistent chemicals in their agriculture and vector control practices and also in many of their industrial practices.

Such factors make India an area of great concern while evaluating the global status, transport and distribution of persistent toxic substances, because of its increasing and uncontrolled use of chemicals, their distinctive climatic conditions, excessive population, multitude of diseases, intensive agriculture, increased industrialization, etc. (Allsopp and Johnston, 2000).

9.2. History of PTS usage in India

The history of vector control in India can be divided broadly into pre-DDT and post-DDT eras. Before 1936, most of the vector control measures used was confined to methods such as the use of larvivorous fishes, oils, Paris green and provision of proper drainage systems (Covell, 1928, 1941; Viswanathan, 1941; Johnson, 1965). In 1944, DDT was introduced in the mosquito control program (Singh, 1962) and later extended to bring several million population under the ambit of National Malaria Eradication Program (NMEP) (Raghavendra and Subbarao, 2002). Later, in areas where local vectors had developed resistance to DDT, HCH and then malathion were used alternatively (Rajagopal, 1977). During the 1980s insecticides belonging to synthetic pyrethroid group were introduced in India in the public health program. Carbamate group have not yet been introduced for public health sprays in India. DDT has been banned from agricultural usage in the 1980s and HCHs had been phased out of the program in the year 1997 (Raghavendra and Subbarao, 2002). India is one of the countries that had been permitted to use DDT for their vector control programs, under Stockholm Convention, and also the chemical has been targeted at present, by the Government of India for phase out over the next few years.

India was a stagnant economy at the time of independence. The turn around in industrial growth seems to have started in the 1980s attaining a growth rate of 12% in the year 1995–1996 (Abid Hussain—Discover India—http://www.meadev.nic.in/). The composition of the industry has also undergone significant transformation since independence in 1947. Now India is considered as the 10th industrially developed nation in the world. The Indian chemical industry has been among the fastest-growing sectors of the Indian economy. The country is rapidly becoming one of the most dynamic generic industries in the world. In fact, between 25 and 33% of all genetic manufacturers worldwide are located here (Dave, 1996). The present day India is a growing giant in the information technology sector apart from the rapid growths in automobile, shipping, aviation, textile industries, each releasing some sort of chemicals in to all the three major compartments of the Indian environment viz. atmosphere, water and soil.

Because of its overcrowded metropolis, as in any other developing country, India also has problem with the management of its varied solid wastes comprising domestic, biomedical, agricultural and industrial wastes. Dumpsites of such wastes have been found to be the sites of production of the most dreaded pollutants of the persistent organic pollutants (POPs) group, the dioxins and furans (Minh et al., 2003; Kunisue et al., 2004).

The other reason for a prominent PTS pollution is, India is yet to formulate a comprehensive policy on pesticides and other chemicals. The Insecticides Act, 1968 does regulate the manufactures, registration, use, export and import of pesticides in the country but does not have much control on its consumers. There are many other policy decisions and Acts on environmental management in India which will be discussed later in this chapter. India has already banned the use of 9 of the 12 POPs slated for ultimate elimination from the world use in a United Nations treaty adopted in Stockholm on May 23, 2001. The three remaining POPs include PCBs, DDT and dioxins and furans.

As a result of such extensive use of agricultural and industrial chemicals and uncontrolled production of wastes the entire Indian environment and biota such as its atmosphere (Ramesh et al., 1989), freshwater sources (Pillai, 1986; Rehana et al., 1996; Babu Rajendran and Subramanian, 1997), estuaries (Bhattacharya et al., 2003), coastal and offshore areas (Sarkar and Sen gupta, 1988a,b; Iwata et al., 1993a; Sarkar et al., 1997), inland soils (Kawano et al., 1992), fish (Babu Rajendran et al., 1992, 1994; Das et al., 2002), birds (Tanabe et al., 1998a), bats (Senthilkumar et al., 1999b), river dolphins (Kannan et al., 1993, 1994; Senthilkumar et al., 1999a; Subramanian et al., 1999), food stuff (Kannan et al., 1992) marine mammals (Tanabe, 2002; Tanabe et al., 1993) and human milk (Tanabe et al., 1990) have been reported to be loaded with multitude of mixtures of POPs.

Apart from the POPs, other persistent organic chemicals such as butyl tin compounds (BTs) (Iwata et al., 1994; Tanabe et al., 1998b; Tanabe et al., 2000; Sudaryanto et al., 2002), polybrominated diphenyl ethers (Ueno et al., 2004) and the compounds like tris(4-chloropheyl) methane (TCPMe) and tris(4-chlrorphenyl) methanol (TCPMOH), the chemicals occurring as impurities in DDT formulations (Minh et al., 2000a) were also reported to be present in various environmental and biotic media of India and surrounding seas.

In spite of all such widespread contamination, the implementing agencies responsible for the control of POPs and other persistent toxic substances (PTS) pollution does not seem to be well informed on the nature and extent of pollution in the Indian environment and biota. It is high time, that India hasten the processes of controlling the use of not only the POPs but also all hundreds of the dangerous organic chemicals now in use for agriculture, disease control and industrial processes, by finding out cleaner alternatives. There is also urgent need for development of gathering information, information exchange, drafting plans, implementation of plans, awareness creation and educating the public, man-power development, research, curbing the production and usage and regular monitoring, in the order of priority.

9.3. Why India is important from global PTS pollution perspective

India is the seventh largest country in the world and the second largest nation in Asia with an area of 3.28 million sq. km. (land 2.97 million sq. km and water 0.31 million sq. km) (CIA – World Fact book; http://www.cia.gov/cia/publications/factbook/geos/in.html). According to Indian census statistics in an area of 2.4% of the total expanse of the world it supports over 15% of the world population. Further, in this land area, India supports 5% of the world's life forms (Gaur, 1994). The country's wild life comprises over 75,000 animal species which include 300 species of mammals and 1200 species of birds. In addition, there are over 15,000 species of flowering plants. On a land mass of only one fiftieth of the world, the diversity of birds is most beautifully exemplified by one sixth of the world's total avian diversity, the creatures of the nature most vulnerable to the organic pollutants.

As already shown in previous paragraphs, being a typical agrarian state India has been using large quantities of agrochemicals. The use of industrial chemicals has been increasing at a faster rate than the other countries with similar economies, because of its higher industrial growth rate among the industrially developing countries. Apart from these factors, the open dumping sites in the suburban areas of its nine metropolis and other cities are contributing to the PTS load by the unintentional production of chemicals like dioxins and furans.

Of course, India is one of the major contributors of certain organochlorine compounds like HCHs and DDTs to Arctic region, along with China and Soviet Union (Macdonald et al., 2000). For example, Macdonald et al. (2000) found that global use of technical HCH and historical measurements of alpha-HCH concentration in the atmosphere of Arctic region showed two significant declines, one in 1983 when China banned the use of technical HCH and another around 1990 when India banned technical HCH usage in agriculture. In an experiment conducted at a paddy field in southern India Tanabe et al. (1991), Ramesh et al. (1991) and Takeoka et al. (1991) noticed rapid volatilization of HCHs, low residues in the soil and paddy plant when compared to their presence in the atmospheric levels and rapid removal to the atmosphere. Such experiments and surveys indicate the prominence of India in the contribution toward global pollution of toxic chemicals.

The climatic conditions in India facilitate its role as a global contamination source for persistent toxic substances. Many geographers characterize the climatic changes in India as violent. There are often abrupt changes on the onset of monsoon rains, sudden flooding, rapid erosion, extremes of temperatures, tropical storms and unpredictable fluctuations in rainfall (www.indianchild.com/climate_india.htm). By all these, India represents wide range of climates.

India, being a vast country, there are sharp variations in temperature from place to place and from season to season. In summer, the temperature may occasionally go up to 55°C in the deserts whereas in winter the temperature goes as low as −45°C at Leh in the Himalayas. Indian temperature and monsoonal changes are very much complex. Indian monsoons are components of large-scale circulation system. Two prominent monsoons, the southwest monsoon (June–October) and northeast monsoon (October–January) occur at various months of the year along the west and east coasts of India, respectively (Ramesh Kumar et al., 1999a,b; Ramesh Kumar and Sreejith,, 2005). All these factors alter the distribution and transport of the semi-volatile persistent organic pollutants and makes India as a prominent contributor to the global contamination of PTS chemicals.

9.4. Persistent toxic substances in the Indian environment

9.4.1. PTS in Indian atmosphere

Many processes lead to translocation of organochlorines within the global environment, e.g., from the continent to the oceans (Goldberg, 1975) or from source regions to less contaminated remote regions (Wania and Mackay, 1993; Wania and Daly, 2002). In this respect, India can very well act as a source for many POPs on a global scale. Volatilization of organic pollutants from Indian soils has been reported by many authors in the late 1980s by measuring the reduction from soil in hot climates (Kaushik, 1989; Samuel and Pillai, 1989) on the two intensively used insecticides in India, DDTs and HCHs. Following this, Ramesh et al. (1989) reported the climatic differences in the levels of DDTs and HCHs in rural Indian atmosphere. The vital contribution of volatile PTS chemicals from India to the global environment has been shown by the schematic representation of HCH release in a paddy field in India (Fig. 9.1) by Takeoka et al. (1991) which shows that more than 99% of the total HCH applied in one crop season is removed to the air before the next cropping season. Even though, the rates of transportation of different organic chemicals differ depending upon their physico-chemical properties, the existing climatic conditions in a tropical country like India may considerably alter the global contamination by persistent toxic substances through long-range atmospheric contamination. In a study in India, Thailand, Vietnam, Solomon Islands, Japan, Taiwan and Australia, Iwata et al. (1994) found apparently higher concentrations of DDTs in the Indian cities, Goa, Bombay (presently Mumbai) and Calcutta (presently Kolkata). Further, the atmospheric distribution of PTS in India implied the presence of sporadic emission sources. Babu Rajendran et al. (1999), in the air samples collected during 1993–1994 from South India reported comparable concentrations of both DDTs and HCHs without any temporal variation.

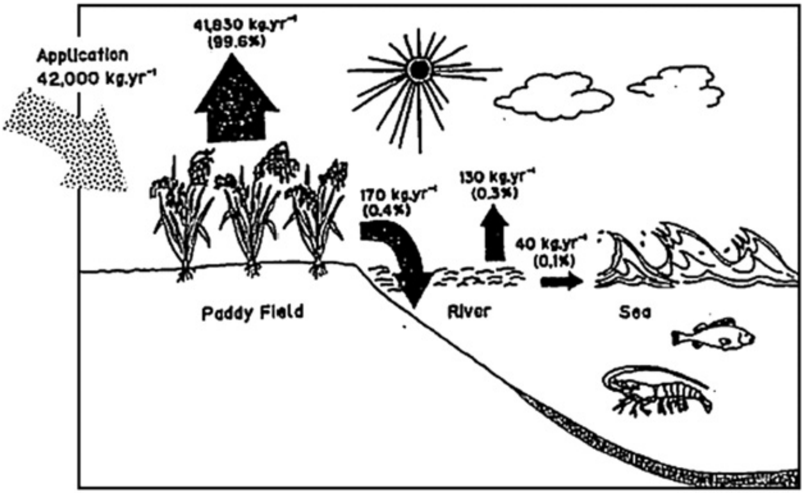


Figure 9.1. Schematic representation of the flux of HCH in Vellar river watershed, South India (*Source*: Takeoka et al., 1991).

Most of the works on the atmospheric concentrations of persistent toxic substances in India are only on the above stated chemicals and as far as our knowledge goes, not much interest has been shown in measuring the atmospheric levels of other organic pollutants in India as was shown on measuring the levels in the aquatic and biotic environment. After the mid-1990s, it seems that measuring the atmospheric levels of persistent toxic substances in the tropical countries slowly waned. The reasons may be the ultra low levels of these chemicals in the air leading to the tedium of measuring them. On the other hand, measurement of PTS in the other environmental compartments like water and sediments and the biota has increased in recent years.

9.4.2. PTS in the aquatic environment of India

Indian scenario of concern over diffuse pollution sources in water quality management may be very much special with its extremely varying rainfall and river flows, traditional as well as modern agriculture, use of water ways for varying life processes like bathing, washing, animal wading, domestic and industrial waste disposal, etc., apart from scant respect for rules, regulations and laws. Surface wash off of pollutants from agricultural sources is dominant only during the peculiarly short flood season and major proportion are normally carried away into the atmosphere leaving only very minor quantities to be transported by the water runoff.

9.4.2.1. Freshwater environment

Agarwal et al. (1986), Ray and Gupta (1986), Singh et al. (1987) and Rehana et al. (1995) on their works conducted on major rivers of India such as Ganga, Yamuna, Tapti, Narmada, Krishna, Cauvery, Godavari, etc. stated that the direct and mostly untreated disposal of waste leads to contamination of rivers and lakes chronically affecting their environment. The discharge of uncontrolled agricultural, industrial and domestic wastes, which is a normal phenomena in any part of India, polluting the streams and rivers, seep into deeper layers of the soil, thus polluting the ground water sources as well as pore waters in the nearby areas.

There are many efforts in measuring the pesticide levels in the water of the major rivers of India from the 1980s to recent years. The works of Pillai (1986) and Aleem and Malik (2005) in River Yamuna, Ansari et al. (2000), Nayak et al. (1995) and Singh et al. (2004) on River Ganges are some such examples of sporadic case studies. Several organochlorines and organophosphorus compounds occur at measurable concentrations in the River Yamuna (Table 9.1) and River Ganges (Table 9.2), two prominent rivers in India. Ramesh et al. (1990), Tanabe et al. (1991) and Takeoka et al. (1991) conducted several case studies and spraying experiments in a South Indian river for a period of more than one year and found that the levels of two of the prominent insecticides HCHs and DDTs fluctuates in line with the cultivation practices and sharp seasonal changes in the year, as a result of which only a meager portion of the pesticides applied in the

Table 9.1. Pesticide residues in the Yamuna River water at Okhla

Pesticide	Concentration (ng l^{-1})
Organochlorines	
T-BHC	25 ± 6.2[a]
T-endosulfan	114 ± 19.8
p,p′-DDE	1.6 ± 0.26
p,p′-DDT	8.8 ± 1.9
o,p′-DDE	3.9 ± 0.86
o,p′-DDT	ND[b]
Dieldrin	2.1 ± 0.34
Aldrin	0.9 ± 0.06
2,4-D	0.6 ± 0.02
Organophosphorus	
Dimethoate	0.9 ± 0.08
Methyl parathion	1.7 ± 0.65
Malathion	1.9 ± 0.72

[a] Mean ± SD.
[b] ND = not detected.

Table 9.2. Residual pesticidal load of Ganga strech at various stations (values are in ppb)

Pesticides	Stations		
	Kachla	Fatehgarh	Kannauj
Organochlorine			
Aldrin (HCH)	2.81	1.17	1.81
α-BHC	1.73	2.33	3.01
DDD (TDE)	0.88	1.30	2.41
DDT	3.33	5.19	5.33
Dieldrin	0.66	4.11	0.49
Endosulfan	ND	ND	0.75
Endrin	ND	1.14	1.04
Lindane	0.56	ND	ND
Organophosphorus			
Dimethoate	0.41	0.49	0.56
2,4-D	0.06	ND	ND
Methylparathion	0.50	0.49	0.16

Note: ND = not detected.

area was drained to the sea via rivers and streams. Their findings were supported by the studies of Babu Rajendran and Subramanian (1997) in the perennial river Kaveri of southern India showing the prominence of these chemicals in the region in wet months and their elimination during hot months. An interesting work is available on the fates of HCHs, DDTs and endosulfan in the surface water samples of the rain fed and snow fed rivers and streams of Himalyas at altitudes ranging from 300 to 1120 m (Sarkar et al., 2003) showing a sharp difference in the patterns of pollution from of the plains in India.

There are documentations of several pollutants in the river basins of India which were not followed-up by continuous monitoring and/or corrective measures. Further, the studies at the same place at the same season of different years or at places very near to each other at the same time reveal varying levels of persistent toxic substances. Based on the available limited knowledge on the PTS levels in Indian ground and surface water resources, it can only be summed up that there is a certain ambiguity of the situation in which Indian people are undergoing considerable life-long exposure. In the case of water studies, data are available from some rivers like Ganges, Gomti, Yamuna, Kaveri, Vellar, etc. but the data are difficult to interpret. The data reveals varying levels of POPs like DDTs, aldrin and dieldrin and also other chemicals like HCHs and BTs in different seasons. Certainly the tedium of sampling and analysis, lack of manpower and facilities and support from the government obviates the Indian scientists from undertaking a full fledged survey on the PTS levels in the Indian aquatic environment. With a visible growth of industries and ever-existing agriculture and public health activities, an entirely new paradigm of activities for surveying and controlling the aquatic pollution by PTS is the need of the hour in India.

9.4.2.2. Seas and oceans

The situation with regard to marine pollution by PTS is particularly important in India from the view point of the enormous and uncontrolled use of pesticides by its mostly illiterate farmers and health workers, increasing use of industrial chemicals for feeding its growing industries, and ever increasing domestic wastes coupled with its tropical climate with high temperature and heavy rains underlining the possibility of global transport of all these chemicals from point sources. There are a number of rivers along the east and west coast of India through which a large amount of PTS are being transported into the marine ecosystem thereby causing a great concern on the quality of the coastal marine environment. Further, India has a long coast line of about 7000 km. Considerable number of monitoring works on the PTS could be seen in the 1980s and the 1990s from the Indian estuaries and coastal environment after which the attention of environmentalists working on Indian samples seems to have diverted to the biotic material.

As early as in 1980, Tanabe and Tatsukawa (1980) observed the existence of all the classical organochlorines (HCHs, DDTs and PCBs) in the air and water samples collected at Bay of Bengal, Arabian Sea and Indian Ocean in various cruises during 1975–1979. Remarkably high concentrations of ΣDDT and ΣHCH in the air and surface waters off the western coast of India in the Arabian Sea than in the Bay of Bengal were observed. The follow up studies by the same authors in the eastern Indian Ocean, western and northern Pacific and Antarctic Oceans (Tanabe et al., 1982a,b, 1983) showed that the HCH levels in the northern hemisphere were higher than in the southern hemisphere depending largely on their extensive use in the Asian continent, especially leading to the spread of HCHs pollution on a global scale from India. In fact FAO (1979) reported that the consumption of technical grade HCH in India during 1975–1977 was 77,000 mt—extraordinarily high in comparison with that of other nearby countries. This has been substantiated by the finding of high concentrations of HCH residues in the western coast of India in the years closely following this (Tanabe and Tatsukawa, 1980; Bidlemen and Leonard, 1982).

Sarkar (1994), in a chapter on the occurrence and distribution of persistent chlorinated hydrocarbons in the seas around India, stated that isomers of HCH, aldrin, dieldrin and PCBs occur in water of different regions of the Indian Ocean and surrounding seas with remarkable variations in the levels of DDT between the coastal and open ocean waters. PCBS were found to be relatively in higher amounts in the surface waters of southwest Indian Ocean than the eastern Indian Ocean which he has attributed to the larger input of these chemicals from the African coast.

Most recently, Babu Rajendran et al. (2004) collected two seawater samples one each from the Chennai commercial harbor and Cuddalore fishing harbor and sediment samples from six stations in the southeast coast of India along the coastal line of Bay of Bengal. They found that the water samples had higher levels of HCHs than DDTs but the sediment samples near the major cities along this coast showed a reverse trend.

Generally, not much work was available in the published literature on the levels of persistent toxic substances in the waters along the coastal areas of India. Most of the data available are on the two classic organochlorine pesticides, DDT and HCH and some sporadic reports on PCBs, BTs, cyclodines and some other organophosphorus pesticides in the coastal environmental samples. Neverthless, some recent works showed the presence of other compounds like PBDEs, BTs, dioxins and related compounds in the Indian terrestrial and aquatic animals, necessitating the need for a survey of the aquatic occurrences for these and many other chemicals in India.

9.4.3. PTS in Indian soils and sediments

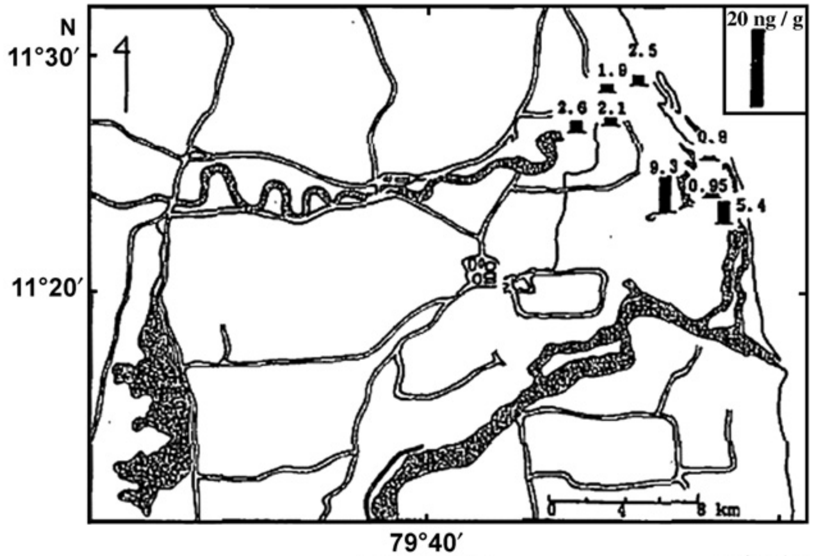
Since the early 1980s, human activity along the coastline of India has developed rapidly. People from inland cities and countryside have migrated to near coastal regions to find work and livelihood based on farming, agriculture, fishery and industry. This has invariably added to the direct inputs of various solid materials into the estuaries, inter tidal and coastal areas. The cumulative effect of the PTS residues in Indian coastal environment can be expected to be considerable in view of the fact that 25% of the India's population lives in the coastal areas (Sarkar, 1994).

Only very few studies have reported the contamination by PTS in the Indian terrestrial soils and riverine and coastal sediments (e.g., Pillai, 1986; Sarkar and Sen Gupta, 1987, 1988a,b, 1991; Ramesh et al., 1991; Sarkar et al., 1997; Sethi et al., 1999; Senthilkumar et al., 2001; Pandit et al., 2002). A review on the available information on PTS in the soils and sediments of India may be an essential prelude for understanding their effects on wildlife and human through bioaccumulation and biomagnification.

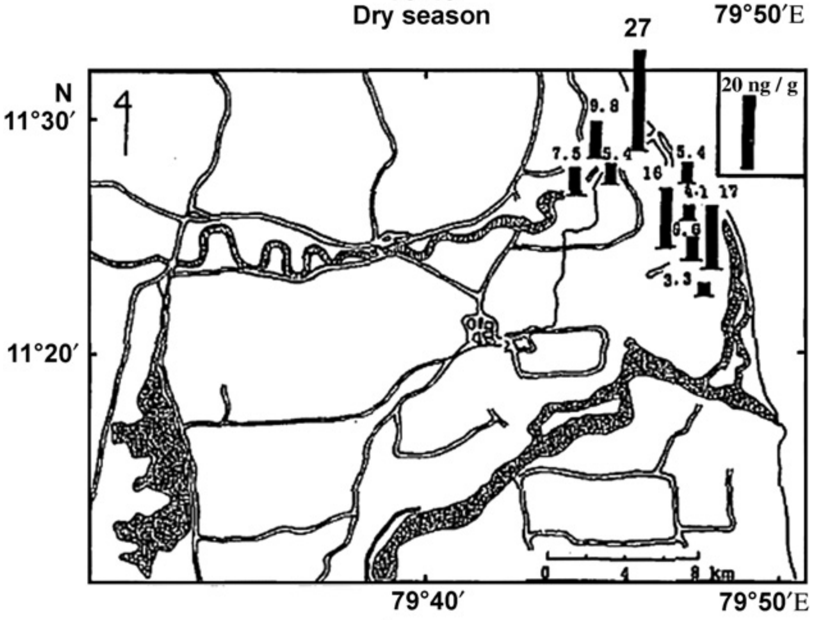
9.4.3.1. Terrestrial soils

Despite the low average consumption of pesticides, in the sporadic reports available, it could be seen that even the roadside dusts, rural and urban soils and the underwater sediments are contaminated. Many pesticides are degrading the Indian environment, even though faster dissipation and possible degradation of POPs chemicals like HCHs and DDTs were observed in Indian soils by the tropical climate of India (Pillai, 1986). Such a phenomenon of dissipation in the dry season was substantiated by Ramesh et al. (1991) in the river sediments (Fig. 9.2). Further, the relative flux of residues into the aquatic environment is smaller than the amount volatilized to the atmosphere in tropical countries like India (Tanabe et al., 1991).

Fast disappearance of HCHs from the paddy soil in India were also reported by Chawla et al. (1984) in Ludhiana, Punjab where the levels in soil decreased by 95% in 112 days, by Kathpal et al. (1984) in Hisar, Haryana where a 99% reduction was noticed after 100 days of application. Samuel et al. (1983) found 50% reduction of the HCH applied on soil in Delhi in 30–45 days. In India, the climatic conditions determine the



Dry season



wet season

Figure 9.2. Spatial distribution of HCH concentrations in Vellar river and Pichavaram mangrove sediments. Numbers on the top of each bar represent the concentrations detected at the respective sampling points (*Source*: Ramesh et al., 1991).

distribution of chemicals in the environment, including the soils (Kawano et al., 1992). Many of the studies in Indian soils (e.g., Ramesh et al., 1991; Tanabe et al., 1991; Babu Rajendran and Subramanian, 1999; Senthilkumar et al., 2001; Suresh Babu et al., 2003) underline the fact that HCHs and possibly other chemicals with similar physico-chemical properties are lost from soil layers under the subtropical conditions in India thus leading to their widespread global distribution. Apart from such studies in the 1980s and early 1990s, not much work is available on the existence of classical organochlorines such as HCHs, DDTs, PCBs levels in the terrestrial soils of India.

Most recent findings showed that the dumping site soils in India ranks third in the average concentrations of PCDDs/DFs next to the Philippines and Cambodia and followed by Vietnam (Minh et al., 2003). The magnitude of contamination in the common and agricultural soils were very much lower than the dumping soils, suggesting that open dumping sites in India are becoming a potential source of dioxins and related compounds. Further, the PCDD/DF homologue profiles of the dumpsite soils from India (Fig. 9.3) synchronized with the profiles reported for the soils representing environmental sources of these chemicals (municipal waste incinerator emissions) from United States (Brzuzy and Hites, 1995). On the other hand, the profile from the control site soil from India resembled those from urban soils, sediments and atmospheric deposition samples from various locations of the world (Baker and Hites, 2000), confirming the fact that the municipal dumping sites of India act as reservoirs and sources of these chemicals.

9.4.3.2. River and marine sediments

Several studies have reported the contamination of PTS in the sediments under Indian rivers, estuaries and coastal waters (Sarkar and Sen Gupta, 1991; Iwata et al., 1994; Sarkar et al., 1997; Sethi et al., 1999; Pandit et al., 2001; Babu Rajendran et al., 2004). Many PTS have been detected in the sediment samples of major rivers in India and especially DDTs, HCHs and cyclodine compounds were found to be predominant. As in the case of water samples, profound seasonal changes in the levels of these chemicals were found in the sediments of the rivers Yamuna and Ganges (Agnihotri et al., 1996; Sethi et al., 1999; Guzzella et al., 2005).

It was often observed that, even after heavy usage of persistent insecticides like HCHs and DDTs in India in the previous three decades, the residues in coastal sediments remained constant and lower than the levels that can not be normally expected after such heavy use (Sarkar and Sen Gupta, 1987; Pandit et al., 2001, 2002). Logically, based on all the

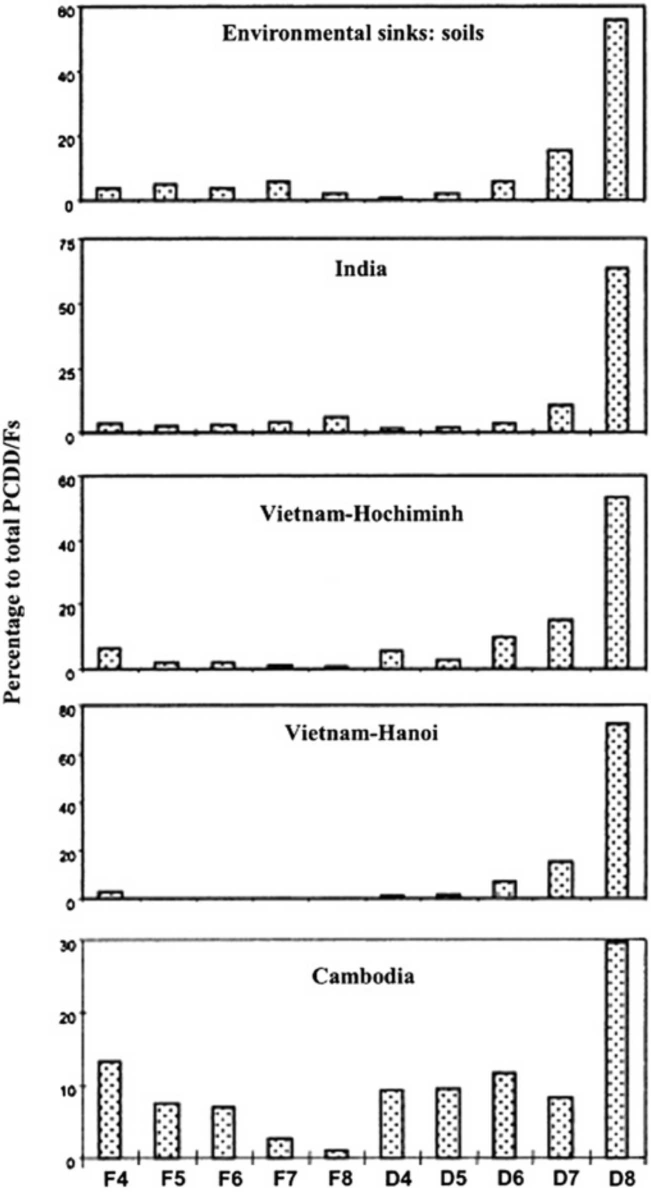


Figure 9.3. Homologue profiles of PCDD/DFs in soils from agricultural and urban areas (control sites) in Asian developing countries in comparison to the profile of samples representing environmental sinks (urban soils). Vertical bars represent the percentage of each homologue to total PCDD/F concentrations. F and D refer to dibenzofurans and dibenzo-*p*-dioxins, respectively. Numbers Figures indicate the degree of chlorination (*Source*: Minh et al., 2003).

available scientific literature, such a phenomenon can be confirmed by the fact that the Indian tropical environment is better suited and more congenial for transportation and decomposition of such chemicals. Most recently, Babu Rajendran et al. (2004), based on the water quality criteria/ guidelines designated some coastal locations of the Bay of Bengal came to the same conclusion of the previous authors that the declining trend on the environmental burden of these persistent pollutants are due to their decreasing usage and also the favorable tropical climate for easy removal from source.

Iwata et al (1994) in their study on the geographical distribution of persistent chemicals in the environmental matrices of Asia and Oceania found that the distribution patterns of organochlorines in the sediments showed smaller geographical variations (Fig. 9.4) when compared to air (Fig. 9.5) and water (Fig. 9.6). When comparing these figures it could be seen that HCH and DDT showed a clear regional trend with higher values in the tropical region than in Japan and Australia. HCH residue levels in air and water were found to be particularly higher in India. But a uniform distribution of these OCs in sediments may be explained by their rapid evaporation from water phase to atmosphere because of the prevailing high temperature.

The studies of Ballschmiter and Wittilinger (1991), Sunito et al. (1988) and Iwata et al. (1994) indicates that levels of semi-volatile chemicals used in India, as in similar tropical countries, are gradually redistributed to colder regions on a global scale, leaving only lower loads in the Indian environmental matrices. Although some of these chemicals show higher values in the environmental compartments (e.g., HCHs in atmosphere), majority of PTS that are used in India will be carried away by air and water to far away regions of the globe with advancement of time, leaving only lower levels of residues in the biota, except in organisms near to local sources.

9.5. PTS in Indian flora and fauna

9.5.1. Plants

India is one among the mega-biodiversity nations in the tropical belt. Both plants and animals belonging to many orders comprising many genera have been analyzed in the world for their PTS content for understanding the levels, toxic effects, metabolism, etc. Starting from zooplankton to human, many animals have been analyzed for their PTS content but not much information is available on plants. Generally, the

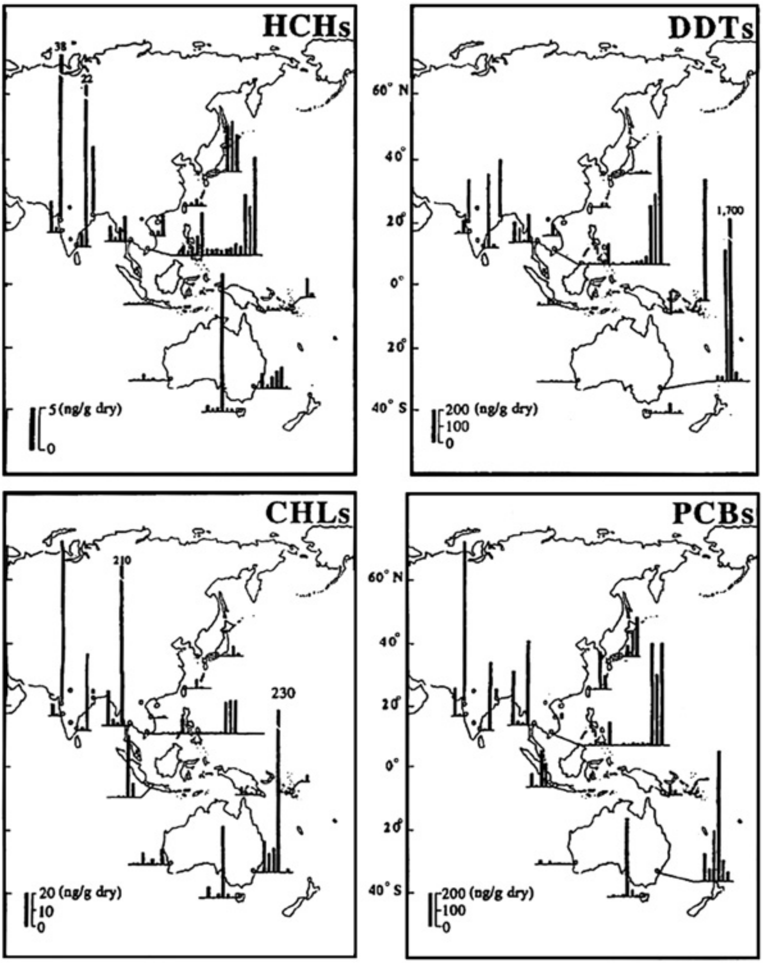


Figure 9.4. Distribution of persistent organochlorines in river and estuarine sediments from the eastern and southern Asia and Oceania (*Source*: Iwata et al., 1994).

available scientific literature on PTS pollution in Indian environment and biota, especially with regard to the information on the floral assemblages of India are less when compared to those available from developed nations, because of the lack of instrumental and manpower facilities. Considerable amount of information is available on the agricultural soils but not actually on the plants themselves. At the same time, some information is available on the plant products (food stuff) of India (See Section 9.7 of this chapter). With regard to paddy plants, it was found that notwithstanding

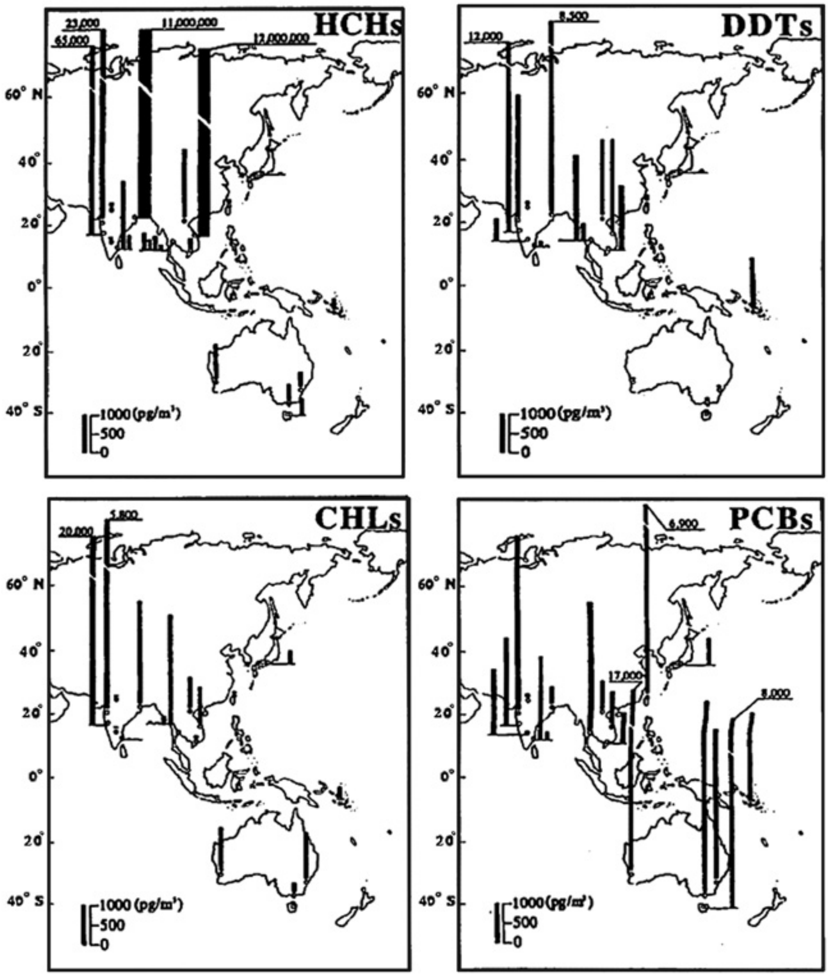


Figure 9.5. Distribution of persistent organochlorines in river and estuarine air from the eastern and southern Asia and Oceania (*Source*: Iwata et al., 1994).

several possible variations, only a meager amount of HCHs sprayed remained in the plant leaves (Fig. 9.7) two weeks after application, the major portion of which was carried over to the atmosphere. In the same way Suresh Babu et al. (2003) found higher amounts of both the chemicals in the husk rather than in the grain, straw and root of Basmati rice (*Oryza sativa*). Even then the levels were low compared with environmental levels. Most of the information in India on samples of plant origin are on the food products rather than on plants.

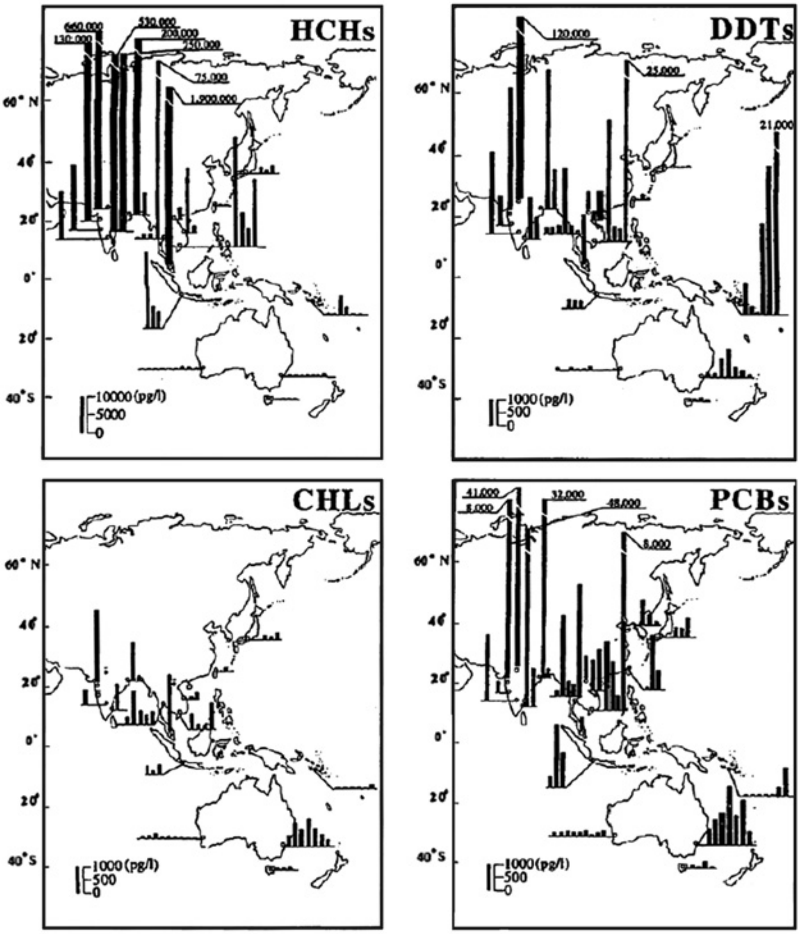


Figure 9.6. Distribution of persistent organochlorines in river and estuarine water from the eastern and southern Asia and Oceania (*Source*: Iwata et al., 1994).

9.5.2. Animals

As in many developed and some developing nations, Indian wildlife have been widely surveyed for the distribution and toxicology of many of the PTS chemicals. The animals widely surveyed are mussels (Ramesh et al., 1990; Kan-atireklap et al., 1998; Sudaryanto et al., 2002), birds (Ramesh et al., 1992; Sethuraman and Subramanian, 2003; Kunisue et al., 2003a,b; Watanabe et al., 2005), bird-eggs and bats (Senthilkumar et al., 2001), fish (Kannan et al., 1995; Das et al., 2002), river dolphins (Kannan

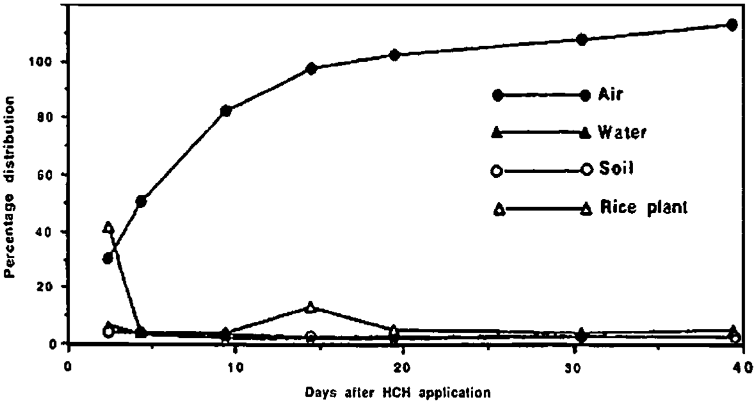


Figure 9.7. Residual amounts (%) of HCH in various compartments of the experimental paddy field (*Source*: Iwata et al., 1994; Tanabe et al., 1991).

et al., 1994; Senthilkumar et al., 1999a; Subramanian et al., 1999) and marine mammals (Tanabe, 1999; Tanabe et al., 1993; Karuppaiah et al., 2005).

9.5.2.1. Zooplankton

Sarkar (1994) while reviewing the occurrence and distribution of persistent chlorinated hydrocarbons in the seas around India found that among these chemicals, compounds of DDT family was abundant in the northeastern Arabian Sea as also observed by various other authors of his group (Kureishy et al., 1978; Kannan and Sen Gupta, 1987; Shailaja and Sen Gupta, 1990; Sarkar, 1991). These authors reported a concentration of up to 500 ppb DDTs in the zooplankton of this region. They have attributed such high concentrations in zooplankton to the input of huge amounts of DDT into the coastal water through agricultural drainage from the adjoining areas and river runoffs and also due to the availability of rich organic matter in the areas on which the OCs adsorb and are in turn fed by the zooplankton. Sarkar (1994) also found varying levels of PCBs (17.6–105 ppb) comprising of 31 congeners in zooplankton from the Arabian Sea, the levels being higher in coastal samples and steadily decreasing towards offshore regions. According to the authors the source of PCBs is the coastal industrial installations. Other than these works, nothing could be seen in the literature on the levels of PTS in Indian planktonic organisms.

9.5.2.2. Mussels

Ramesh and co-workers found that in green mussels (*Perna viridis*), the concentration ranges of OCs are in the order of HCHs > DDTs > PCBs (Ramesh et al., 1990). The green mussels collected from the same or nearby locations in India by Ramesh et al. (1990), Kan-atireklap et al. (1998) and Monirith et al. (2003) showed a clear chronologically decreasing trend in the case of HCHs and DDTs (Fig. 9.8), showing that the restrictions imposed on their usage by the Government of India are effective and the Indian environment is becoming cleaner in the case of these classical organochlorines. Further Kan-atireklap et al. (1998) found measurable levels of butyl tin compounds (ΣBTs = MBT + DBT + TBT) which were lower in international comparison, in most of their green mussel samples.

HCHs was always higher in the mussel samples in India in international comparison during all the above years showing that India has been using enormous quantities of this chemical since its introduction. The DDTs levels were also comparatively higher than the developed countries, but the PCBs, HCB, CHLs and BTs levels were lower. Further, the continuing contamination by one or the other chemicals in the coastal region of India as revealed by the available literature on mussels is a matter of concern. Other than the above-cited literature, to our knowledge, no other work on the PTS chemicals in mussels of India has been carried out so far. It may be informative, if the mussels are analyzed in future to render a clear picture on the PTS contamination in India (Tanabe and Subramanian, 2006).

9.5.2.3. Fish

Ramesh et al. (1992) by carrying out an elaborate survey in the Bay of Bengal region on the trends of persistent organochlorine contaminants in wildlife stated that, unlike in the case of birds where a wide variation could be seen, differences of OCs in fish were generally comparable to values reported from other locations of the world, suggesting that the bioavailability of the contaminants to the aquatic fauna is less due to the smaller flux and shorter residence time of these chemicals in the tropical climate of India. Interestingly, the works of Das et al. (2002) on DDTs in the catfish (*Tachysurus thalassinus*) from the Bay of Bengal region south of Bangladesh, Guruge and Tanabe (2001) in mullets from Sri Lanka and Senthilkumar et al. (2001) in the different fish species collected from southern Bay of Bengal points out the complicated sources of

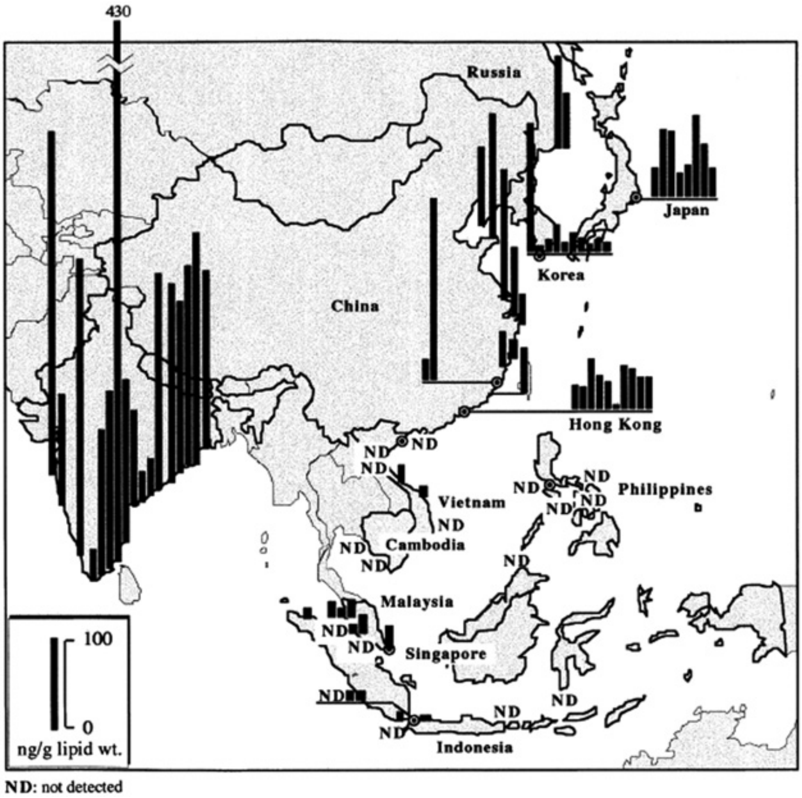


Figure 9.8. Distribution of concentrations of HCHs in mussels collected from coastal waters of some Asian countries (*Source*: Monirith et al., 2003).

contamination to the coastal waters of Bay of Bengal by the input from surrounding countries.

Generally, the contamination of HCHs and DDTs in fish (both inland and marine) reflects the trends of their usage in the adjacent terrestrial area during the time of sampling. Greater concentrations of HCHs than DDTs in Indian fish, despite the higher bioaccumulation potential of DDTs might be due to the increased consumption of HCHs and the phasing out of DDTs from usage in agriculture earlier than HCHs. The trend is slowly changing and the levels of both these pesticides are going down in Indian wildlife and foodstuff, which is evident from our most present data.

Apart from POPs chemicals, data are available on butyltin contamination in Indian fish. Similar to some Oceanian countries, these chemicals were widely detected in fish muscle tissues from many Asian countries including India, suggesting their widespread contamination. Kannan et al. (1995) analyzed few samples from several countries and found that fish from Bangladesh contained relatively high butyltin concentrations with a maximum of 109 ng g^{-1} wet wt. followed by those from India up to 79 ng g^{-1} wet wt. (Table 9.3).

The authors further found that in India, the marine fish collected from the coastal regions of the cities Mumbai (Bombay) and Kolkata (Calcutta) contained higher concentrations of buytltin than those from the inland city Delhi because the marine fish might have been greatly contaminated by antifouling paints and sewage from inland areas compared to those from inland fish (mainly freshwater species).

In general the dietary intake of classical organochlorines like DDTs, HCHs, etc. are decreasing at present and that of the other modern chemicals like BTs also do not exceed the average daily intake (ADI) in India. But the varying conditions of contamination in fish depending on multitude of parameters warrants a continued surveillance of the sources and factors that control the concentrations of these chemicals in fish, which are one of the major food items and also a major source of persistent chemicals to humans.

9.5.2.4. Birds

India is a haven for bird and has over 1200 species of birds from 20 orders and 17 families and also receives millions of migrating birds every year (Ali, 1979; Gaur, 1994). But only limited numbers of publications are available on the occurrence and effects PTS levels in Indian birds. It has long been reported that migratory as well as resident avian species of India gets contaminated by various PTS chemicals to different extent. Infochange India News (http://infochangeindia.org/toxictours) has stated that the Saurus cranes and white peaked vultures living in India are in danger of pesticide toxicity, by the chemicals like aldrin, dieldrin, heptachlor and DDT.

As early as in 1981, Kaphalia and co-workers reported measurable levels of organochlorine pesticide residues in some wild Indian birds. Later, a report from the Mahala water reservoir of Jaipur, India (Misra and Bakre, 1994) has reported the presence of HCHs, aldrin and DDTs in the resident and migratory bird species like fantail snipe, red wattled lapwing, blackwinged stilt, flamingo and pied wagtail. Several reports were published by the research group at the Center for Marine Environmental Studies at Ehime University of Japan on the occurrence of PTS chemicals in Indian birds through their work in the last two decades

Table 9.3. Concentration ranges (ng g^{-1} wet wt.) of BTs in fish from different regions of the world

Location (year surveyed)	MBT	DBT	TBT	References
Alaska, USA (1981–1984)	na	na	280–900	Short and Thrower, 1986
East, Gulf and Pacific Coast, USA (1986–1991)	20–190	17–1300	26–610	Krone et al., 1995
The Netherlands (1993)	23–41	13–183	9.2–67	Stab et al., 1996
River Elbe and North Sea, German (1993)	89[a]	55[a]	66–490	Shawky and Emons, 1998
Baltic Sea, Poland (1997)	8.0–43	8.0–530	17–2700	Senthilkumar et al., 1999
Japan (1992)	na	3.9–49	8.9–450	Suzuki et al., 1992
Otsuchi Bay, (1994–1995)	<9.0–66	1.8–60	4.2–210	Takahashi et al., 1999
Otsuchi Bay, Japan (1996)	na	na	10–20	Harino et al., 1998a
Osaka Port, Japan (1996)	25–83	2.0–18	11–250	Harino et al., 1998b
Australia (1990–1992)	<4.0–42	<0.36–3.1	<0.13–13	Kannan et al., 1995a
Oceanian countries (1990)	<4.0–8.0	<0.36–0.98	<0.13–0.15	Kannan et al., 1995a
India (1989)	<5.6–78	<0.36–0.65	<0.13–1.6	Kannan et al., 1995a
Bangladesh (1994)	<5.6–170	<0.36–15	0.47–3.0	Kannan et al., 1995a
Thailand (1994)	<5.6	1.6–2.6	1.3–13	Kannan et al., 1995a
Vietnam (1990)	<5.6	<0.36–0.78	<0.13–0.90	Kannan et al., 1995a
Taiwan (1990)	<5.6–13	0.36–2.1	0.13–5.2	Kannan et al., 1995a
Taiwan (1997)	2.8–11	5.8–16	nd	Hung et al., 1998
Malaysia (1998)	2.5–7.4	<1.3–13	2.4–190	Sudaryanto et al., 2004
Indonesia (1991)	<5.6–10	0.41–4.8	<0.13–3.7	Kannan et al., 1995a
Indonesia (1998)	0.93–14	<1.5–18	1.4–52	This study

Note: All values originally reported as butyltin-Sn or butyltin-Cl concentrations are converted here to butyltin ions, nd = not detected, na = no data available.

[a] Maximum concentration.

Table 9.4. Mean concentration (ng g^{-1} wet wt.) of organochlorines in Indian wild birds according to feeding habit

Trophic group	*n*	HCHs	DDTs	PCBs	HCB
Inland piscivores and scavengers (cattle egret, pond heron, Brahmney kite, pariah kite)	17	1400	480	25	0.20
Coastal piscivores (Kingfisher, brown-headed gull, black-headed gull)	7	680	380	36	0.98
Insectivores (swallow, lapwing, Kentish, plover)	8	250	190	42	0.24
Omnivores (chicken, house crow, jungle crow)	17	190	64	15	0.08
Granivores/occasionally insectivores (duck, Water hen, parakeet)	7	23	1.9	7.0	0.07

(Ramesh et al., 1992; Tanabe et al., 1998a; Tanabe 2000; Senthilkumar et al., 2001; Kunisue et al., 2003a,b). Sethuraman and Subramanian (2003) also found considerable levels of HCHs and DDTs in several species of migratory and resident birds collected from the state of Tamil Nadu, southern India. Very clear differences in the PTS loads based on feeding habits of the birds from India were observed as inland piscivores & scavengers > coastal piscivores > insectivores > omnivores > granivores (Table 9.4) by these authors identical to the pattern that was observed by Fybe et al. (1991) in Latin American birds and Frank et al. (1977) in the birds collected from Kenya.

All these reports showed that the HCH residue levels in Indian birds were quite high, while the PCB and DDT concentrations were lower than in the birds from developed nations. One of these studies (Tanabe et al., 1998a) also showed that the migrating birds that stop over in India are heavily exposed to HCHs.

Trends of PTS in the birds from India can classified as those in (1) strict residents (living in the same region for their entire life span), (2) local migrants (which migrate only between Himalaya and South Indian regions), (3) short-distance migrants (those breeding in central Asia, southern Russia, central China, Gulf of Oman, eastern Russia, southern Europe and the Middle East) and (4) long-distance migrants (which have their breeding grounds in northern Europe, eastern to southeastern Russia, western Europe to eastern Russia, Arctic Russia, the Middle East, Papua New Guinea and Australia). Residue patterns of organochlorines in most resident birds were in the order of HCHs > DDTs > PCBs > CHLs = HCB. In general, the contamination pattern observed in the birds collected in India indicates higher exposure to HCHs and DDTs and low concentrations of PCBs in strict residents and local migrants (Senthilkumar et al., 1999b).

It is interesting to note that from the variations in the levels of dominant organochlorines in the migratory birds wintering and breeding in India, their species-specific migratory routes could be determined. It was reported that the migratory birds collected from India have their stopover sites and breeding grounds in China, Russia or around Persian Gulf, Red Sea, Caspian Sea and Mediterranean Sea regions (Fig. 9.9) (Kunisue et al., 2003a).

While Tanabe et al. (1998a) found clearly low concentrations and body burdens of PCBs, DDTs and HCHs in females of little ringed plover, common redshank and white-cheeked tern collected from India, sex related tissue accumulation was not found in Indian birds by Ramesh et al. (1992).

Highest concentrations of HCHs, DDTs and PCBs were found in the egg yolks of house crow followed by sparrow, red jungle fowl, spotted dove, collard dove, white wag tail, turkey, baya weaver and blue rock pigeon by Senthilkumar et al. (2001). In general, in the granivorous or paaserine birds, accumulation of organochlorines in eggs was less than that in omnivorous birds like house crow and sparrow.

A recent finding that the residue levels of organochlorines and PCDDs/DFs and their toxic equivalents (TEQs) in the breast muscle of crows from Perungudi, the dumping site for the municipal wastes of Chennai city were significantly higher than those from Chidambaram, the reference site situated 250 km south of the dumping site reiterates the earlier findings in the soils by Minh et al. (2003). The estimated bioconcentration factors of individual congeners indicated soil as one of the prime sources of dioxins and related chemicals to crows and also the molecular size of the congeners play a significant role in their bioconcentration (Watanabe et al., 2005).

The residue levels of HCHs observed in the birds collected during 1995 (Tanabe et al., 1998a) were greater than those observed by Ramesh et al. (1992) in the birds collected during 1987 and 1991 in the same location. Levels of DDTs and PCBs have also increased slightly during this period, showing the continued exposure or increased pollution by these compounds in India during the period. Because of the recent ban or restrictions on HCHs and DDTs in India, the concentrations in biota may go down, but it may be expected that PCBs contamination in India may increase due to rapid industrialization. Further, the detection of other PTS chemicals like PCDDs/DFs in Indian birds indicates a new paradigm of pollution erupting in Indian birds and the birds wintering there.

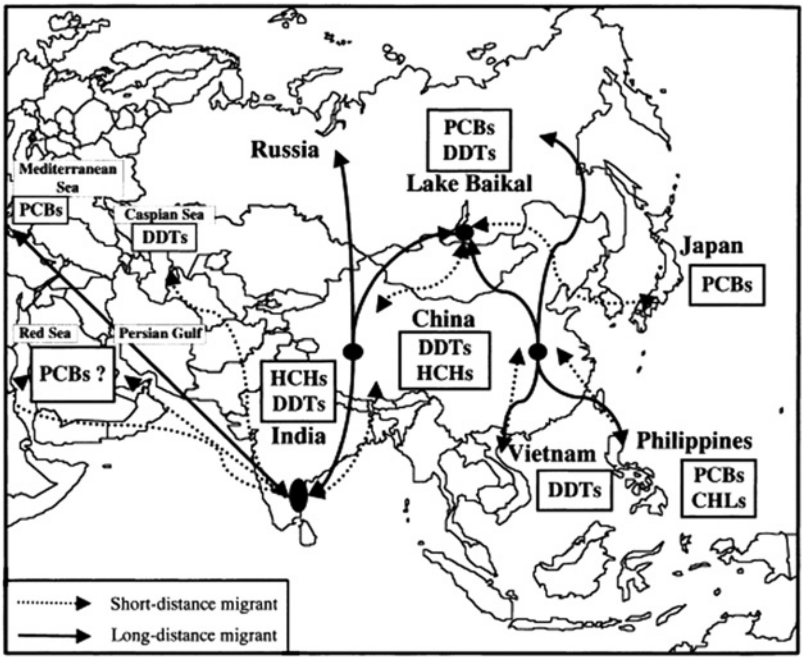


Figure 9.9. Migratory patterns predicted from accumulation features of organochlorines in migratory birds collected from the Philippines, Vietnam, India and Lake Baikal (Russia). Organochlorines in a square represent dominant contaminants in respective area (*Source*: Kunisue et al., 2003a).

9.5.2.5. Mammals

9.5.2.5.1. Terrestrial mammals

In land-based mammals of India most of the works were carried out in the animals which are normally used as food by humans. For example Seth and Kaphalia (1983) found low levels of DDTs and high levels of HCHs in the slaughter house samples. Another Indian study (Nigam et al., 1998) found 10–33 $\mu g\ kg^{-1}$ DDT and 10–295 $\mu g\ kg^{-1}$ HCH in food animals. Some of these have been reviewed by the Global Environmental Facility under the umbrella of the United Nations Environment Programme (UNEP Chemicals, 2002). There are many other data available on the mammalian food animals and their products from India and we will give a brief account under Section 9.7 of this chapter.

9.5.2.5.2. Aquatic mammals

While browsing through the literature we could find only very few publications on the levels of HCHs, DDTs and PCBs in three species of marine mammals of India, *Sousa chinensis*, *Tursiops truncatus and Stenella longirostris* (Tanabe et al., 1993; Karuppaiah et al., 2005) and one species of river dolphin, *Platanista gangetica* (Kannan et al., 1993; Subramanian et al., 1999; Senthilkumar et al., 1999a). Later the samples from some of the above specimens were used for measuring the other organic contaminants like butyltin compounds (Iwata et al., 1994) and tris(4-chlorophenyl)methane (TCPMe) and tris(4-chlorophenyl)methanol (TCPMOH) (Minh et al., 2000a) and also to explain certain parameters in organochlorine accumulation in cetaceans (Kannan et al., 1994; Minh et al., 2000b).

Among the organochlorine compounds measured in these three species of marine mammals from the southeast coast of India, Tanabe et al. (1993) found that the concentrations of DDTs ranked first, followed by PCBs, HCHs and HCB (Table 9.5). In spite of its low levels in the Indian environmental samples and terrestrial biota (Ramesh et al., 1989, 1990, 1991, 1992; Tanabe et al., 1990; Kannan et al., 1992) DDTs were found to be predominant in the blubber tissues of the dolphins collected from the coastal areas of southeastern India.

A wide range of organochlorines were detected in the blubber, muscle, liver and kidney of four Ganges river dolphin (*Platanista gangetica*) specimens (Kannan et al., 1993) in the order of DDTs $>$ PCBs $>$ HCHs $>$ aldrin and dieldrin$>$heptachlor and heptachlor epoxide$>$HCB, similar to that observed by Tanabe et al. (1993) in the dolphins of Bay of Bengal. Levels of DDTs in the blubber were 10–30-fold higher than those of PCBs. Subramanian et al. (1999) analyzed further specimens of Ganges river dolphins and one milk sample collected from different locations of river Ganges and found that the accumulation pattern of organochlorines as DDTs $>$ PCBs $>$ HCHs $>$ CHLs $>$ HCB was same as previously reported in Ganges river dolphins by Kannan et al. (1993) and in marine dolphins of India by Tanabe et al. (1993).

In the blubber samples of three spinner dolphin (*Stenella longirostris*) specimens, Iwata et al. (1994) found very low levels of butyl tin compounds (2 ng g^{-1} wet wt.) of tri-, di- and monobutyl tins. In the same three specimens Minh et al. (2000a) found 31 ng g^{-1} (8.7–63) of TCPMe and 36 ng g^{-1} (10–58) of TCPMOH in the blubber which are lower than the values found in marine mammals from the colder mid-latitude oceans. Other than the above-cited works, we could not find any other literature providing information on the quantities of persistent toxic substances in the tissues of aquatic mammals of India.

Prudente et al. (1997) compared the data from humpback dolphin and spinner dolphin of Bay of Bengal (Tanabe et al., 1993) in a global comparison of PTS in 11 species of male odontoceti and (Fig. 9.10) and found

Table 9.5. Concentration of persistent organochlorine residues in blubber of dolphins from Porto Novo (Bay of Bengal) coastal waters, South India

	Concentrations (ng g^{-1} wet wt.)												
Sample no.	α-HCH	β-HCH	γ-HCH	δ-HCH	ΣHCH	*p,p′*-DDE	*p,p′*-DDD	*o,p′*-DDT	*p,p′*-DDT	ΣDDT	PCBs	HCB	Fat (%)
Spinner dolphin (*Stenella longirostris*)													
DO(01)90	63	160	27	19	270	1700	3800	540	3400	9400	470	13	22
DO(03)90	94	230	39	12	380	16,000	1600	150	4700	22,000	580	13	48
DO(07)90	27	110	10	11	160	11,000	1000	96	3300	15,000	410	3.6	69
DO(08)90	16	36	4.2	3.6	60	3700	140	43	630	4500	240	1.1	43
DO(01)91	410	330	100	21	860	23,000	2600	610	9200	35,000	950	13	48
Bottlenose dolphin (*Tursiops truncatus*)													
DO(02)90	24	82	15	10	130	4700	1000	12	160	5900	390	4.8	69
DO(05)90	33	90	15	4.1	140	6100	840	5.4	59	7000	370	12	53
DO(09)90	5.8	50	3.8	3.8	63	2100	17	6.5	9.8	2100	670	13	40
DO(02)91	15	160	12	5.2	190	9200	3700	46	1300	14,000	630	2.8	67
Humpback dolphin (*Souse chinensis*)													
DO(04)90	29	150	18	2.8	200	5600	1500	40	3700	11,000	960	4.6	52
DO(06)90	110	960	47	6.3	1100	10,000	850	20	690	12,000	1800	0.5	93
DO(03)91	39	150	19	9.4	220	9300	2000	20	3100	14,000	920	2.6	91

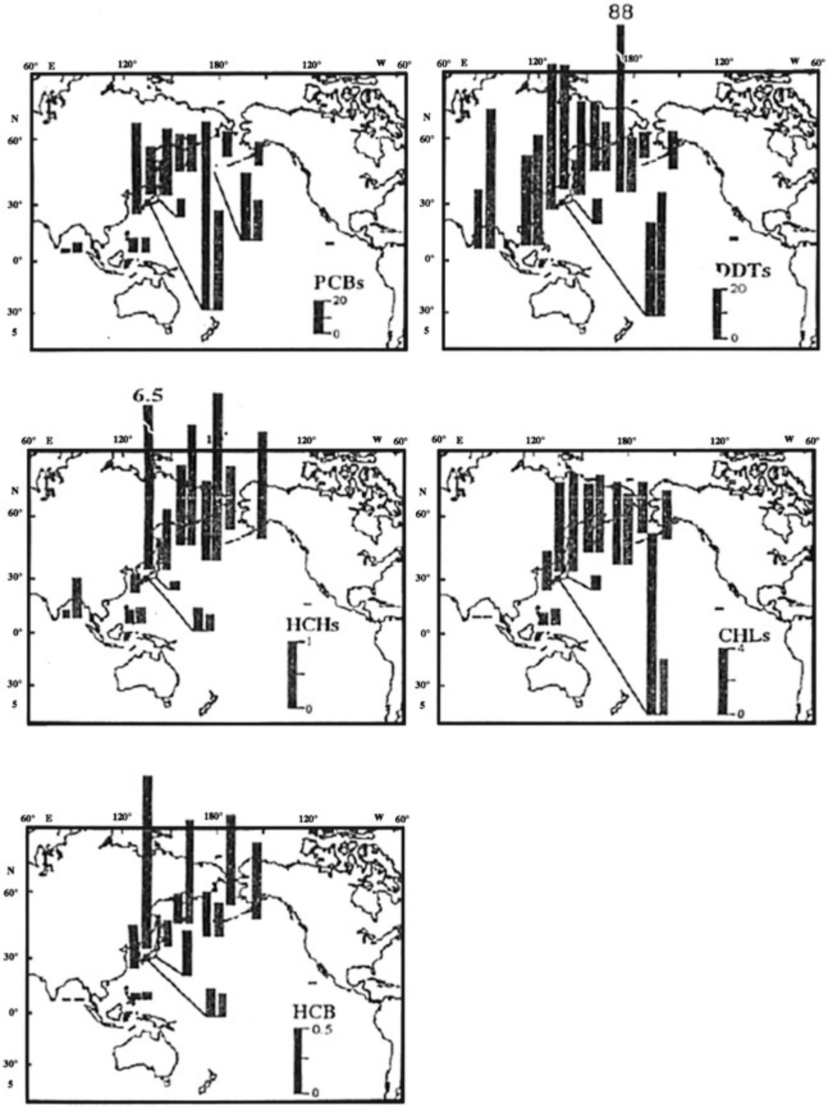


Figure 9.10. Distribution of DDTs, PCBs, HCHs, CHLs and HCB residue levels μg g^{-1} wet wt.) in odontoceti animals from various locations of the North Pacific, Indian Ocean and nearby seas (*Source*: Maricar et al., 1997).

high concentrations of DDTs in the blubber of tropical water species, indicating the current usage of DDT in the tropics and the less movable nature of this compound via long-range atmospheric transport. HCH levels in animals inhabiting cold and temperate waters were higher than those inhabiting tropical waters, a result that was perhaps reflective of easier atmospheric transport of the chemical from the tropical source to northern sinks.

Minh et al. (2000a) while comparing the contamination of persistent endocrine disruptors in cetaceans from the North Pacific and Asian coastal waters including Indian specimens showed that the latitudinal distribution of TCPMe and TCPMOH in cetaceans from North Pacific Ocean and Asian coastal waters was similar to DDTs, suggesting the less transportable nature of these compounds. Toxic evaluation of coplanar PCBs using TEQs concept indicates an increasing impact on the animals of mid-latitudes. On the other hand, the cetaceans at lower and higher latitudes, including the dolphins from Bay of Bengal, India are not under threat by dioxin like congeners of PCBs.

Apart from the above species, it was shown by Kannan et al. (2005) that the Irrawaddy dolphins from the Chilika Lake (Chilika Lagoon) of India had the same pattern of distribution of OCs as observed in the above four species of aquatic mammals of India, with DDTs as the predominating compound followed by HCHs, PCBs, HCB, TCPMe and TCPMOH in order.

9.6. PTS in Indian human

In spite of the large amount of data available on the classical organochlorines and other chemicals in wild animals all over the world only very limited works are available on PTS levels in human samples, most of the recent works being in human breast milk (Tanabe and Subramanian, 2006). From the late 1990s there has been a steady increase in the works on PTS in Indian human samples. The most widely used samples from human are the human milk followed by blood, liver, hair, muscle and urine.

9.6.1. Blood

Testing of the blood serum samples conducted in India regularly by some research groups, especially by the National Institute of Occupational Health (NIOH) shows temporal reduction of HCHs, DDTs and HCB in the blood serum of healthy volunteers from Ahmedabad area in the year 2001 when compared with the samples of the 1980s (Bhatnagar, 2001; Bhatnagar et al., 2004) which may be due the imposition of restrictions on the usage of these chemicals for agriculture in India. Levels of DDTs reported from Delhi in the year 1980 (Ramachandran et al., 1984) and

1985 (Saxena et al., 1987) were higher than in Ahmedabad. HCHs in the year 1982 (Ramachandran et al., 1984) from different cities of India were very much higher than those reported by Bhatnagar (2001) and Bhatnagar et al. (2004) in Ahmedabad samples. Studies from another urban area (Lucknow) in the samples of the 1980s showed comparable levels to Ahmedabad samples (Kaphalia et al., 1981; Siddiqui et al., 1981a) while Rao and Banerji (1989) found somewhat higher levels of PCBs in human blood samples from Bombay (Mumbai), showing the tedium in having a generalized picture of human PTS contamination in India.

An attempt by the scientists at the NIOH, Ahmedabad, India to provide a database on the residues of total PTS chemicals in Indian human blood serum showed that the total organochlorine insecticide content is in an average of 200 ppb with a range of 58.3–321 ppb. Among these chemicals HCHs and DDTs were the chief contaminants and the order of persistency was HCH $>$ DDT $>$ dieldrin $>$ oxychlordane $>$ heptachlor $>$ aldrin. Heptachlor epoxide and HCB were not present (Bhatnagar et al., 1992).

Interestingly, a study on German children and adolescents showed that two girls of the age of 10 and 13 (born to an Indian father and a German mother), who had a holiday stay in India had DDE plasma levels of 11 and 12 μ gl^{-1} while the range values for samples from 130 children were between 1.46 and 2.09 μ gl^{-1}, respectively. DDTs were also higher in those two children (1.44 and 1.11 μ gl^{-1}) while the corresponding range values were from 0.02 to 0.06 μ gl^{-1}, respectively. The authors have argued that higher accumulation of these chemicals might have probably obtained through exposure in India during their recent holidays (Heudorf et al., 2003) showing the possibility of the higher amount of exposure to these chemicals by Indian resident population.

9.6.2. Urine

Almost all the PTS chemicals being lipophilic, non-degradable and not easily excreted from animal bodies were not found in considerable concentrations in the animal excreta like feces and urine. The only study by Singh et al. (2004) on impact assessment of sewage treatment plants on the environmental quality of the waste disposal area in Varanasi and Kanpur, two big cities in India showed that the mean values of HCHs and DDTs in the urine samples of the people in the exposed area were higher than those living in unexposed areas, the levels being lower than those in blood of the same subjects. Other than these, we could not find any other data available in the published literature on the levels of PTS in Indian human urine or feces.

9.6.3. Fat

The presence of organochlorine pesticides in Indian human fat samples have been reported by various authors as early as from the 1960s (Dale et al., 1965; Ramachandran et al., 1973, Bhaskaran et al., 1979; Siddiqui et al., 1981a). Studies conducted to monitor pesticide residues in autopsy fat samples from different parts of India indicated a nationwide variation (Anonymous, 2001), increasing age trends of organochlorines with the maximum DDT residues in age group of 20–39 years and no sex difference for both the chemicals (Jeyaratnam, 1985). Later, Bhatnagar (2001) in his review article on pesticide pollution in India told that the wide variation of HCHs and DDTs seen among different populations may be due to the geographical variations in consumption and usage pattern, chemical intensity, efficiency of absorption, age, nutritional status and integrity of the organs.

Apart from such complications that may occur during the accumulation of PTS chemicals in humans, interesting chronological patterns of the ratios between HCHs and DDTs were observed in the studies conducted in the 1960s and 1980s in India. For example DDT concentrations in Indian human adipose tissue collected in the year 1964 were nearly 18 times higher than the HCHs (Dale et al., 1965) than in the samples collected during 1971 by Siddiqui et al. (1981b) in which the DDTs were only 1.5 times higher than HCHs. Increased usage of HCHs both in agriculture and vector control and the restrictions imposed on DDT usage in between those years might be the reason for such a temporal increase of HCH levels in human tissues in India (Tanabe et al., 1990).

In an interesting work in Farah, Mathura District, India, Dua et al. (1998) collected the skin lipids from face and blood from the occupationally exposed and unexposed volunteers and found that the levels of both HCHs and DDTs were higher in the samples obtained from the exposed group. They have also found an increase in the levels of both the compounds in Delhi population when compared with the data reported in previous publications on the concentrations in the adipose tissue collected a decade before in Delhi (Ramachandran et al., 1984) and several other parts of India (Kaphalia and Seth, 1983), reflecting the intensive use of these pesticides for malaria control in the sampling area.

9.6.4. Milk

Indian breast milk could be used as a sort of indicator for understanding the biological specificity in the accumulation of organochlorines in the tropical environment as well as assessing the extent of environmental pollution in similar countries by these chemicals (Tanabe et al., 1990). In an interesting study in the southeastern locations, Madras (Urban), Chidambaram (semi urban), Nattarasankottai (rural) and Parangipettai (fishing village) (Table 9.6), HCHs concentrations followed the different exposure patterns of the donors. At Chidambaram and Nattarasankottai, where higher levels of HCH isomers were observed in breast milk all the donors were living in an agricultural area and had some connection with agriculture and most of them were vegetarians. Lower levels of HCHs were found in the samples from Madras and Parangipettai, where all the donors were nonvegetarians. This indicates the fact the intake of HCH isomers through foodstuff of animal origin is not significant in India. Indeed high levels of HCHs have been documented in vegetables (Lal et al., 1989), cereals (Noronha et al., 1980) and edible oils and oil seeds (Dikshith et al., 1989) from India.

Unlike HCH isomers, regional differences in DDT concentrations and effect of dietary habits on human uptake were found to be smaller (Tanabe et al., 1990). The authors also reported the occurrence of PCBs in Indian human breast milk for the first time (120 ng g^{-1} fat wt.) which were very much lower than those in developed nations like Japan (1100 ng g^{-1} fat wt.—Yakushiji et al., 1979) and USA (1500 ng g^{-1} fat wt.—Wickizer et al., 1981) but were only slightly higher than in Vietnam (100 ng g^{-1} fat wt.) and Thailand (60 ng g^{-1} fat wt.) (WHO, 1988). Unlike in developed countries where fish were found to be the prime source of PCBs to human through diet (Watanabe et al., 1979; Noren, 1983), the milk samples from fisherwomen of Parangipettai, who consumed fish almost every day did not have higher concentrations of PCBs or other OCs, implying that the major source of OCs contamination is not present in coastal areas in India but probably lie in the inland regions. Further to this, in the northern Indian state of Punjab, the human milk samples from intensive cotton growing areas had significantly higher concentrations of both HCHs and DDTs than those in samples from areas where cotton is sparsely grown (Kalra et al., 1994), the median values of DDTs (0.52 μg g^{-1} fat wt.) and HCHs (0.19 μg g^{-1} fat wt.) in samples of human milk from cotton growing areas being higher than those from most other countries in the world.

Banerjee et al. (1997) found 3.4 times higher levels of HCHs in 61 milk samples from Delhi than those from Lucknow (Siddiqui et al., 1981a). Sanghi et al. (2003) found endosulfan, malathion, chloropyrifos, methylparathion and HCHs in human milk samples collected from Bhopal, India. Again, with respect to the classical organochlorine pesticides in mothers' milk in big cities and rural areas in the present decade, Nair et al. (1996) found 1.27 mg l^{-1} fat wt. of DDTs and 0.33 mg l^{-1} fat wt. of

Table 9.6. Concentration of HCHs, DDTs, and PCBs (ng/g of fat) in human milk from South India

Sample no.	Fat content (%)	HCHs					DDTs				
		α-HCH	β-HCH	γ-HCH	δ-HCH	ΣHCH	*p,p′*-DDE	*p,p′*-DDD	*p,p′*-DDT	ΣDDT	PCHs
CM1	0.48	2100	18,000	310	320	21,000	770	< 1.0	260	1000	27
CM2	1.9	270	4700	19	29	5000	370	9.5	100	640	21
CM3	3.3	290	6700	28	17	7000	840	< 1.0	160	1000	660
CM4	2.2	380	4500	40	30	5000	1300	17	240	1600	23
CM5	0.26	1300	6500	150	130	8100	340	< 1.0	160	500	26
CM6	0.80	310	1100	130	100	1600	32	< 1.0	71	100	30
CM7	1.5	410	7200	49	56	7700	880	< 1.0	210	1100	72
CM8	2.4	490	3800	51	82	4400	180	< 1.0	69	250	30
CM9	3.1	160	3200	6.3	9.3	3400	1700	< 1.0	210	1900	270
CM10	1.5	1600	24,000	52	54	26,000	2100	< 1.0	270	2400	770
CM11	3.4	360	6900	21	21	7300	750	< 1.0	96	850	52
Mean		700	7900	78	77	8800	840	2.4	170	1000	180
		(8)	(90)	(1)	(1)	(100)	(83)	(0.2)	(17)	(100)	
CP1	15	100	940	12	15	1100	68	< 1.0	46	110	7.0
CP2	4.1	160	1800	21	20	2000	960	< 1.0	320	1300	19
CP3	4.4	110	950	23	29	1100	240	< 1.0	100	340	190
CP4	4.1	270	3700	51	17	4000	4700	30	1400	6100	47
CP5	1.3	140	2200	0.0	13	2400	300	< 1.0	110	410	32
Mean		170	2200	24	20	2400	1600	6.0	400	2000	72
		(7)	(91)	(1)	(1)	(100)	(80)	(0.3)	(20)	(100)	
M1	3.3	410	3300	76	26	3800	79	14	140	230	480
M2	4.3	150	2800	4.4	96	3100	1300	16	< 1.0	1300	26
M3	1.7	240	1600	17	27	1900	590	10	230	830	20
M4	2.0	190	1800	14	8.2	2000	650	13	64	730	37

Table 9.6. (*Continued*)

Sample no.	Fat content (%)	HCHs					DDTs				
		α-HCH	β-HCH	γ-HCH	δ-HCH	ΣHCH	*p,p′*-DDE	*p,p′*-DDD	*p,p′*-DDT	ΣDDT	PCHs
M5	2.0	140	2400	16	20	2600	290	14	160	460	21
M6	0.95	170	3500	25	11	3700	790	18	240	1000	86
Mean		220	2600	25	31	2900	620	14	140	760	110
		(8)	(90)	(1)	(1)	(100)	(81)	(1)	(18)	(100)	
N1	1.8	1100	16,000	46	25	17,000	3500	43	390	3900	29
N2	2.7	490	11,000	82	29	12,000	2500	33	440	3000	31
N3	5.1	340	1500	63	51	1900	95	<1.0	48	140	3.3
		640	9500	60	35	10,000	2000	25	290	2300	21
		(6)	(93)	(0.6)	(0.4)	(100)	(87)	(1)	(12)	(100)	

Note: Values in parentheses indicate percentage compositions of HCH isomers and DDT compounds.

HCHs in Delhi mothers' milk. Most recently, the mothers in four villages near Agra had around 170–179 ng g^{-1} fat wt. of DDTs and 123–131 ng g^{-1} fat wt. of HCHs in their milk (Kumar et al., 2006). Further, Nair et al. (1996) found in mothers from Delhi that their breast milk contained 4.5 times higher DDTs than in blood serum and also there was a significant positive correlation between both these levels. They also found that the breast milk sampled during first feeding after childbirth showed 80% more residues of DDT and HCH when compared to maternal blood. Also, the primipara mothers showed 1.15 and 2.3 times more DDT and HCH residues in the breast milk, respectively when compared to multipara mothers. Most recently Kumar et al. (2006) found DDT and its metabolites and HCHs in 95% of the mothers' milk samples collected from the remote villages in Agra region of northern India.

Apart from classical organochlorines, not much literature is available on the occurrence of other PTS compounds like butyltins, polybrominated diphenyl ethers, etc. in Indian human breast milk. Indian Council of Medical Research (ICMR) in their news bulletin of the year 2004 has indicated that they could detect PCDDs and PCDFs in the human milk samples collected from Ahmedabad, Vadodara and Surat cities (http://icmr.nic.in). They have found that the TEQs of dioxins and related compounds in their samples ranged from about 2 to 16 pg g^{-1} lipid weight of human milk.

These compounds are the byproducts of incineration, uncontrolled burning and industrial processes. These may reach the people living around these sites via inhalation or through food chain by the consumption of products from farm animals and birds grazing in those sites; this will be certainly reflected in the milk of mothers living around these sites.

This has prompted Kunisue et al. (2004) to quantify the levels of dioxins and related compounds (DRCs) such as polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans and coplanar polychlorinated biphenyls in the human breast milk from women living near dumping sites of municipal wastes in India and compare them with the samples from a reference site and also with similar sites from other developing countries. DRCs were found in all the samples from Indian dumping and reference sites demonstrating that residents of both the sites were exposed to these contaminants. They have also found that the mean concentrations of PCDDs in human breast milk from Indian dumping sites were the highest among the samples from Asian developing countries they have analyzed. The range and mean concentrations were in the decreasing order as India (290 (150–780) pg g^{-1} lipid wt.) $>$ Philippines (190 (29–730) pg g^{-1} lipid wt.) $>$ Cambodia (49 (14–170) pg g^{-1} lipid wt.) $\geq$ Vietnam (32 (15–130) pg g^{-1} lipid wt.). At the same time the concentrations of PCDFs were in the decreasing order as follows: India > Philippines ≥ Vietnam ≥ Cambodia. In India, the concentrations of PCDD/DFs in human breast milk from dumping site were significantly higher than those from reference sites, whereas levels of these contaminants in human breast milk from Cambodia and Vietnam were not very much different between the dumping and reference sites. These results indicate that significant pollution sources of PCDD/DFs are present in the dumping site of India and that the residents living near them have been exposed to relatively higher levels of these contaminants than residents in the other countries evaluated in this study. Further studies in Kolkata and various other cities in India reveal similar patterns of OCs including DRCs (Kunisue, unpublished data). Kashyap et al. (2004) also made some preliminary observations on the levels of DRCs in human milk from Ahmedabad, India.

Further, a comparison of TEQ levels of these chemicals (PCDDs/DFs and coplanar PCBs), calculated using WHO TEFs in Indian human milk with other developing and developed nations showed that the Indian value (38 pg TEQs g^{-1} lipid wt.) were comparable with or higher than those from developed nations, suggesting that Indians residing near the dumping sites are exposed to DRCs as the general population of developed nations; the TEQs levels in Cambodia (9.2 pg TEQs g^{-1} lipid wt.), the Philippines (12 pg TEQs g^{-1} lipid wt.) and Vietnam (13 pg TEQs g^{-1} lipid wt.) were lower. There are reports claiming that the DRCs in human breast milk decreased recently in developed nations (La Kind et al., 2001) because of the installation of highly efficient incinerators and strict regulations on the production and usage of such chemicals. In this context, the fact that the levels of DRCs are higher in Indian human milk is noteworthy, not only from the viewpoint of local pollution but also from a global point of view.

Another interesting new finding by Sudaryanto et al. (2005) has revealed the occurrence of the popular flame retardant chemicals, polybrominated diphenyl ethers (PBDEs) in human milk collected during 2000–2004 from urban areas of the Asian countries, Japan, Korea, China, Philippines, Vietnam, Cambodia, Indonesia, Malaysia and India. They have also deducted the popular organochlorines in all those milk samples. The order of magnitude of the organohalogens is DDTs > PCBs > HCHs > CHLs > HCB > PBDEs., Unlike OCs, concentrations of PBDEs did not correlate with the age of the mother and parity, possibly because of the relatively short period of the usage of PBDEs in India and the different exposure pathways of PBDEs and OCs. Unlike HCHs and DDTs, the mean level of PBDEs in Indian milk samples is low when compared with other countries; yet the finding attains its importance from the fact that India is a fast developing country, especially in the field of electronics and computers, in the manufacture of which PBDEs and related compounds are used in plenty.

9.7. PTS in Indian food items

Despite the fact that the average consumption of pesticides are still low in India, (05 kg ha^{-1}) against 6.6 and 12 kg ha^{-1} in Korea and Japan, respectively, there has been widespread contamination of food commodities with pesticide residues, basically due to their non-judicious use. In a recent review Gupta (2004) has stated that in India, 51% of food commodities are contaminated with pesticide residues and out of these, 20% have residues above the maximum permissible residue levels on a worldwide basis.

The first report of contamination of food commodities in India was the report of pesticide poisoning of wheat flour in 1958 (Karunagaran, 1958). Following this, there are plenty of market and field surveys of almost all the vegetarian and non-vegetarian food items of India mostly on the pesticides rather than other PTS chemicals, reviewing all of which will be a task more than the necessity of the present review.

Regular food contamination surveys in India are being conducted since the 1970s (Agnihotri et al., 1974; Joia et al., 1978; Noronha et al., 1980; Kalra et al., 1983; Lal et al., 1989; Kannan et al., 1992; UNEP Chemicals, 2002). As a general rule, milk and its products followed by edible oil were found to contain the highest levels of residues, unlike in the developed nations where fish and meat had the highest levels (Dikshith et al., 1989; Dhaliwal, 1990; Kannan et al., 1992, 1997; John et al., 2001; Battu et al., 2004, 2005). Apart from these, almost all the Indian foodstuff like cereals, rice, wheat, meat, egg, vegetables infant formulae and human milk were found to be contaminated with different PTS chemicals, and most of them with at least the classical organochlorine pesticides, DDT and HCH (Kaphalia and Seth, 1981; Kaphalia et al., 1985; Lal et al., 1989; Kunisue et al., 2004). Above these, assessment of vegetarian and non-vegetarian diets was undertaken by Gupta et al. (1982), Rekha et al. (2006) and Battu et al. (2005). These works reported that 21% of the total pesticide residues intake via Indian food is contributed by milk. Organochlorines were observed in higher concentrations in rice and wheat follwed by carbamates, organophosphorus and pyrethrites. It was also reported that dairy products are the prime sources for both HCHs (70%) and DDTs (87%) while dairy products (31%), pulses (27%) and vegetable oils (20%) are the three main sources of PCBs for human in India (Fig. 9.11) (Kannan et al., 1992).

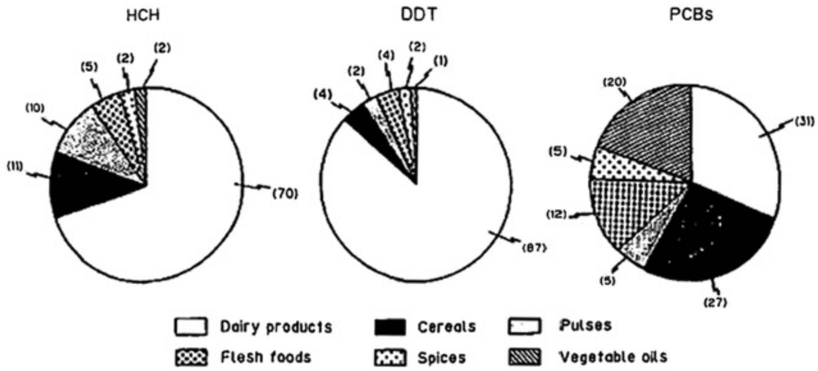


Figure 9.11. Contribution by different classes of foodstuffs toward the dietary intakes of ΣHCH, ΣDDT, and PCBs by Indians. [Figures in parentheses indicate the percentage (*Source*: Kannan et al., 1992).]

9.8. Management of toxic chemicals in India

In 1976, when Indian parliament passed the 42nd amendment of its constitution safeguarding the environment, it became the first country in the world to do so. Essentially, The Water (Prevention & Control) Act, 1974 can be considered to be truly the first regulation on environmental management in India. At present, there are several pollution regulations in India (Harish C. Sharma—www.petroleumbazaar.com/Library/Pollution) viz.:

1. The Water (Prevention & Control of Pollution) Act, 1974 and its amendments;
2. The Water (Prevention & Control of Pollution) Cess Act, 1974 and its amendments;
3. The Air (Prevention & Control of Pollution) Act, 1981 and its amendments;
4. The Environment (Prevention) Act, 1986 and its amendments (a) National Environmental Tribunal Act of 1955 and (b) National Environmental Appellate Authority Act of 1977;
5. Hazardous Waste (Management and Handling) Rules, July 1989 and
6. The Public Liability Insurance Act, 1991 (Sharma, 1994, 1999).

The Public Liability Insurance Act 1991 is the first regulation which gives strong power to the other five pollution regulations. These Acts regulate the agencies polluting various environmental and biotic matrices. Even before this, India already had The Insecticides Act, 1968 to regulate the manufacture, registration, use, export and import of pesticides in the country. There existed already is the Prevention of Food Adulteration Act (PFA) 1954, giving power to the government for punishing food adulteration with unwanted materials including toxic chemicals.

Under the Water Act, 1974, Central Pollution Control Board and State Pollution Control Boards were formed and given power to govern all the pollution regulations since then and any other to be put in regulations in the future. The Chairman and members of the Boards are appointed by respective governments from various interest groups such as corporations, public health, engineering, agriculture, forestry, fishery, etc. The boards advise their respective governments on any matter concerning the prevention and control of pollution in their area of jurisdiction. The boards have authority to take samples and analyze any matter from the industries and other polluted environments and make recommendations to the government.

Apart from the above regulations, the government issued many policies such as:

1. The National Forest Policy;
2. The National Wildlife Action Plan;
3. Forest (Conservation) Act;
4. The Policy Statement for Abatement of Pollution;
5. The National Conservation Strategy;
6. Policy Statement on Environment and Development, etc.

At present the regulatory agencies are now enforcing the regulations fairly strictly by taking legal actions against the erring industries and persons. There has been some control on the unmindful pollution by industries at present because of the enforcement of the principle "Polluter pays" for the damage. The Ministry of Environment and Forests and some related departments of Government of India are empowered to take steps even for the summary closure of polluting industries and to curtail the activities of the polluting agencies. There are many NGOs and public interest groups keeping a watchdog approach in order to prevent possible violations of environmental regulations by big farming societies and industries.

The government encourages measurement of the pesticide and other chemical contamination of soil, water and food that has been a much-researched subject in India since the 1970s. Several national and international agencies carry out regular research on toxic chemicals, especially on pesticides in India. In 1986, The Indian Council of Medical Research (ICMR) began a project on surveillance of food contaminants in India and found that 51% of the food items tested were contaminated with various pesticides and 20% of them had pesticide levels above the maximum permissible residue limits. The National Institute of Oceanography (NIO) began research on pesticides in 1984. According to a research report by Dr. Anupam Sarkar and others, Indian marine environment has been contaminated by different classes of pesticides. The Department of Science and Technology of the Government of India set up a Programme Advisory Group in 1988 for regular monitoring of food grains and pulses for their pesticide levels. In 1992–1993, The Consumer Education Research Centre (CERC), Ahmedabad, along with the National Institute of Nutrition (NIN), undertook the testing of pesticide residues in food. The CERC, in another investigation (Insight—the consumer magazine, May–June 2000), found that the most of the wheat flour brands of India are contaminated with lindane, DDT, aldrin, dieldrin and ethion. Studies by Toxic Link found various toxic persistent chemicals in water, fish and clams collected from India (Toxic Link, Nov. 2000).

Green Peace in an effort in evaluating the levels of toxic chemicals in Asian countries such as India, Pakistan, Nepal and Bangladesh found that several of the locally banned or severely restricted pesticides are freely available in these countries. The Pesticide Action Network, Asia and the Pacific based in Malaysia undertook case studies on endosulfan poisoning in the State of Kerala, jointly with International POPs Elimination Network (IEPN) based in Kerala State, India. The scientists from the Center for Marine Environmental Studies of Ehime University, Japan under the Asia Pacific Mussel Watch Program surveyed the countries surrounding Indian Ocean region for several of the POPs chemicals. Dr. Shinsuke Tanabe, the Leader of the Program, as one of the findings of their still continuing research efforts in the region, states that almost all the countries in the region, India, Vietnam, the Philippines, Cambodia, etc. act as global pollution sources of different classes of POPs chemicals. In their work together with scientists from Annamalai University, India they found that foodstuffs and other wildlife collected from different regions of India contained PTS Chemicals like HCHs, DDTs, PCBs, PBDEs, BTs, etc. They found India as a main source of HCHs to global environment while Vietnam is the source for DDTs and Japan for PCBs in the region they have surveyed.

Even beyond all such rules and policies and efforts of the Government of India and other non-governmental agencies, it is an obvious fact that the levels of many of the persistent toxic chemicals in the Indian environment, food stuff, wildlife and human are one among the highest in the world. As opined by many of the public interest groups and NGOs, India has no shortage of strong teethed regulations to control the pollution by PTS chemicals starting from their source(s) to the environment. What is obviously lacking is the strict enforcement of the existing rules and regulations.

9.9. Conclusion

Apart from the legal formalities and several ethical, religious and social problems that are to be considered in collecting wildlife and environmental samples, especially in India, a very much religious country, where a considerable proportion of the subjects are illiterate, considerable amount of literature is available on PTS in India; an evaluation of which shows a wide spread contamination of organochlorine pesticides and other industrial chemicals in the environment, wildlife and humans to the levels which can cause serious concern because of their severe and already proven toxic implications.

In a popular news article that appeared in www.newindpress.com on October 1, 2004, a study by the Mumbai (Bombay, India) based Blackstone Research Institute has stated that the onset of slowdown among the men in Delhi is at the age of 35 years while Mumbai men begin to suffer from it only at 41. Kolkata and Chennai men were on par, experiencing the slowdown at 45 years of age. The news article also has shown that men experience such andropause due to decline of testosterone levels in their blood. Already it has been shown that many PTS chemicals are having endocrine disrupting and estrogenic characteristics. These chemicals cause disruptions in sex characteristics of individual animals and also decrease fertility rates in some wild species (Colborn et al., 1996; Reijnders et al., 1999; Tanabe, 2000). Sexual dysfunction in many marine species like fish and shellfish and eggshell thinning in some bird species led to reduced reproductive success in individuals having high POPs concentrations in tissues and organs (Reijnders et al., 1999; Konstantinou et al., 2000; Van der Oost et al., 2003). One of our earlier studies has also shown that the testosterone levels in the blood of Dall's porpoises decreased significantly with increase in the levels of DDTs in their blubber (Subramanian et al., 1987).

Interestingly, evaluation of the data obtained in India on the levels of OCs, especially DDTs, were found to be higher in many of the environmental and biotic samples. This fact may be considered as a matter of serious concern. There may be several medically proved factors that may cause the 'slow down' of the Indian men at an early stage. But the fact remains; higher levels of PTS chemicals in Indian environment and human may also have an added effect on their early andropause; this may also have teratogenic effects on perinatal children by transfer through placenta and breast milk from mother. So far, no direct evidence is available linking human sexual dysfunction and fertility problems and the PTS chemicals. But there is ample evidence to believe that in countries like India with uncontrolled usage of estrogenic chemicals, the environmental levels are sufficient enough to cause several toxic implications in wildlife as well as human. This is certainly high time for the government and related agencies take a serious look on the matter and take urgent necessary steps.

The data available on the Indian POPs pollution scenario shows need for every concern. But the interest shown by the concerned agencies is very minimal for reasons obvious. The participation by NGOs and public is not encouraged in this critical issue. Effort by the scientific community is waning for want of encouragement and should be stimulated in a systematic and coordinated fashion. As a first step to this, available information on the existence of PTS, their distribution, transport and bioaccumulation in the Indian environment and biota should be gathered in a systematic manner.

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Chapter 10

Persistent Toxic Substances in Thailand

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Abstract

Thailand was one of the Asian countries that are very conservative with regard to the import, introduction and usage of any toxic chemical. The first ever known usage of such a chemical in Thailand was the application of DDT in the early 1950s followed by the chemicals like dieldrin, aldrin, endrin, toxaphene and BHC. The first official report on the import statistics of these chemicals was made only in 1971, even though the country has been busy tackling the occupational health and environmental problems systematically and at national level, even from the early 1960s. There were increases and decreases year by year from the 1950s until various chemicals were banned in different years starting from the ban of DDTs for agricultural use in the year 1983. Studies initiated by Thailand's National Environment Board found organochlorine and organotin compounds as the most common pollutants in the major rivers of Thailand followed by their detection in almost all the environmental and biotic media. In order to control the utilization of toxic substances for various purposes the "Toxic Substance Act of 1967" was first promulgated in Thailand in 1967 and the import, export, manufacture and possession of hazardous substances have been controlled under the Hazardous Substances Act 1992. Even beyond these Acts and several other control measures initiated by the Government of Thailand, the demand for agricultural productivity and the expansion of industry is now causing a rapid increase in the use of many chemicals in Thailand. As a result, wide spread contamination of several persistent chemicals were noticed in almost all the environmental and biotic matrices. Most recently, improved government policy has resulted in better control of chemical management. Even then, the present status of chemicals pollution in Thailand indicates that it may take several more years to reduce the levels of these chemicals considerably from the Thailand environment. Until then, a continuous

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survey for monitoring the present persistent organic pollutnats and several new chemicals that may come in to use in future is an absolute necessity.

10.1. Introduction

Thailand is located in the center of the Southeast Asian region and share borders with four neighboring countries, namely Myanmar in the north and west, Laos in the northeast, Cambodia in the east, and Malaysia in the south. Thailand is the third largest country in Southeast Asia, with a total land area of 513,115 km^2, next only to Indonesia and Myanmar. The borders around Thailand are totally ~8031 km long, of which 5326 km are inland and the other 2705 km are coastlines, including 1840 km of coastlines of the Gulf of Thailand and 865 km along Andaman seaside. Thailand is blessed with four geological features. In the North, high mountains give rise to several rivers and streams. In the northeast is a high plateau while an enormous plain covers the central region. The south is bordered on both sides by seas, namely the Andaman Sea and the Gulf of Thailand, which is part of the Malay Peninsula. Thailand is situated in the tropical zone; the temperature is rather high throughout the year. The climate is monsoonal in character with dry season during October–April and wet season during May–September. However, occasionally the weather turns unusually cold under the influence of a cold mass of air from China and Mongolia during December–February.

The population of Thailand is ~62.42 million in 2005 (Bureau of Registration Administration, 2006), which is currently increasing at an annual rate of ~2% (www.chem.unep.ch/pops). Thailand's economy has been dominated by agriculture during the period from the 1950s to the early 1970s; ~70% of the population was engaged in agriculture sector that provided most of the country's export earning. At present, roughly 47% of Thailand's population is employed in agriculture sector with rice as the country's most important crop. Other agricultural commodities produced in significant amounts include tapioca, rubber, corn, coconuts, and soybean. Thailand has used organochlorine compounds as pesticides to control pests in agriculture and malaria vector control for several decades. However, the demand for organochlorine pesticides is declining sharply and replaced gradually by other chemicals of less persistence.

During the last three decades, Thailand was one of the rapidly developing nations in Southeast Asia. Increasingly diversified industrial sector contributed to the growth of Thailand's economy with a growing number of industrial plants using hazardous chemicals. Between 1970 and

1985, the number of industries registered as using hazardous chemicals increased from ~19,700 to 51,500 (Ross, 1995). Recently, the number has increased to 122,300 in 2005 (Department of Industrial Works, 2006). Such an increase in Thailand's industrial sector is suggestive of greater production and usage of toxic chemicals and exposure of humans and wildlife leading to environmental problems and toxic implications on wildlife. Thus the demand for both agricultural productivity and industrial expansion caused a rapid increase in the usage of chemicals. Thailand's import of chemicals increased from 600,000 MT in 1978 to 13,124,438 MT in 1988 and to 60,395,565 MT in 2003 (National Research Center for Environmental and Hazardous Waste Management, 2004). A rapid increase of urbanization and use of chemicals in industrial and agricultural activities impose potential risk for considerable contamination by chemical substances in the environment (Hungspreugs et al., 1989).

Increase in Thailand's chemical trade is suggestive of greater production and usage of toxic chemicals and exposure of humans and wildlife to those chemicals. Therefore, corresponding environmental problems caused by hazardous chemicals are of great concern in Thailand. This chapter will give information on the sources, transport, persistence in the environment, and biota, import, usage, and control and management of some persistent chemicals in Thailand.

10.2. Sources of persistent toxic substances

Due to the extensive agriculture activities, manufacture and use of pesticides increased dramatically in Thailand. Figure 10.1 shows pesticides from one of the toxic groups of chemicals imported increasingly, from 19,456 MT in 1978 to 29,696 MT in 1993 (Department of Agriculture, 1993). Organochlorine pesticides have been widely used in Thailand for pest control in agriculture as well as for public health purposes (Siriwong et al., 1991). During the last three decades, most of the developed nations have banned or restricted the use of such persistent toxic chemicals, because their extensive usage has resulted in severe environmental problems and human health hazards (Tayaputh, 1996). During the period from 1950 to 1970, most of the imported pesticides were organochlorines including those specified POPs chemicals such as DDT, toxaphene, drins, heptachlor, and others. The trends of organochlorine residues seen in various environmental media showed an increasing trend even after the ban on their use. Under strict enforcement of the ban, the demand for organochlorine pesticides is declining sharply, being replaced gradually by organophosphorus pesticides that are degradable in the

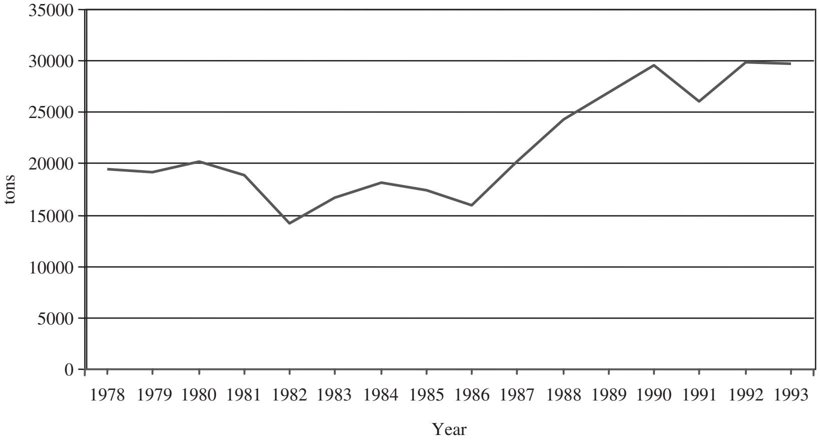

Figure 10.1. Pesticide imports of Thailand between 1978 and 1993. (*Source*: Raw data obtained from Department of Agriculture, 1993. Also see Kan-atireklap et al., 2002)

environment and less accumulative in food chain (Hungspreugs et al., 1989; Tayaputh, 1996).

After the Second World War, DDT (1,1,1-trichloro-2,2-*bis* (*p*-chlorophenyl) ethane) was first introduced for malaria control in a northern province in 1949 by the Ministry of Public Health of Thailand. During those days, malaria epidemic was very serious and caused over 38,000 deaths at the rate of 201.5 persons per 100,000 population. After the initial use of DDT, it was gradually expanded to cover all malaria transmission areas. During the 1970s to the 1980s, DDT has been widely applied with a dosage of $2\,\mathrm{g\,m^{-2}}$ and two cycles per year in mountainous and high malarial areas. However, DDT has not only been used for malaria control but also in agriculture for pest control. Although DDT has been banned for agriculture purpose in 1983 and for vector control since 1995 by the Ministry of Public Health, the left over stocks are still being used in remote mountainous areas. However, it was also reported that the Ministry of Public Health used the leftover stockpile until 1999. Since 1995, DDT has been replaced by deltamethrin for vector control and DDT was phased out from 1996 in Thailand (Ministry of Public Health of Thailand, 2003). DDT was used mainly for malaria vector control till 1998 in national boundary areas, such as Cambodia in the east, Myanmar in the west, and Malaysia in the south (Boonyatumanond et al., 2002).

Under the Stockholm Convention, 12 organochlorine compounds were designated as persistent organic pollutants (POPs) and called for their immediate control because they were the most dangerous among all the persistent pollutants released into the environment by human activities. POPs were grouped into three categories, namely pesticides: aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, mirex, and toxaphene; industrial chemicals: hexachlorobenzene and polychlorinated biphenyls (PCB); and generated unintentionally as by-products of various industrial processes: dioxins and furans. In fact, only seven specified POPs pesticides were imported in Thailand, namely aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, and toxaphene, whereas hexachlorobenzene and mirex have never been imported (Wong-ek, 2000).

Information on the import of the 12 specified POPs chemicals has not really been collected from the very beginning of its usage in the country. Until the mid-20th century, Thailand was very conservative with regard to the import, introduction, and usage of any toxic chemical. The first ever known usage of such a chemical was the application of DDT in Chiangmai Province for control of malaria and later used very widely from the year 1951 for disease control. In the year 1953, DDT was first applied to control the epidemic of grasshopper and then on cotton bole worm from the year 1955. Following DDT, the chemicals like dieldrin, aldrin, endrin, toxaphene, and BHC were first imported in the year 1955.

PCBs were first used in small quantities in industrial fluids for hydraulic systems and gas turbines, and as plasticizers. The other main purpose for which they were used in a relatively large quantity was as dielectric fluid for electric capacitors. PCB was totally banned in the year 1975. But, reports by the Electricity Generating Authority of Thailand (EGAT), Metropolitan Electricity Authority (MEA), and Provincial Electricity Authority (PEA) indicate possession of PCBs containing transformers and capacitors.

The first official report on the import statistics of these chemicals was made in 1971. After this, the import of POPs chemicals increased year by year. There were increases and decreases year by year until various chemicals were banned in different years. For example DDT was banned for agricultural use in the year 1983 and totally in the year 1994; aldrin in the year 1988; dieldrin in 1986; endrin in 1981; heptachlor in 1988; toxaphene in 1982; HCB in 1980; and PCBs in the year 1975. Only chlordane remained in use until 1996 (www.chem.unep.ch/pops-Inc/).

At present, Thai government initiated systems for monitoring import of hazardous materials which is now successfully implementing and able to give fairly accurate import statistics of hazardous materials. For example, although dieldrin was banned since 1988, this monitoring system showed that dieldrin is being imported until recently (Danutra and Ratanasatian, 2002). They have also shown that, even after all of the specified POPs pesticides were banned in Thailand before the year 2000, small amounts of some organochlorine pesticides, namely DDT, aldrin, dieldrin, and endrin, were imported during the period 2001–2005.

Organotin compound is one of the organometalic chemicals, which are widely used for industrial and agriculture purposes. The first application was as a mothproofing agent in 1925 and for stabilizing chlorinated benzenes and diphenyls used in transformers and capacitors in 1932. Since the biocidial properties of trialkylated organotins were recognized in the 1950s, an increasing number of organotin compounds were developed and used as important industrial and agricultural commodities (Champ and Pugh, 1987). At present there are three major areas of utilization of organotin compounds, namely heat stabilizers for polyvinyl chloride polymers, industrial and agricultural biocides, and industrial catalysts (Fent, 1996).

Application and usage statistics of organotin compounds was first compiled by the International Tin Research Institute (ITRI), which was initially financed by five of the major tin producing countries of the world, viz. Indonesia, Malaysia, Nigeria, Thailand, and Zaire. Although Thailand is one of the major tin producing countries, use of organotin compounds in Thailand is limited mainly because the chemicals must be imported from abroad, making them more expensive and not competitive with other compounds having similar application values (Visoottiviseth, 2001). The biocidial use of organotin compounds were estimated to account for ~30% of total present use.

Among the organotin compounds, the trialkyltins are mainly used as biocides. Tributyltin (TBT) is used as an antifouling agent in paints applied on boats and fishnets, lumber preservatives, and as slimicides in cooling systems. Dibutyltin (DBT) is used as a polyvinyl chloride stabilizer and as a catalyst in some industrial processes (Maguire, 1987). The biocidial use as antifouling agent in paints applied on boats give rise to the largest proportion of free butyltin in the aquatic environments. The aquatic pollution by butyltin compounds arising from antifouling paints has been of great concern in many countries due to their effect on non-target marine organisms, which occur even at few nanograms per liter of aqueous TBT concentrations (Alzieu and Heral, 1984; Alzieu and Portmann, 1984; Beaumont and Budd, 1984; Bryan and Gibbs, 1991). These adverse effects prompted the restriction of TBT usage in many countries like USA, France, UK, Switzerland, New Zealand, and Japan (Alzieu, 1991; Waite et al., 1991; Dowson et al., 1993; Horigushi et al., 1994; Smith, 1996; Tóth et al., 1996). Although TBT use on small vessels of length less than 25 m was banned in many countries, TBT-based antifouling paints are still being used on larger or far sea vessels, particularly on commercial ships, which utilize ~75% of the total TBT used as antifouling paints. The number of commercial vessels loading and unloading in Thai coastal waters increased from 73,292 in 1998 to 103,482 in 2004 (Marine Department, 2006) and still increasing. In addition, an increasing demand for antifouling paints is predicted in the Asia-Pacific region including Thailand (Layman, 1995; Reisch, 1996), and hence the aquatic environment in this region may face serious organotin pollution in future.

On the other hand, triphenyltin acetate and triphenyltin hydroxide were the first commercial products introduced during the early 1960s followed by triphenyltin chloride, tricyclohexyltin hydroxide, bis(trineophenyltin) oxide, and tricyclohexatin-1,2,4-triazole, respectively. Triphenyltin hydroxide was one of the recommended pesticides for rice and necessary for countries like Thailand where rice is a major component of both domestic and export markets (Visoottiviseth, 2001).

At present, the usage of organotin compounds in Thailand is still unclear. Before 1998, the import data of organotin compounds was lacking. Recent data show that tributyltin fluoride as one of butyltin compounds was used as a biocidial agent in Thailand and imported increasingly from 1.4 MT in 1998 to 6.3 MT in 2001 as shown in (Kan-atireklap et al., 2004). The purpose and usage statistics of this compound in Thailand is not known. To our knowledge, the usage of organotin compounds in Thailand is not yet controlled and the possible usage of butyltin compounds as antifouling agents in paints in the country is also not clear. Further, data on the occurrence of butyltin compounds in environment of Thailand is very much lacking.

10.3. Status of contamination

10.3.1. Abiotic environment

Very limited information is available, either in the scientific literature or in popular literature available through Internet. Thapinta and Hudak (2000) in their report on the pesticide use and residual occurrence in Thailand reviewed the import and usage statistics of different pesticides and also their residual levels in different environmental samples. Thailand is a country where the climatic conditions make it suitable for cultivating a wide range of tropical and semi-tropical crops. Recently, Thailand is improving fast in the industrial sector, all these activities leading to the import of many chemicals from several nations. Chemicals import, especially those of pesticides to Thailand have increased rapidly over the past decade—more than double between 1987 and 1996, that is from 20,357 MT in 1987 to 45,071 MT in 1996 (DOA, 1996).

Table 10.1. Pesticide residue levels in water samples from main rivers in Thailand, 1985–1988 (*Source*: Thapinta and Hudak, 2000)

Chemical	Type	Concentration ($\mu g\,L^{-1}$)				Standard ($\mu g\,L^{-1}$)
		1985	1986	1987	1988	
Aldrin	OC	NA	NA	0.01–0.44	0.01–0.02	0.1
Alpha-BHC	OC	0.01	NA	NA	<0.01	0.02
Beta-BHC	OC	0.04	NA	NA	NA	0.2
Gamma-BHC	OC	0.01–0.02	NA	NA	NA	–
DDT	OC	0.01–0.02	NA	0.02–0.55	0.10–0.35	1.0
Dieldrin	OC	0.01–0.13	NA	0.003–0.10	0.01–0.13	0.1
Heptachlor	OC	NA	NA	0.01–0.14	0.01–0.3	0.2
Heptachlor epoxide	OC	0.01–0.07	NA	NA	NA	0.2
Lindane	OC	NA	NA	0.04	0.04	–
Methyl parathion	OP	0.01–0.20	NA	0.09–0.68	0.01–0.68	–
Dimethoate	OP	0.03–0.24	NA	0.06	0.06	–
Diazinon	OP	0.19	NA	0.07–0.28	0.01–0.28	–
Carbofuran	C	0.01–1.37	NA	0.01–1.37	NA	–

Source: Office of the National Environment Board (1991).
Note: NA (data not available); OC (organochlorine insecticide); OP (organophosphate insecticide); C (carbamate insecticide).

Studies initiated by Thailand's National Environment Board (ONEB, 1991) found that various organochlorine pesticides occurred frequently in water samples of the main rivers of Thailand (Table 10.1). Further, a study by Thailand's Pollution Control Department (PCD, 1977a, b) showed that organochlorine insecticides are the most common pollutants in the ground water samples from agricultural areas in Thailand (Table 10.2). At the same time, organophosphate concentrations were found to be higher than organochlorine levels, because of their wide use in the country. However, some organochlorine insecticides were banned a decade before the sampling for this study. Recently, a monitoring study conducted by a group of scientists from the Environmental Research and Training Center of the Department of Environment Quality Control of the Ministry of Natural Resource and Environment during 2002–2003 on a batch of 48 water samples collected from four main rivers namely The Chao Pharya River, The Mae-Klong River, The Bang-Pakong River, and The Tha-Chin River has reported very low concentrations of OCs like DDTs, CHLs, endrin, dieldrin, aldrin, etc. (http://landbase.hq.unu.edu/Country reports/2000/Thailand2002.htm). It was also suggested in that study that the tropical climatic conditions facilitated the loss of residues from the soil and heavy

Table 10.2. Pesticide residues in water samples from agricultural areas of Thailand 1996–1997 (*Source*: Thapinta and Hudak, 2000)

Chemical	No. of samples	Type	Concentration ($\mu g\,L^{-1}$)		Standard ($\mu g\,L^{-1}$)
			1996[a]	1997[b]	
Alpha-BHC	47	OC	NA	0.002–0.005	0.02
Beta-BHC	78	OC	NA	0.001–0.024	0.2
Gamma-BHC	61	OC	NA	0.001–0.032	–
Aldrin	38	OC	NA	0.001–0.006	0.1
DDT	56	OC	0.007	0.001–0.089	1.0
Dieldrin	33	OC	0.003–0.576	0.006–0.017	0.1
Endrin	21	OC	NA	0.003–0.011	0.0
Endosulfan	79	OC	0.003–1.350	0.001–0.460	–
Heptachlor	57	OC	NA	0.001–0.006	0.2
Heptachlor epoxide	79	OC	NA	0.001–0.300	0.2
Methyl parathion	21	OP	0.007–8.720	NA	–
Methamidophos	11	OP	0.002–0.011	NA	–
Mevinphos	21	OP	0.014–47.500	NA	–
Permethrin	10	PY	2.81	NA	–
Dicofol	21	A	0.007–10.510	NA	–

Source: Pollution Control Department (1997a).

Note: NA (data not available); OC (organochlorine insecticide); OP (organophosphate insecticide); PY (pyrethroid insecticide); A (acaricide).

[a] Data collected from northern part of Thailand.

[b] Data collected from eastern part of Thailand.

rainfall carried away the chemicals to the coastal regions of the Andaman Sea. A study conducted by the Department of Agriculture in five main rivers of Thailand showed detection of organochlorines in 40.6% among the 805 water samples (range <0.02–$1.21\,mg\,l^{-1}$) and in 46.6% of 693 sediment samples (range <0.01–$7.43\,mg\,kg^{-1}$).

With regard to sediments, in an earlier study Menasveta and Cheevaparanapiwat (1981) detected organochlorines, especially DDT and its metabolites but no PCBs in the sediments of the mouths of rivers Mae Klong, Tha Chin, Chao Pharya, and Bang-Pakong. Most recently, Boonyatumanond et al. (2007), in their work on four sediment cores collected from an offshore transect in the upper Gulf of Thailand found a subsurface maximum ($\sim$2000 $pg\,g^{-1}$) of PCBs in layers corresponding to the 1970s, indicating the effectiveness of regulation of PCBs in Thailand, which was enforced in the year 1975. The authors have also suggested possible leakage of PCBs from the transformers and capacitors in use and in storage at present in the country contributing to ambient soils and sediments. Apart from POPs, Kan-atireklap et al. (1997a) found that the coastal sediments of Thailand are contaminated by butyltin compounds, the levels being consistently related to various activities like commercial vessel transport, coastal mariculture, etc. (Table 10.3).

Vulnerability studies of agricultural soils and 90 wells at three different provinces of Thailand conducted by Thapinta and Hudak (2003) for several pesticides using Geographical Information Systems showed that the depth of the wells was the most significant vulnerability factor followed by soil texture, percent slope, and average monthly rainfall. As a result, they found that the agricultural areas in Central Thailand characterized by fine-textured soils and unconsolidated aquifers reduce the threat of pesticide contamination in the region. While the data on the actual levels of different persistent chemicals are limited in the soils and sediments of Thailand, various studies were conducted on the effects of different soil types (Parkpian et al., 1998) and water flow and percolation patterns (Ciglasch et al., 2005; Chatupote and Panapitukku, 2005) on the distribution of pesticides in the country.

10.3.2. Wildlife

Since 1979, several studies have detected the presence of organochlorine pesticides in various environmental compartments such as agricultural commodities, soil, fresh and marine waters, and marine organisms in Thailand (Menasveta & Cheevaparanapiwat, 1981; Thoophom et al., 1984; Siriwong et al., 1991; Ruangwises et al., 1994; Kanatharana et al., 1994; Impithuksa et al., 1995; Kan-atireklap et al., 1997b; Chamrasakul et al., 1999). During the last three decades, improved governmental policy through legislation and monitoring has resulted in better control of pesticides. Since 1979, numerous samples from different sources were collected and analyzed each year. Relatively small amounts of organochlorine pesticides were found in different percentages of samples collected. During 1987–1994, organochlorine pesticide residues were detected in relatively lower levels and percentages of samples (Wong-ek, 2000). Most samples were reported to contain a very few parts per billion or even at non-detectable level of several compounds.

Tanabe et al. (2000) by their analyses of the organochlorines PCBs, DDTs, CHLs, HCHs, and HCB by collecting the green mussels (*Perna viridis*) from 21 locations in Thailand, 13 locations in the Philippines, and 19 locations in India during the years 1994–1997 found widespread contamination of all the compounds in all the three countries. There were subtle differences in the mean values which were not statistically significant (Fig. 10.2). In this study, concentrations of PCBs in green mussels from coastal waters of Thailand exhibited a smaller variation among locations. Relatively high levels of PCBs were detected at some locations around

Table 10.3. Concentrations (ng g^{-1} dry wt.) of butyltin compounds in sediments from various areas in the world (*Source*: Kan-atireklap et al., 1997a)

Location	Year	MBT	DBT	TBT	References
Vancouver Harbour, Canada	1982–1985	nd–3400	nd–8500	nd–11,000	Maguire et al. (1986)
Poole Harbour, UK	1985–1987	NA	10–570	20–520	Langston et al. (1987)
Boston Harbor, USA	1988	nd–130	nd–316	nd–518	Makkar et al. (1989)
East, Gulf, and Pacific coasts of USA	1986–1991	NA	NA	<10–770	Krone et al. (1996)[a]
Mediterranean Sea (French, Italy, Turkey, and Egypt coasts)	1988	nd–670	nd–830	70–3400	Gabrielides et al. (1990)
Marina area, Hong Kong	1988–1989	NA	NA	60–1160	Lau (1991)
	1994	NA	NA	nd–130,000	Ko et al. (1995)
Auckland, New Zealand	1990	NA	NA	<2–1360	de Mora et al. (1995)
Bohemia River, Chesapeake Bay, USA	1991	0–13	4–110	15–590	McGee et al. (1995)
Portland and Boothbay Harbor, Maine, USA	1990–1992	NA	15–2240	24–12,400	Page et al. (1996)
Coasts, Thailand	1995	7–410	2–1900	4–4500	This study

Note: All concentrations expressed as tin (Sn) we converted to MBT, DBT, and TBT cation by a factor of 1.48, 1.96, and 2.44, respectively; nd (not detected); NA (no data available).

[a] ng g^{-1} wet wt.

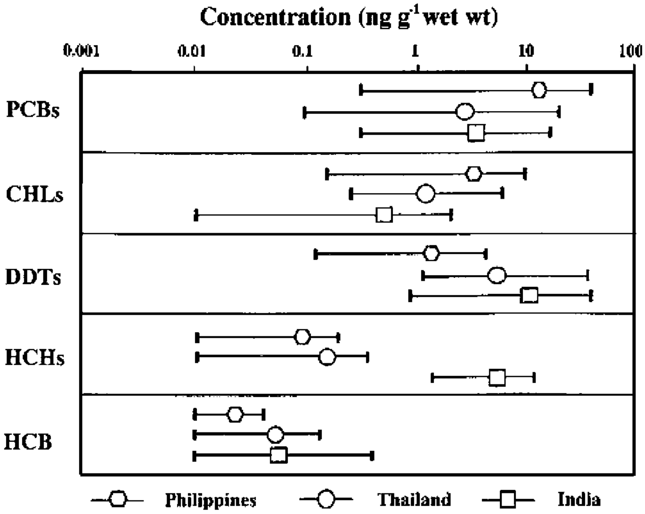

Figure 10.2. Comparison of organochlorine residue levels in green mussel (*Perna viridis*) from India, the Philippines, and Thailand. (*Source*: Tanabe et al., 2000.)

populated and industrialized cities like Samut Prakan and Chonburi. Transformers and capacitors imported by Electric Authority of Thailand were considered as major PCB pollution source in Thailand. Watanabe et al. (1996) also found in an earlier work that the dumped electrical appliances were also a prime source of PCB pollution proximal to the estuary of Chao Pharya River at the suburbs of Bangkok.

DDT and its metabolites (DDTs) have been reported to be present in green mussels along the coastal waters of Thailand, ranging from 32 to 42 ng g^{-1} in 1979 (Menasveta and Cheevaparanapiwat, 1981), 0.39–7.41 ng g^{-1} in 1989 (Siriwong et al., 1991), 0.74–5.38 ng g^{-1} in 1991 (Ruangwises et al., 1994), 1.3–38 ng g^{-1} in 1994 and 1.2–15 ng g^{-1} in 1995 (Kan-atireklap et al., 1997b), 0.05–5.7 ng g^{-1} during 1997–1999 (Boonyatumanond et al., 2002), and 0.86–2.11 ng g^{-1} in 1998 (Noicharoen, 2000).

DDTs were also detected in marine fish collected from market in Bangkok during 1989–1993, ranging from 0.48 to 19 ng g^{-1} (Kannan et al., 1995b) and from coastal water areas along the east coast of the Gulf of Thailand during 1999–2000, ranging from $<$0.01–17.48 ng g^{-1} (Kan-atireklap et al., 2002). In general, *p,p′*-DDE the metabolite of *p,p′*-DDT under aerobic condition was predominant, showing a possible decrease in the usage of DDT. Even though the usage of DDT for agriculture purposes has been banned since 1983 and for vector control purposes since 1995, DDT was used mainly for malaria vector control till 1998 in the boundary areas between Myanmar, Cambodia, and Malaysia (Boonyatumanond et al., 2002).

Considerable proportion of *p,p'*-DDT in DDTs was found in green mussel, oyster, and marine fish from several locations during the period of 1998–2000 (Noicharoen, 2000; Saisith, 2002; Boonyatumanond et al., 2002; Kan-atireklap et al., 2002). This may indicate the presence of significant current sources of DDT in Thailand related to public health issues.

In the fresh water environment, Kumblad et al. (2001) found DDT and its metabolites in four species of fish (Sactophagus argus, Protosus canius, Channa striata, and Zonichthys nigrofasciata) from Songkhla Lake. The mean $\sum$DDT concentrations in fish from different locations of the lake ranged from 33 to 170 ng g^{-1} lipid wt. (0.086–7.7 ng g^{-1} fresh wt.), which is well below the recommended maximum residue levels for aquatic animals (5000 ng g^{-1} fresh wt.) in Thailand. The authors have attributed such low concentrations in fresh water fish, in spite of wide use, may be due to the high volatilization and degradation of DDT in the tropical condition in Thailand and/or due to the high biological productivity in the lake leading to dilution and degradation of the pollutants.

Chlordane compounds (CHLs) were detected in green mussel, ranging from 0.3 to 5.9 ng g^{-1} in 1994 and 0.25–3.5 ng g^{-1} in 1995 (Kan-atireklap et al., 1997b) and 0.22–12.0 ng g^{-1} during 1997–1999 (Boonyatumanond et al., 2002). However, the CHLs were detected in marine fish which showed a similar range of concentration from 0.1 to 15 ng g^{-1} during 1989–1993 (Kannan et al., 1995b) and from $<$0.01 to 4.7 ng g^{-1} during 1999–2000 (Kan-atireklap et al., 2002).

Hexachlorocyclohexanes (HCHs) were found in fish from Bangkok, ranging from 0.22 to 1.8 ng g^{-1} during 1989–1993 (Kannan et al., 1995b), whereas the range of concentrations was from $<$0.01 to 1.15 ng g^{-1} during 1999–2000. These may be because the usage of HCHs in Thailand has been banned since 1980. Lower residence time of HCHs in the aquatic environment of this tropical country might be because of the prevailing high temperature leading to easy volatilization and transport from the point source as observed by Takeoka et al. (1991) in India.

Hexachlorobenzene (HCB) contamination seems to have originated from the usage of fungicides or as an impurity in pesticide formations, a by-product of various chlorination processes and the combustion of industrial and municipal wastes (Kannan et al., 1995b). The earlier studies showed low concentrations of HCB in green mussels, ranging from $<$0.02 to 0.31 ng g^{-1} in 1989 (Siriwong et al., 1991), $<$0.02–0.21 ng g^{-1} in 1991 (Ruangwises et al., 1994), $<$0.01–0.09 ng g^{-1} in 1994, and $<$0.01–0.12 ng g^{-1} in 1995 (Kan-atireklap et al., 1997b), whereas in the fish collected during 1999–2000 HCB was not detected (Kan-atireklap et al., 2002).

However, in recent studies on marine organisms collected from east coast of the Gulf of Thailand during 1999–2000, several organochlorine pesticides were detected in some marine fish, namely monocle bream (*Scolopsis* spp.), threadfin bream (*Nemipterus* spp.), lizardfish (*Saurida* spp.), goatfish (*Parupeneus* spp.), and common squid (*Loligo* spp.) with ranges of <0.01–$17.48\,\mathrm{ng\,g^{-1}}$ for DDTs, <0.01–$1.15\,\mathrm{ng\,g^{-1}}$ for HCHs, and <0.01–$4.74\,\mathrm{ng\,g^{-1}}$ for CHLs, whereas HCB was not detected. Among the organochlorine pesticides examined, DDTs were found to be the highest, followed by CHLs and HCHs, respectively (Kan-atireklap et al., 2002).

In general, earlier results showed that DDT residues were the highest among various pesticides analyzed, followed by CHLs, HCHs, and HCB, in that order. On the other hand, higher levels of CHLs than DDTs were detected in mussels during 1997–1999 (Boonyatumanond et al., 2002). These results may indicate that the usage of DDT in several locations in Thailand decreased after the ban, whereas CHLs were being widely used until its ban in the year 2000.

From the public health point of view, high DDT levels in fish and squid collected during 1999–2000 did not exceed the Extraneous Residues Limit (ERL) of $1000\,\mathrm{\mu g\,kg^{-1}}$ (wet weight basis) for meat and entrails of aquatic animals, issued by the Ministry of Public Health of Thailand as shown in Fig. 10.3 (Kan-atireklap et al., 2002), and $300\,\mathrm{\mu g\,kg^{-1}}$ for poultry meat, as recommended by FAO/WHO (FAO/WHO, 2000). Based on the average daily consumption (57 g/day/person) of fish by Thai (FAO, 1991 cited by Kannan et al., 1995a) of 60 kg body weight and using the values on the levels of DDTs in marine fish and squid collected during 1999–2000, the daily intake of DDTs by Thai were estimated. The average dietary intake value of Thai was found to be 0.062 μg/person/day with the highest value of 0.996 μg/person/day. The dietary exposure to DDTs from marine fish and squid by Thai was lower than that of the Provisional Tolerable Daily Intake (PTDI) of 600 μg/person/day recommended by FAO/WHO (FAO/WHO, 2000). However, the dietary intake of DDTs was likely to be an underestimation of the actual consumption because the values were obtained from fish only.

Up to now, some studies have reported the contamination by organotin compounds in Thailand. Tributyltin contaminations in sea water, fish, bivalves, and sediments collected from Thailand have been reported (Kannan et al., 1995a; Kan-atireklap et al., 1997a, b; Tiensing, 1997; Lommettra, 2001; Kan-atireklap et al., 2004) and imposex widely reported as being caused by tributyltin was also recorded in gastropods in the coastal areas of the Gulf of Thailand and Andaman Sea (Swennen et al.,

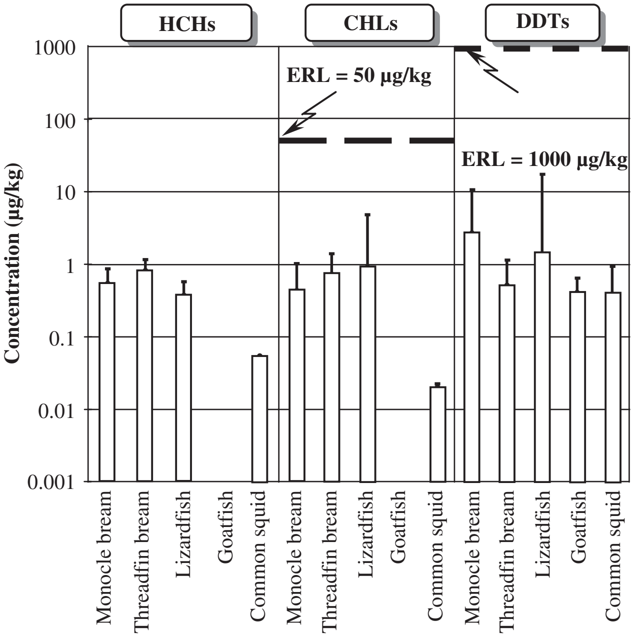

Figure 10.3. Average (white bar) concentration levels of organochlorine pesticides contaminated in marine organisms from Eastern coast of the gulf of Thailand comparing to Extraneous residue Limit (ERL). (*Source*: Kan-atireklap et al., 2002.)

1997; Bech, 1999). These observations indicate that butyltin compounds are widespread in Thai waters.

The occurrence of organotin compounds in Thailand was first reported in fish, namely Silver pomfret, Indian mackerel, and Giant seaperch collected from Bangkok in 1994 (Kannan et al., 1995a). Concentrations of total butyltin compounds in fish muscles ranged from 2.9 to 16 $\mathrm{ng\,g^{-1}}$ on wet wt. Among various butyltin derivatives, tributyltin was a predominant compound found in muscle of fish with the range of 1.3–13 $\mathrm{ng\,g^{-1}}$ on wet wt. Similarly, tributyltin was also detected in muscles of demersal fish collected from offshore of east coast of the Gulf of Thailand in 2000, ranging from 0.2 to 10.1 $\mathrm{ng\,g^{-1}}$ wet wt., whereas the concentration range of total butyltin compounds was from 0.2 to 11.5 $\mathrm{ng\,g^{-1}}$ wet wt. (Kan-atireklap et al., 2004).

During 1994–1995, butyltin compounds in green mussels (*P. viridis*) collected along the coastal areas of Thailand, both in the Gulf of Thailand and Andaman Sea were widely detected in a range of 4–800 $\mathrm{ng\,g^{-1}}$ wet wt., suggesting a widespread contamination along the coastal waters of Thailand. Relatively high concentrations of butyltin compounds in green mussel were found in high boating activity and coastal aquaculture areas, implying the usage of tributyltin as a biocide in antifouling paints used on boat hulls and marine aquaculture facilities (Kan-atireklap et al., 1997b). Concentration ranges were from <3 to 45 ng g^{-1} wet wt. for monobutyltin, 1–80 ng g^{-1} wet wt. for dibutyltin, and 3–680 ng g^{-1} wet wt. for tributyltin. The composition of butyltin derivatives in mussel was in the order of tributyltin > dibutyltin > monobutyltin, suggesting also the presence of significant and recent butyltin source in coastal Thailand. Butyltin residual pattern in green mussels revealed higher levels in aquaculture than in boating activity sites. Butyltin compounds in marine fish (Kan-atireklap et al., 2004) was lower than sediments (Kan-atireklap et al., 1997a) and mussel (Kan-atireklap et al., 1997b) (Fig. 10.4). Further, a study on the distribution of BTs in green mussels (*P. viridis*) by Kan-atireklap et al. (1997b) showed a widespread contamination all along the coastal areas of Thailand (Fig. 10.5). Recently, 10 ng l^{-1} has been designated as the safe level for all coastal areas in Thailand (PCD, 2006).

In addition, Tiensing (1997) determined tributyltin residues in sea water and oyster (*Saccostrea cucullata*) samples collected from the high boating activity along the east coast of the Gulf of Thailand and detected these compounds in ranges of 62.2–93.9 ng l^{-1} for sea water and 19.7–237 ng g^{-1} wet wt. for oyster. In 2000, butyltin compounds in the eastern coast of the Gulf of Thailand were detected in the ranges of 43.1–277.1 ng l^{-1} in sea water, 2.3–73.4 ng g^{-1} wet wt. in bivalves, and 8.7–63.9 ng g^{-1} wet wt. in marine fish (Lommettra, 2001). On the other hand, a recent investigation

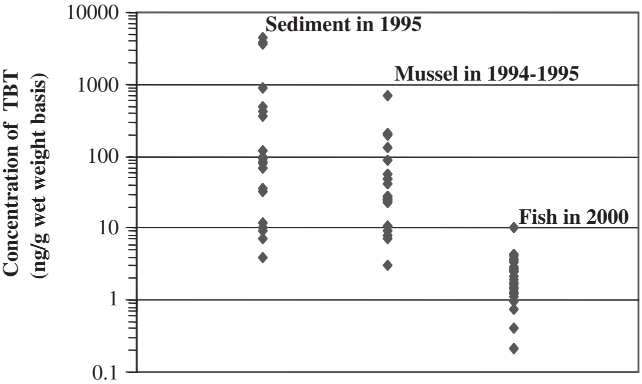

Figure 10.4. Comparison of TBT in environmental samples from Thailand. (*Source*: Kan-atireklap et al., 1997a,b; Kan-atireklap et al., 2004.)

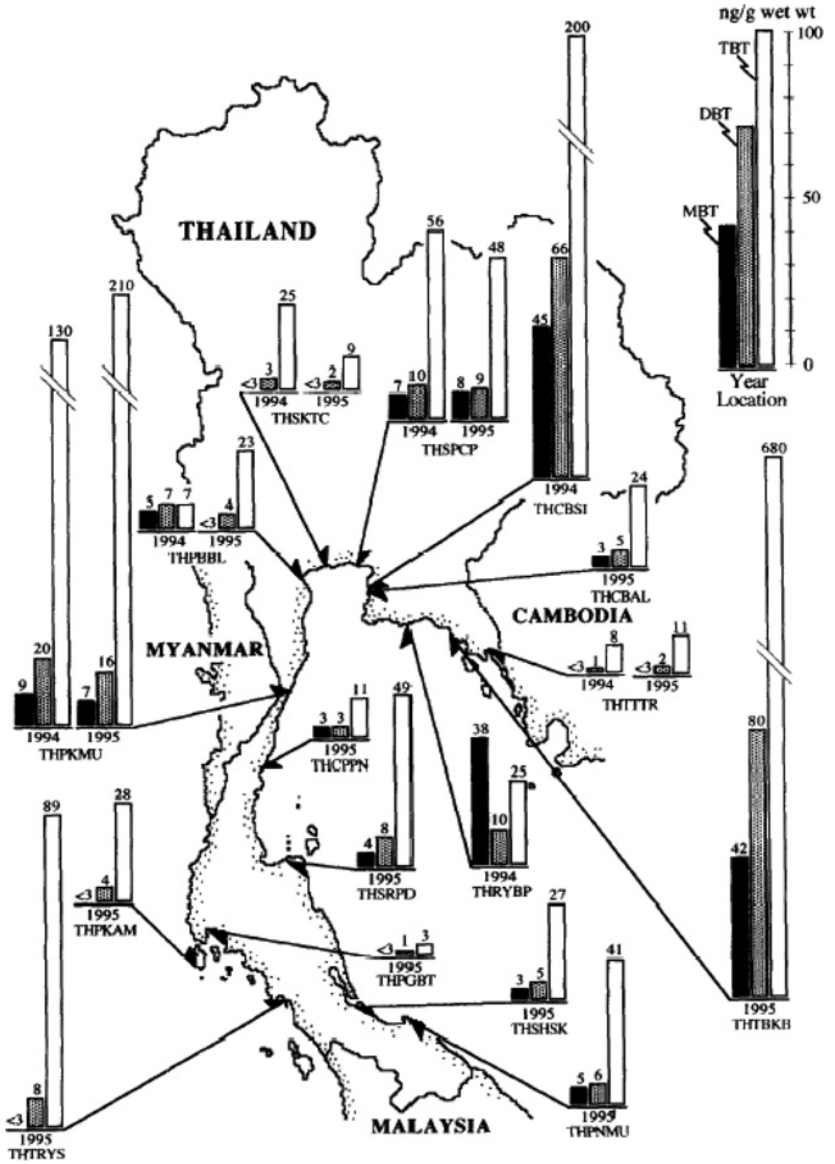

Figure 10.5. Distribution of butyltin compounds in green mussel (*Perna viridis*) from Thailand coastal waters. (*Source*: Kan-atireklap et al., 1997b.)

has shown the presence of lower concentrations of tributyltin in coastal fish than those from offshore areas far from tributyltin sources (Kan-atireklap et al., 2004). According to a monitoring survey of Pollution Control Department of Thailand, tributyltin concentrations in sea water collected from coastal areas of Thailand in 2003 ranged from 2 to $52\,\mathrm{ng\,l^{-1}}$ (Pollution Control Department, 2004). The high TBT concentration levels were found in high shipping areas.

Numerous investigations have shown that there is a significant correlation between incidence of imposex and the concentration of tributyltin in the tissue of gastropods (Gibbs et al., 1990). Recent studies showed widespread occurrence of imposex in coastal waters of Thailand (Swennen et al., 1997; Bech, 1999). Swennen et al. (1997) reported the percentage of occurrence of imposex in gastropods from high shipping areas was 100% in some locations along the east coast of the Gulf of Thailand and 86% in southern part of Thailand. Nearly 100% of *Thais bitubercularis* female had imposex in the harbor area and up to 1 km from any known source of tributyltin (Bech, 1999).

Recently, imposex in *Thais distinguenda* increased significantly from 1996 to 2000 at Phanga Bay along the east coast of Phuket Island, Thailand. The area of occurrence of females with imposex increased, extending from 3.5 km in 1996 to 10 km from the harbor areas in 1999 and 2000 (Bech, 2002). Even the less sensitive species of gastropods *Morula musiva, M. granulata, M. margariticola*, and *Thais rufotincta* also developed imposex at three main areas of intense shipping and tourism activities in the region. The author has also mentioned that his results suggest that TBT contamination is worsening, against global trends, because regulations prohibiting the use of TBT-paints do not exist in Thailand.

According to some earlier studies, detection of butyltin compounds in sediments (Kan-atireklap et al., 1997a) and mussels (Kan-atireklap et al., 1997b) of Gulf of Thailand suggest the source of tributyltin is the usage of antifouling paints in coastal aquaculture and in far sea vessels or boating activities. High concentrations of butyltin compounds were found in mussels from coastal aquaculture areas and high fishing boat activities, whereas far sea vessel areas were lower. On the other hand, high butyltin levels were detected in sediments from commercial or far sea vessel areas, whereas the levels in high fishing boat and coastal aquaculture areas were lower. Despite early restriction on the use of tin-containing boat paints, a considerable amount of butyltin compounds is still stored in polluted sediments with a half-life of several years (Sarradin et al., 1994, 1995; de Mora et al., 1995). Therefore, butyltins in sediment might exhibit earlier contamination, whereas mussels may reveal a present contamination of butyltin compounds in respective aquatic environment. This pattern implies that butyltin usage in coastal aquaculture in Thailand might have increased from the past to present, while usage in far sea vessels or boating activities were in a steady state or could have slightly increased.

Additionally, continuous input of tributyltin into the coastal waters of the Gulf of Thailand may also provide a plausible explanation for the higher ratio of tributyltin found in fish samples (Kan-atireklap et al., 2004). The usage of organotin compounds in antifouling paints and other purposes was not controlled in Thailand yet. Fent (1996) suggested butyltin contaminations must be regarded as a global problem, particularly where no regulation has been implemented, such as in countries in Asia, Africa, and South America. In addition, an increasing demand for antifouling paints is predicted in the Asia-Pacific region (Layman, 1995). Considering the unregulated usage and the increasing demand of butyltin compounds in Thailand, organotin contamination in aquatic environment may increase in the future.

10.3.3. Human

Since the 1960s, monitoring programs of persistent compounds in human tissues have been implemented in many industrialized and some developing countries (Tanabe and Subramanian, 2006) for assessing environmental pollution and to estimate the body burden as well as their toxic risks. Thailand has been using organohalogen compounds from the middle of 20th century, but over the past 20 years many of these compounds, especially the organochlorines were banned by Thai government. In spite of such widespread use and ban based on various estimates of the levels of pollutants in the environment and wildlife, information on the human levels of PTS in Thailand is very much scanty.

In earlier attempts Schecter et al. (1989a) found that the human milk samples of Thailand contained higher levels of DDT and its metabolite DDE than in USA and Germany. They have also reported detection of PCDD/DF in the human milk from Thailand. It was also reported by Schecter et al. (1991) that the human blood samples from Thailand contained measurable levels of PCCDD/DF and also PCBs. Further, the same group of authors (Schecter et al., 1989b) reported that the soy milk preparations and cow milk from Thailand, to which the newborn infant changes after weaning, contained quite low levels of dioxins and dibenzofurans as compared to human milk, pointing out to a matter of severe concern in Thailand.

A survey on the levels of organochlorine pesticides in human milk from Hmong hill tribes in northern Thailand (Stuetz et al., 2001) reported considerable levels of heptachlor ($125\,\mathrm{ng\,g^{-1}}$ lipid), heptachlor epoxide

(177 ng g^{-1} lipid), DDE (8210 ng g^{-1} lipid), and DDT (2600 ng g^{-1} lipid). Further, the estimated daily intakes of DDT, heptachlor, and heptachlor epoxide by the infants exceeded up to 20 times the acceptable daily intakes recommended by the FAO and WHO. The authors found that HCB values in many of their samples also exceeded the tolerable daily intake guidance values recommended by WHO. Even though the use of many of the organochlorines are banned in Thailand, it may take 10–20 years before low levels of OCP residues, such as those in developed countries at the end of the 1990s, can be reached.

10.3.4. Food items

As early as in 1991, Tanabe et al. analyzed the raw food items like fish meal, meat, farm products, etc. from Bangkok, Thailand, for their organochlorine pesticide levels and found that PCBS, DDTs, HCHs, HCB, aldrin, dieldrin, and heptachlor epoxide were found at least in trace amounts in all the samples analyzed (Tanabe et al., 1991). They found higher HCH levels in the farm products whereas DDTs were higher in fishes including fish flakes and fish meal. Meat samples contained higher DDTs and dieldrin. PCBs were also found in low levels. However the levels were lower than the food safety levels set forth by FAO/WHO/FDA. Food contamination in Bangkok by HCB, heptachlor, and heptachlor epoxide was comparatively lower. Earlier to this report, Schecter et al. (1989b) found measurable levels of PCDDs/DFs in soy preparations and in cow's milk of Thailand indicating a severe concern on infant health. In their attempt in reviewing the organotin levels in seafood of several countries, Belfroid et al. (2000) have stated that the literature data on TBT show that the Tolerable Average Residue Level (TARL) is exceeded in one or more samples in developed nations such as Canada, France, Italy, Japan, and USA and in some developing countries such as Taiwan, Korea, and also Thailand. Other than these, not much information is available on the levels of persistent toxic chemicals as has been available from developed and some other developing nations.

10.4. Management of hazardous substances

10.4.1. Laws, regulations, and implementation

Ever since the early 1960s, Thailand has been busy tackling the occupational health and environmental problems systematically and at national level. At present, there are many government agencies responsible in the field of chemical control and management. Before 1967, production, import, export, sale, or handling of toxic substances in Thailand was not controlled. In order to control the utilization of toxic substances for various purposes, the "Toxic Substance Act of 1967" was promulgated in Thailand in 1967. In 1973, some more measures on registration of manufacturers of toxic substances were added to the amendment of the Act, which was promulgated as the "Toxic Substance Act, 2nd Amendment of 1973."

Later, a large number of hazardous substances, other than those specified in the above Acts, were used in various industries and agriculture in Thailand. Several Ministries, bureaus, and departments administered the then existing laws. As a consequence, different proclamations were made during different periods of time, resulting in discrepancies and incomprehensiveness of the provisions of the existing Acts. So, concerned agencies collaborated in the revisions and integration of the then existing laws into one law known as Hazardous Substance Act of 1992. By definition, the "Hazardous Substance" means any of the following substances: explosives, flammable, oxidizing agents and peroxides, toxic, infectious, radioactive, mutant causing (mutagens), corrosive, irritating, and other substances either chemicals or otherwise which may cause injury to humans, animals, plants, properties, or the environment. Three ministries, namely the Ministry of Industry, the Ministry of Agriculture and Cooperatives, and the Ministry of Public Health are directly involved in the control of hazardous substances.

The Ministry of Industry has established quality standards and control of industries and factories involved with chemicals, particularly those generating hazardous or toxic chemicals under the provision of the Factory Act of 1969 (amended in 1972, 1975, 1979, and 1992). The Ministry of Agriculture and Cooperatives has the authority to control toxic substances in agriculture, particularly pesticides. Under the same Act, the Ministry of Public Health also controls the toxic substances used as consumer products and for some purposes of human health. After 1992, those ministries included a lot of hazardous substances in the Ministerial Notification by periodically following the evaluation of such substances, either old or newly introduced.

The Ministry of Natural Resources and Environment is responsible for developing policies, strategies, and action plans to achieve environmental quality standards and pollution control. This ministry is composed of various departments, such as Department of Environmental Quality Promotion, Pollution Control Department, and Office of Natural Resources and Environmental Policy and Planning. Recommendations have been made with regard to the maintenance of environmental quality standards and control of pollution by toxic chemicals as protective measures under the Enhancement and Conservation of National Environmental Quality Act of 1975, 1978, 1979, and amended in 1992. In addition, Ministry of Natural Resources and Environment, Ministry of Agriculture and Cooperatives, and Ministry of Public Health have done a great deal of monitoring and analysis of residues of hazardous substances including those of POPs chemicals.

The Customs Department under the Ministry of Finance is responsible for prevention and control of smuggling of all goods and other illegal products including import, export, and re-export of hazardous substances, chemical products, and hazardous wastes. This agency is not directly responsible for control of pollution but works in collaboration with other agencies in order to play a role in controlling substances or chemicals that are imported for use as a raw material or catalyst in some industrial processes.

10.4.2. Bans and restrictions

Import, export, manufacture, and possession of hazardous substances have been controlled under the Hazardous Substances Act, 1992. However, banning of the import or severely restricted uses of chemicals had been notified in the Ministerial Notifications since 1977. Two insecticides, namely chlordimeform and leptophos were the first two of the banned chemicals in 1977. According to the Act, Ministerial Notifications of the Ministry of Industry were issued to banning of nine specified POPs pesticides usage since 1980 (Table 10.4). Only seven specified POPs pesticides were imported and widely used in Thailand, namely aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, and toxaphene, whereas hexachlorobenzene and mirex have never been imported. Although

Table 10.4. List of banned specified persistent organic pollutants (POPs) pesticide in Thailand (*Source*: Wong-ek, 2000)

POPs pesticides	Date of banned
Aldrin	September 1988
Chlordane	May 2000
DDT	March 1983, 1995
Dieldrin	May 1988
Endrin	July 1981
Heptachlor	September 1988
Hexachlorobenzene	March 1980 and never been imported
Mirex	Never been imported
Toxaphene	March 1983

hexachlorobenzene was never been imported, it was the first one to be banned in 1980, followed by endrin in 1981 and toxaphene in 1983. DDT has been used both in agriculture and for malaria control but it was banned for agricultural uses from 1983 and for malaria control in 1995 pending availablity of other alternatives. Dieldrin, aldrin, and heptachlor were banned in 1988. Chlordane was the last one to be banned in 2000. On the other hand, the regulation prohibiting the usage of other organohalogen chemicals and organotin compounds in industrial and agriculture sections do not exist now in Thailand.

10.5. Conclusion

The demand for agricultural productivity and the expansion of industry is now causing a rapid increase in the use of many chemicals in Thailand. Most chemicals, organic and inorganic were imported from ~40 countries including developing and developed countries and were widely used in almost all over the country. As a result, widespread contamination of several persistent chemicals were noticed in almost all the environmental and biotic matrices. In the past 20 years, improved government policy has resulted in better control of chemical management including legislation and management. Import of many chemicals, including those of specified POPs chemicals have now been prohibited for all uses. In spite of these control measures the levels of some of the banned chemicals still appear in the environment as well as biota, some times even above the safety levels specified by international agencies. It may take few more years to few decades for those chemicals to disappear from Thai environment and biota, depending on the persistence and bioavailability of the chemical. Apart from these, several new chemicals, whose existence in the environment and biota are not yet known, may be detected. Continuing a clear vision on environmental issues and monitoring the chemical(s) under concern are the need of the hour in Thailand.

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Chapter 11

Persistent Organic Pollutants in Vietnam: Levels, Patterns, Trends, and Human Health Implications

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Abstract

This chapter provides an overview of the contamination by persistent organic pollutants (POPs) in Vietnam on the basis of the results of extensive monitoring studies conducted in our laboratory during the last two decades. Surveys conducted in the framework of Asia-Pacific Mussel Watch Program during early 1990s indicated widespread contamination by polychlorinated biphenyls (PCBs) and organochlorine (OC) insecticides, particularly DDTs and HCHs in various environmental compartments such as air, water, soils, sediments, and fish collected from different parts of Vietnam. Recent studies have revealed elevated contamination by DDTs in fish, mussels, and birds from Vietnam. Interestingly, DDT residue concentrations in fish and birds from Vietnam are among the highest values reported for the countries in Asia-Pacific region, suggesting the role of Vietnamese environment as a potential emission source of DDTs in this region. Open dumping sites for municipal wastes in some major cities such as Hanoi and Hochiminh City is a matter of concern with regard to environmental pollution, particularly contamination by dioxins (PCDDs) and related compounds such as dibenzofurans (PCDFs) and coplanar PCBs. Soils collected in dumping sites in Hanoi contained higher PCDD/F residues as compared to general soils collected far from dumping sites. PCDD/F concentrations in a few soil samples from Hanoi exceeded the environmental guideline values, suggesting potential health effects on humans and wildlife living near these dumping sites. Daily intakes of DDTs via seafood estimated for Vietnamese general population were among the highest values reported for East Asian countries. In the open dumping sites, intakes of dioxins by residents were significantly greater than those living far from dumping sites. Particularly, the estimated intakes of

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dioxins via soil ingestion and dermal exposure for children were higher than those for adults, suggesting greater risk of dioxin exposure for children in dumping sites. Future studies should be focused on the temporal trends of POPs in biota in Vietnam to predict the future trends of contamination and to understand possible toxic impacts on organisms. In addition, human exposure and possible toxic effects, particularly on children should be considered as priority research as they are the most susceptible group and have higher exposure levels to dioxins.

11.1. Introduction

Global contamination and toxic effects of persistent organic pollutants (POPs) have been an emerging environmental issue and received considerable attention during the past four decades. Although the extent of contamination by POPs has been dominant in industrialized nations, an increasing number of recent investigations have highlighted the role of Asia-Pacific region as a potential source of emission for these chemicals, particularly to pristine areas such as the Arctic and the Antarctic (e.g., see review by Tanabe et al., 1994; Tanabe, 2002).

Vietnam is located at the center of the Southeast Asian region (Fig. 11.1); it has more than 300 km coastal lines and two major agricultural production areas: the Red River Delta in the north and the Mekong River Delta in the south. These two deltas inhabited by approximately more than 30 million people and are two of the most densely populated areas in the world. The Mekong River Delta has recently become one of the most productive agricultural regions of Southeast Asia. Such a strategic geographical position and rapid agricultural development of Vietnam have made this country become an important subject for extensive studies dealing with environmental pollution during the last three decades.

This chapter provides a comprehensive review of the studies dealing with persistent organic substances in Vietnam. Available data of POP contamination in Vietnam were compiled on the basis of various investigations in frame of the Asia-Pacific Mussels Watch Program, the Core University Program supported by Japan Society for the Promotion of Science (JSPS), which were conducted in our laboratory during the last decade. In addition, results from other laboratories were also reviewed to help improve insight into the distribution, transport, and fate, bioaccumulation feature and possible toxic implications for environmental quality and human health. This paper focuses on the organochlorine (OC) insecticides such as 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDTs) and its metabolites

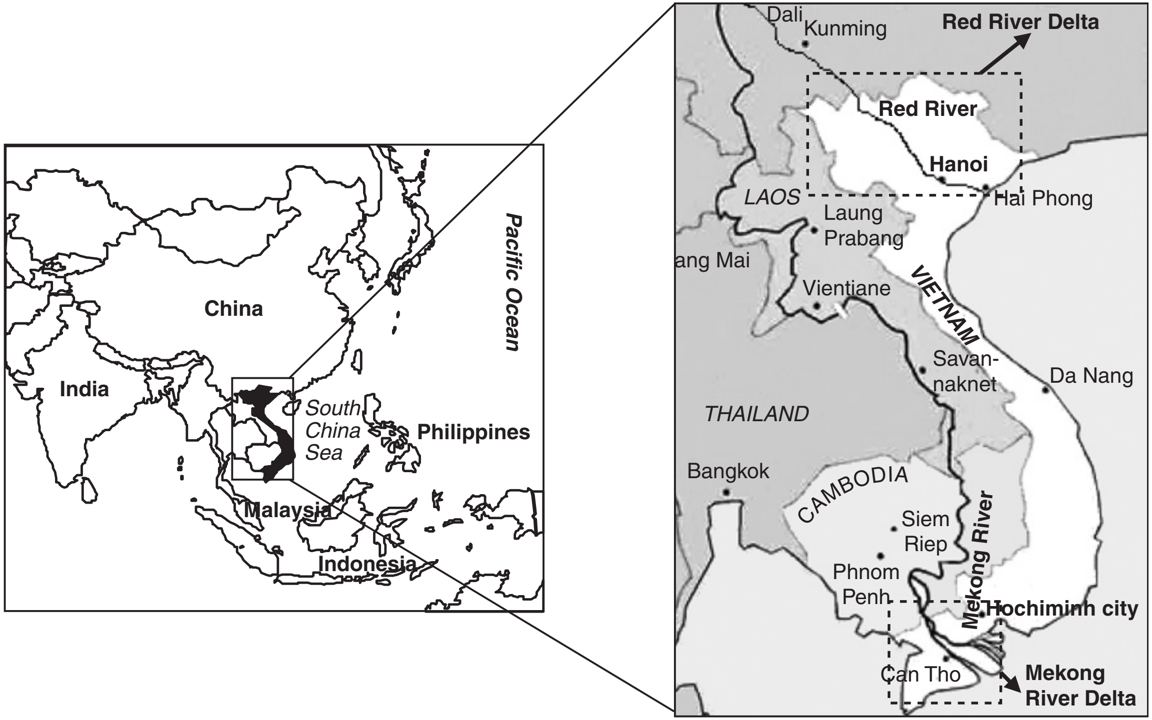

Figure 11.1. Map of Vietnam.

(DDTs), hexachlorocyclohexane isomers (HCHs), chlordane compounds (CHLs) and hexachlorobenzene. Residues levels of industry-derived contaminants such as polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) were also reviewed. Concentrations of these contaminants in different environmental compartments were expressed as unit equivalent to part-per-billion (ppb) level, unless otherwise specified. The cited values of concentrations from various literature sources were rounded to two significant digits for comparison. A number of factors can influence the concentrations in biological samples. Therefore, whenever possible, for biological samples the lipid normalized concentrations were cited for comparison.

11.2. Production and usage of persistent organic pollutants in Vietnam

In general, information on the production and usage of POPs, particularly OC insecticides and PCBs in Vietnam as well as some other developing countries in East Asian region are still limited or obscure. Systematic inventory of toxic man-made chemicals is lacking in these countries due to their limited capacity to conduct comprehensive monitoring surveys. Recently, the United Nations Environment Programs has initiated various monitoring programs for POPs at regional and global levels and the results have been summarized at different workshops. According to the reports, active ingredients for insecticides were not produced in Vietnam. In fact, before 1985, pesticides such as DDT and HCB were imported from former Soviet Union and some socialistic countries with the quantity of ~6500–9000 tons year^{-1} (Sinh et al., 1999). The statistical data showed that the total quality of DDT imported to Vietnam for malaria control from 1957 to 1990 was 24,042 tons. During 1986–1990, approximately 800 tons have been used (Sinh et al., 1999). These amounts are still lower than those in some other countries in region such as Malaysia, Indonesia, and India. DDT usage for malaria control ceased in Vietnam in 1995 and some other chemicals such as pyrethroid compounds have been used as substitutes for DDT (Sinh et al., 1999).

The information about usage of PCBs in Vietnam is still obscure. Statistical data showed that ~27,000–30,000 tons of oils contaminated by PCBs were imported from former USSR, China, and Rumania (Sinh et al., 1999). In addition, electrical equipments like transformer containing PCBs were also imported from Australia until the mid-1980s (Kannan et al., 1995). Other possible source of PCBs in Vietnam could be the weapons which were extensively used during the Indochina War (Thao et al., 1993). Regarding dioxins, the main source in Vietnam in the past was the Agent

Orange and other herbicides sprayed in South Vietnam during the American War. Recently, Stellman and co-workers (Stellman et al., 2003) provided revised estimates on the amounts of herbicides used in Vietnam. During 1961–1971, at least ~45 million liters of Agent Orange were sprayed (Stellman et al., 2003). 2,4,5-T, a constituent of Agent Orange is known to be contaminated with 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). However, the combustion-derived sources of dioxins in Vietnam have been unknown. Various kinds of combustion processes may be facilitating the widespread contamination of dioxins and related compounds in Vietnam.

11.3. Widespread contamination

11.3.1. Air, water, sediments, and soils

Comprehensive monitoring surveys have been conducted during the early 1990s to examine the distribution of POPs such as PCBs, DDTs, HCHs, and HCB in air, water, and sediments from estuarine environments from various countries in Asia-Pacific comprising Japan, India, Vietnam, the Philippines, Thailand, Indonesia, Malaysia, the Philippines, and Australia (Iwata et al., 1994). These investigations reported the presence of higher residues of DDTs and HCHs in air and water from coastal and estuarine areas in the developing countries of tropical and subtropical regions (India, Thailand, and Vietnam), rather than developed nations (Japan and Australia). A compilation of available data of POPs in water, soils, and sediment from Vietnam is given in Tables 11.1 and 11.2. The distribution in air, water, and sediments from northern, central, and southern regions of Vietnam showed relatively higher DDT concentrations, indicating a widespread contamination of this insecticide throughout the country. This result suggests extensive use of DDT for agricultural purposes in the past and for malaria control until very recently. Interestingly, in a survey conducted ~10 years later (1998/99) covering an extended area along Red River and Duong River, the two biggest rivers in northern Vietnam, elevated concentrations of DDTs, HCHs, and CHLs were found (Hung & Thiemann, 2002). The levels of DDTs, HCHs, and CHLs in Red and Duong River were apparently higher than those reported in the 1990s surveys. In addition, wastewater collected near to areas having extensive human activities areas such as canals of Tu Liem district, suburb Hanoi (northern Vietnam) and Thi Nghe River, Hochiminh City (southern Vietnam) contained elevated concentrations of DDTs (Table 11.1). It is interesting to note that the levels examined in a recent survey (in suburb Hanoi; Hung &

Table 11.1. Concentrations (ng L^{-1}) of persistent organochlorines in water from Vietnam

Location	Sample	Year	*N*	DDTs	HCHs	CHLs	PCBs	Reference	Remark
Red River, Hanoi	River water	1990	1	0.68	3.2	0.045	0.84	Iwata et al. (1994)	DDTs: sum of *p,p′*-DDE, *p,p′*-DDD, and *p,p′*-DDT; HCHs: sum of α-, β-, and γ-HCH; CHLs: sum of *cis*-chlordane, *trans*-chlordane, *cis*-nonachlor, *trans*-nonachlor, and oxychlordane; PCBs: quantified by an equivalent mixture of Kanechlor preparations (KC-300, KC-400, KC-500, and KC-600)
Phu Loc Lake, Hue	Lake water	1990	1	0.29	18	0.21	1.2	Iwata et al. (1994)	
Huong River, Hue	River water	1990	1	1.1	1.9	0.07	1.6	Iwata et al. (1994)	
Nha Be River, Hochiminh City	Estuarine water	1990	1	4.7	31	0.55	2.7	Iwata et al. (1994)	
Gua Canal, Cu Chi	River water	1990	1	0.6	9.5	0.16	1.9	Iwata et al. (1994)	
Long Tau River, Hochiminh City	Estuarine water	1990	1	0.55	5.2	0.13	0.57	Iwata et al. (1994)	
Thi Nghe Canal, Hochiminh City	Estuarine water	1990	1	25	19	1	8	Iwata et al. (1994)	
Red River and Duong River, northern Vietnam	River water	1998/1999						Hung and Thiemann (2002)	DDTs: sum of *p,p′*-DDE, *p,p′*-DDD, *p,p′*-DDT, *o,p′*-DDE, *o,p′*-DDD, and *o,p′*-DDT; HCHs: sum of α-, β-, γ-, and δ-HCH; CHLs: sum of heptachlor and heptachlorepoxide
Dry season			18	44 (0.55–320)[a]	17 (1.6–83)	21 (0.81–110)	–		
Rainy season			18	56 (8.4–230)	29 (3.1–97)	27 (1.6–130)	–		
Lakes in Hanoi: West Lake, Thuyen Quang Lake	Lake water	1998/1999						Hung and Thiemann (2002)	
Bay Mau Lake and Ba Mau Lake									
Dry season			4	2.1 (0.21–3.6)	0.69 (0.26–2.16)	2.9 (1.1–4.8)	–		
Rainy season			4	5.1 (0.65–15)	32 (0.69–120)	13 (2–51)	–		
Irrigation canal, Tu Liem, suburb Hanoi	River water	1998/1999						Hung and Thiemann (2002)	
Dry season			6	59 (8.2–130)	7.2 (1.6–18)	6.9 (6.0–7.5)	–		
Rainy season			6	50 (11–110)	17 (5.5–26)	15 (1.2–25)	–		
Wells, Gia Lam, suburb Hanoi	Groundwater	1998–1999						Hung and Thiemann (2002)	
Dry season			2	0.17 (0.11–0.23)	0.21 (0.19–0.22)	0.17	–		
Rainy season			2	0.09	0.04	<0.5	–		

[a] Mean (range).

Table 11.2. Concentrations (ng g^{-1} dry wt) of persistent organochlorines in sediments and soils from Vietnam

Location	Sample/sampling site characteristic	Year	*N*	DDTs	HCHs	CHLs	PCBs	Reference	Remark
Phu Da, Hue	Sediment, paddy field	1990	1	0.52	0.43	0.072	0.65	Iwata et al. (1994)	DDTs: sum of *p,p′*-DDE, *p,p′*-DDD, and *p,p′*-DDT; HCHs: sum of α-, β-, and γ-HCH; CHLs: sum of *cis*-chlordane, *trans*-chlordane, *cis*-nonachlor, *trans*-nonachlor, and oxychlordane; PCBs: quantified by an equivalent mixture of Kanechlor preparations (KC-300, KC-400, KC-500, and KC-600)
A Luoi, Binh Tri Thien	Sediment, municipal sewage	1990	1	68	2.4	0.79	0.18	Iwata et al. (1994)	
Long Giang Canal, Duyen Hai	Sediment, paddy field	1990	1	8	1.1	0.42	3.7	Iwata et al. (1994)	
Lo Giang River, Duyen Hai	Sediment, paddy field	1990	1	1	0.45	0.15	2.2	Iwata et al. (1994)	
Don Canal, Duyen Hai	Sediment, paddy field	1990	1	3.3	0.94	0.21	2.1	Iwata et al. (1994)	
La Canal, Duyen Hai	Sediment, paddy field	1990	1	10	2.3	0.58	9.7	Iwata et al. (1994)	
Ben Nghe Canal, Hochiminh City	Sediment, municipal sewage	1990	1	120	5.2	8.8	140	Iwata et al. (1994)	
Tan Binh, Tay Ninh	Sediment, paddy field	1990	1	7.8	0.7	0.31	–	Iwata et al. (1994)	
Gua Canal, Cu Chi	Sediment, paddy field	1990	1	0.37	0.63	0.24	0.22	Iwata et al. (1994)	
Song Long Tau, Duyen Hai, Hochiminh City	Sediment, paddy field	1990	6	17 (2.1–47)	0.82 (0.5–1.3)	0.26 (0.14–0.46)	6.2 (2.3–8.9)	Iwata et al. (1994)	
Thi Nghe Canal, Hochiminh City	Sediment, municipal sewage	1990	3	530 (360–790)	8.5 (6.0–12)	20 (19–20)	570 (440–630)	Iwata et al. (1994)	
Thinh Liet, Thanh Tri, Hanoi	Soil, paddy field	1990	1	330	18	–	39	Thao et al. (1993)	DDTs: sum of *p,p′*-DDE, *p,p′*-DDD, *p,p′*-DDT, and *o,p′*-DDT; HCHs: sum of α-, β-, γ-, and δ-HCH; CHLs: sum of cis-chlordane, trans-chlordane, *cis*-nonachlor, *trans*-nonachlor and oxychlordane; PCBs: quantified by an equivalent mixture of Kanechlor preparations (KC-300, KC-400, KC-500, and KC-600)
Vinh Quynh, Thanh Tri, Hanoi	Soil, paddy field	1990	2	76 (31–120)	30 (4–55)	–	11 (5.5–17)	Thao et al. (1993)	
Yen Duyen, Thanh Tri, Hanoi	Soil, paddy field	1990	2	47 (19–74)	1.8 (1.3–2.3)	–	21 (13–28)	Thao et al. (1993)	
Phu Da, Binh Tri Thien	Soil, paddy field	1990	1	38	2.8	–	8.6	Thao et al. (1993)	
Hong Ha, A luoi, Binh Tri Thien	Soil, paddy field	1990	1	23	4.7	–	5.2	Thao et al. (1993)	
Ta Bat, Aluoi, Binh Tri Thien	Soil, paddy field	1990	1	11	1.4	–	2.6	Thao et al. (1993)	
Son Thuy, Aluoi, Binh Tri Thien	Soil, paddy field	1990	1	1300	5.7	–	12	Thao et al. (1993)	
Hong Kim, Aluoi, Binh Tri Thien	Soil, paddy field	1990	1	9.7	0.31	–	0.61	Thao et al. (1993)	
An Hoa, Hue	Soil, paddy field	1990	1	69	5.3	–	5	Thao et al. (1993)	

Table 11.2. (Continued)

Location	Sample/sampling site characteristic	Year	*N*	DDTs	HCHs	CHLs	PCBs	Reference	Remark
Phu Loc, Hue	Soil, upland	1990	4	1.9 (0.73–4.4)	0.15 (0.09–0.21)	–	2.1 (1.4–4.0)	Thao et al. (1993)	
Binh Khanh, Duyen Hai, Hochiminh City	Soil, paddy field	1990	2	27 (24–30)	1.5 (1.4–1.5)	–	3.9 (1.6–6.1)	Thao et al. (1993)	
Tan Thuan, Nha Be, Hochiminh City	Soil, paddy field	1990	1	64	4	–	12	Thao et al. (1993)	
My Hung, Cu Chi	Soil, paddy field	1990	1	7.9	0.23	–	1.5	Thao et al. (1993)	
Ba Diep, Hooc Mon	Soil, upland	1990	1	280	0.79	–	130	Thao et al. (1993)	
An Phu, Cu Chi	Soil, upland	1990	3	14 (1.9–37)	2.3 (1.9–2.5)	–	3.7 (3.0–4.2)	Thao et al. (1993)	
Tan Binh, Tan Bien, Tay Ninh	Soil, paddy field	1990	1	5.5	0.15	–	1.6	Thao et al. (1993)	
Thanh Phu, Tan Bien, Tay Ninh	Soil, paddy field	1990	1	350	3.4	–	320	Thao et al. (1993)	
Duong Minh Chau, Tay Ninh	Soil, paddy field	1991	1	1.9	2	–	2.3	Thao et al. (1993)	
Duong Minh Chau, Tay Ninh	Soil, green bean field	1991	1	2.4	0.57	–	1.8	Thao et al. (1993)	
Tan Bien, Tay Ninh	Soil, paddy field	1991	1	6.6	0.78	–	2.3	Thao et al. (1993)	
Hoa Thanh, Tay Ninh	Soil, sugarcane and peanut	1991	1	5.1	1.3	–	1.6	Thao et al. (1993)	
Tan Chau, Tay Ninh	Soil, rubber plantation	1991	1	1.6	1.4	–	1	Thao et al. (1993)	
Tan Chau, Tay Ninh	Soil, sugarcane	1991	1	290	0.27	–	0.45	Thao et al. (1993)	
Tan Chau, Tay Ninh	Soil, harvested crop	1991	5	88 (1.0–270)	0.92 (0.09–2.3)	–	34 (0.95–150)	Thao et al. (1993)	
Tan Bien, Tay Ninh	Soil, paddy field	1991	1	5.7	0.42	–	1	Thao et al. (1993)	
Go Dau, Tay Ninh	Soil, harvested crop	1991	1	130	0.46	–	32	Thao et al. (1993)	
Trang Bang, Tay Ninh	Soil, harvested crop	1991	1	150	0.47	–	38	Thao et al. (1993)	
Duong Minh Chau, Tayninh	Non-cultivated soil	1991	1	1.5	0.8	–	5	Thao et al. (1993)	
Tan Bien, Tay Ninh	Non-cultivated soil,	1991	1	13	1.8	–	92	Thao et al. (1993)	
Tan Chau, Tay Ninh	Non-cultivated soil, US bombed site	1991	1	0.46	0.95	–	25	Thao et al. (1993)	

Tan Bien, Tay Ninh	Non-cultivated soil	1991	6	11 (0.25–38)	0.71 (0.09–1.9)	–	4.8 (0.23–13)	Thao et al. (1993)	
Tan Uyen, southern Vietnam	Non-cultivated soil	1991	2	14 (2.0–26)	1.3 (0.44–2.1)	–	8.0 (3.1–13)	Thao et al. (1993)	
Saigon River, Hochiminh City	River sediment	Q	11	80 (1.8–250)	–	–	220	Phuong et al. (1998)	DDTs: sum of *p,p*′-DDE, *p,p*′-DDD, and *p,p*′-DDT; PCBs: sum of 6 congeners
				DS/RS[a]	DS/RS		DS/RS		
Hanoi	Sediment, irrigation canal, northwest Hanoi	1995/1996	1	6.9/13	0.14/0.07	–	4.1/0.98	Nhan et al. (1998)	DDTs: sum of *p,p*′-DDE, *p,p*′-DDD, and *p,p*'-DDT; PCBs: quantified by Arochlor 1260; HCHs: γ-HCH only
Hanoi	Sediment, paddy field, southwest Hanoi	1995/1996	1	7.5/14	0.41/0.16	–	6.0/1.3	Nhan et al. (1998)	
Ba Lat Estuary, Red River, northern Vietnam	Sediment	1995/1996	1	7.1/3	0.5/0.05	–	1.1/0.7	Nhan et al. (1998)	
Cua Lan Estuary, Thai Binh coast lines, northern Vietnam	Sediment, intertidal mudflat areas	1995/1996	1	5.8/4.9	0.48/0.025	–	0.87/0.41	Nhan et al. (1998)	
Tra Ly Estuary, Thai Binh coast lines, northern Vietnam	Sediment, intertidal mudflat areas	1995/1996	1	7.3/5.1	0.62/0.13	–	0.36/0.32	Nhan et al. (1998)	
Diem Dien Estuary, Thai Binh coast lines, northern Vietnam	Sediment, intertidal mudflat areas	1995/1996	1	6.2/4.6	0.36/0.11	–	0.23/0.11	Nhan et al. (1998)	
Tra Co beach, Mong Cai, northern coast of Vietnam	Marine sediment, intertidal mudflat areas	1997	1 (pooled)	10	34	–	22	Nhan et al. (1999)	DDTs: sum of *p,p*′-DDE, *p,p*′-DDD, and *p,p*′-DDT
Mong Duong, northern coast of Vietnam	Marine sediment, intertidal mudflat areas	1997	1 (pooled)	8.1	4.1	–	0.51	Nhan et al. (1999)	HCHs: sum of α-, β-, and γ-HCH
Ha Long, northern coast of Vietnam	Marine sediment, intertidal mudflat areas	1997	1 (pooled)	7.2	1.8	–	11	Nhan et al. (1999)	PCBs: sum of 13 congeners
Hai Phong, northern coast of Vietnam	Marine sediment, intertidal mudflat areas	1997	1 (pooled)	6.7	1.7	–	18	Nhan et al. (1999)	

Table 11.2. (*Continued*)

Location	Sample/sampling site characteristic	Year	*N*	DDTs	HCHs	CHLs	PCBs	Reference	Remark
Ba Lat estuary, northern coast of Vietnam	Marine sediment, intertidal mudflat areas	1997	1 (pooled)	6.3	1.2	–	0.33	Nhan et al. (1999)	
Cau Dien, Nhue River, suburb Hanoi	Sediment, canal, densely populated industrial area	1997	2	43 (15–71)	0.34 (0.09–0.58)	–	1.7 (0.97–2.51)	Nhan et al. (2001)	DDTs: sum of *p,p′*-DDE, *p,p′*-DDD, *p,p′*-DDT, *o,p′*-DDE, *o,p′*-DDD, *o,p′*-DDT, and DDMU; PCBs: sum 13 congeners; HCHs: sum of α-, β-, and γ-HCH; CHLs: sum *cis*-chlordane, *trans*-chlordane, and *trans*-nonachlor
Nhue River, suburb Hanoi	Sediment, canal, rural area	1997	1	8.3	0.78	–	0.74	Nhan et al. (2001)	
Nhue River, suburb Hanoi	Sediment, canal	1997	1	21	0.32	–	18	Nhan et al. (2001)	
Hanoi downtown	Sediment, canal, densely populated industrial area	1997	1	13	0.44	–	5.3	Nhan et al. (2001)	
ToLich River, suburb Hanoi	Sediment, canal, densely populated industrial area	1997	2	59 (36–81)	2.0 (0.85–3.12)	–	29 (24–34)	Nhan et al. (2001)	
Thuong Tin, suburb Hanoi	Sediment, canal, southern Hanoi city	1997	2	37 (24–50)	1.3 (0.59–1.98)	–	20 (16–24)	Nhan et al. (2001)	
Thuong Tin, suburb Hanoi	Sediment, canal, rural area, southern Hanoi city	1997	1	7.4	0.65	–	3.1	Nhan et al. (2001)	
Gia Lam, suburb Hanoi	Sediment, canal, rural area, eastern Hanoi city	1997	1	17	0.46	–	1.9	Nhan et al. (2001)	
Dong Anh, suburb Hanoi	Sediment, canal, rural area, Northern Hanoi city	1997	1	23	0.07	–	1.8	Nhan et al. (2001)	
Ha Long Bay, northern Vietnam	Estuary sediment	1998	–	28	6.1	–	37	Viet et al. (2000)	
Viet Tri, northern Vietnam	Industrial areas	1998	–	5.2	0.68	–	2.3	Viet et al. (2000)	

Hanoi	Soils, municipal dumping sites	1999–2001	7	21 (2.2–58)[b]	0.75 (0.3–2.2)	0.3 (0.08–1.5)	14 (2.2–20)	Minh et al. (2004)	DDTs: sum of *p,p′*-DDE, *p,p′*-DDD, and *p,p′*-DDT; HCHs: sum of α-, β-, and γ-HCH; CHLs: sum of *cis*-chlordane, *trans*-chlordane, *cis*-nonachlor, *trans*-nonachlor, and oxychlordane; PCBs: quantified by an equivalent mixture of Kanechlor preparations (KC-300, KC-400, KC-500, and KC-600)
Hanoi	Soils, reference areas relative to the Municipal dumping sites	1999–2001	1	6	0.35	<0.03	6.9	Minh et al. (2004)	
Hochiminh City	Soils, municipal dumping sites	1999–2001	7	23 (0.2–93)	0.56 (<0.01–0.9)	1.2 (0.12–2.5)	22 (0.82–40)	Minh et al. (2004)	
Hochiminh City	Soils, reference areas relative to the Municipal dumping sites	1999–2001	3	5.5	0.54	0.2	7.5	Minh et al. (2004)	
Canal, Can Tho, Mekong River, southern Vietnam	Sediment, canals in Cantho city	2003–2004	4	2.8 (1.8–4.3)	0.04 (<0.02–0.11)	0.2) (0.12–0.35	1.8 (0.12–3.7)	Iwata et al. (2004)	DDTs: sum of *p,p′*-DDE, *p,p′*-DDD, and *p,p′*-DDT; HCHs: sum of α-, β-, and γ-HCH; CHLs: sum of *cis*-chlordane, *trans*-chlordane, *cis*-nonachlor, and *trans*-nonachlor; PCBs: quantified by an equivalent mixture of Kanechlor preparations (KC-300, KC-400, KC-500, and KC-600)
Hau River, Mekong River delta, southern Vietnam	Sediment, river	2003–2004	7	0.96 (0.043–1.9)	<0.02–0.044	0.06 (0.025–0.13)	0.21 (0.12–0.54)	Iwata et al. (2004)	
Canals, Hochiminh city, Saigon River, southern Vietnam	Sediment, canals, densely populated areas	2004	5	37	–	–	81	Minh et al. (2005)	
Saigon River, Hochiminh City	Sediment, river	2004	5	6.9	–	–	8.5	Minh et al. (2005)	
Saigon River, downstream and coastal areas	Sediment, downstream and coastal areas	2004	9	1.2	–	–	0.92	Minh et al. (2005)	

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[a] Dry season/rainy season.

[b] Mean (range).

Thiemann, 2002) were even higher than those reported a decade ago (Iwata et al., 1994). Although backgrounds of analytical methods and sampling locations are different among those studies, these observations suggest that the use of DDT for malaria control were relatively extensive until very recently in both northern and southern Vietnam.

Geographical distribution of OCs in sediments from Vietnam showed little variability compared to air and water (Fig. 11.2 and Table 11.2). Consistent results were also observed when considering distribution in Asia-Pacific region (Iwata et al., 1994). A recent survey also indicate rather uniform distribution of DDTs in sediments along the coasts of northern Vietnam, from the sites near the border of China downward to the Red River estuary (Table 11.2, Nhan et al., 1998, 1999). Shorter residence time in water phase and rapid volatilization POPs from sediments of due to the high temperate in tropical region could be reasons for this uniform distribution (Iwata et al., 1994; Tanabe, 2000). However, an interesting result was observed for HCHs, showing relatively higher concentrations in Mong Cai, a site near the border of China than other locations towards the southern areas (Fig. 11.2 and Table 11.2). China has been known as one of the top global HCH users (Li, 1999), and this may be possible reason for such high concentrations in Mong Cai.

As for soils samples, an extensive survey carried out on various soils in northern and southern Vietnam indicated higher concentrations of DDTs in soils from paddy fields than those in soils from upland areas (Table 11.2, Thao et al., 1993). This clearly reflects the status of DDT use as insecticide in the past. Elevated PCB levels were recorded in some specific sites in Tay Ninh, southern Vietnam, where the former US Army Base was located (Thao et al., 1993). A recent survey in soils from the open dumping sites for municipal wastes in Hanoi and Hochiminh City, the two largest metropolitan cities in Vietnam revealed that residue concentrations of DDTs and PCBs in soils collected from dumping sites were much higher than those in paddy field soils collected far from the dumping sites (Fig. 11.3, Minh et al., 2006). PCBs and OC insecticides were likely to be originated from continuous loading of municipal wastes containing residues of these compounds. The open dumping sites therefore, may act as sources of PCBs and OC insecticides.

To understand the magnitude of contamination of POPs in Vietnam, residue concentrations in air, water, and sediments were compared with those in other countries in Asia-Pacific (Fig. 11.4). Higher contamination of DDTs in Vietnamese coastal environments was recorded, again indicating the extensive use of this insecticide in Vietnam. Interestingly, elevated PCB residues were also observed in water and sediments from Mekong River estuary, southern Vietnam; and the levels were comparable to those

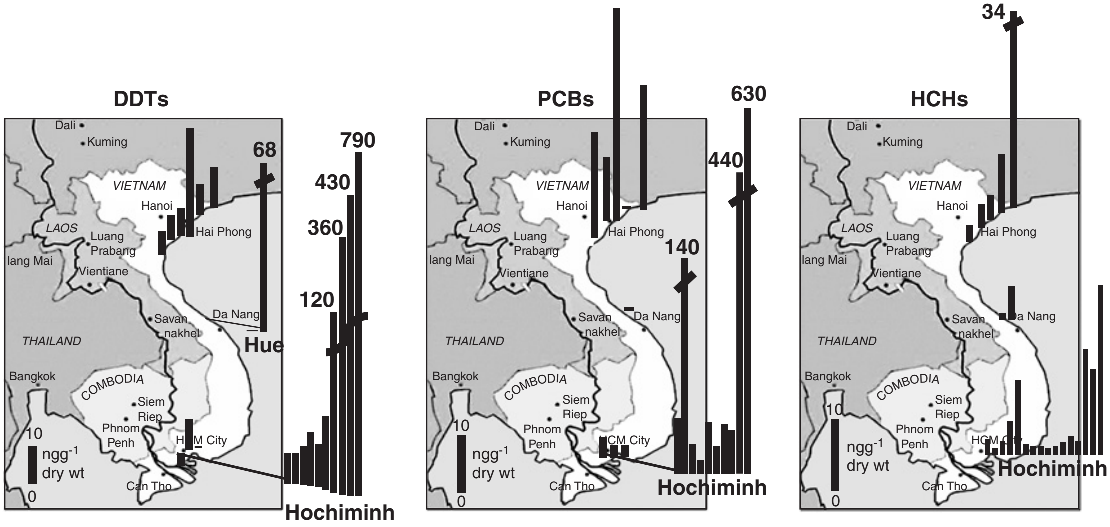

Figure 11.2. Distribution of persistent organochlorines in sediment from various locations in Vietnam.

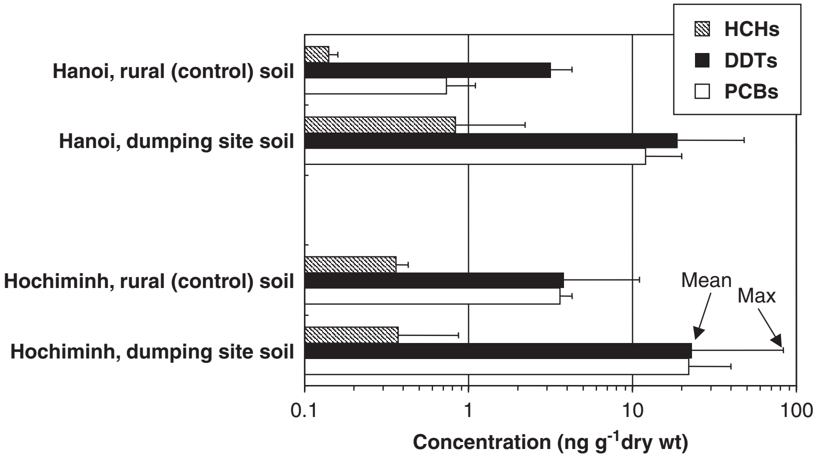

Figure 11.3. Residue concentrations of persistent organochlorines in soils from open dumping sites and rural areas (control sites) in Hanoi and Hochiminh City, the two biggest cities in Vietnam.

reported in some locations in India, Japan, and Australia (Fig. 11.4). High PCB contamination in Vietnam observed during our survey in early 1990s could be derived from both the electrical equipments imported from industrialized nations like former Soviet Union and Australia and the leakages from army weapons extensively used in Indochina War during 1961–1971 (Thao et al., 1993).

Available data on the worldwide comparison for PCBs and OC insecticides levels in open dumpsites are rather scarce. A comparison of PCBs and DDTs residue levels in dumping sites from Vietnam with those in soils from other countries were given in Fig. 11.5. In general, the levels of PCBs in the dumping sites were higher than those in background soils from various countries including industrialized nations such as United States, Russia, Italy, etc, where high contamination of PCBs are commonly reported (Meijer et al., 2003; Minh et al., 2004). Our survey indicated that DDT levels in the dumping site soils were comparable to those found in agriculture soils collected in early 1990s from various countries such as Russia (Iwata et al., 1995), Ireland (McGrath, 1995), and Slovak Republic (Marta et al., 1997), and higher than most of the urban soils recently collected in many countries like Egypt (Ahmed et al., 1998), Korea (Kim & Smith, 2001), and the reference sites in this study (Fig. 11.5). This observation highlights the role of the open dumpsites in Asian developing countries including Vietnam as significant pollution sources of PCBs and DDTs.

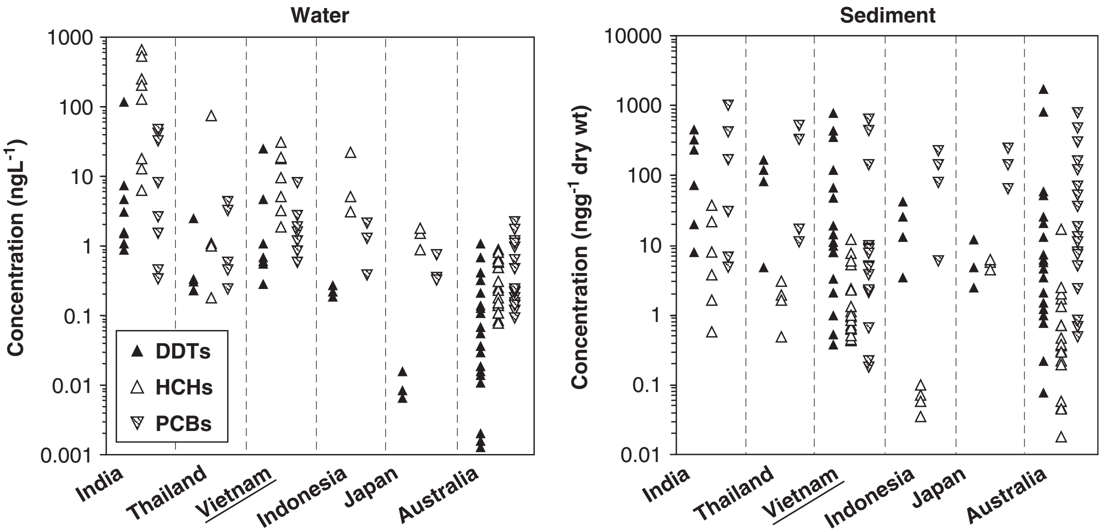

Figure 11.4. Comparison of persistent organochlorine residues in surface water and sediment from different countries in Asia-Pacific.

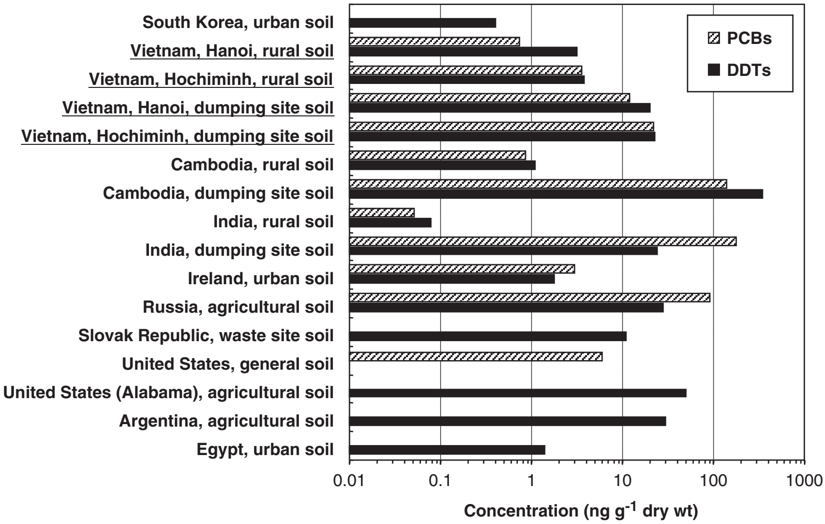

Figure 11.5. Comparison of organochlorine residue levels in soils from different countries in the world.

11.3.2. Biological samples (fish, bivalves, and birds)

Extensive studies on OC contamination in fish and mussels from Asia-Pacific countries including Vietnam were carried out by Kannan et al. (1995) and Monirith et al. (2003). Similar to sediment samples, a relatively uniform distribution of OCs was observed in fish in various countries in the Asia-Pacific region. In Vietnam, residues levels of DDTs were relatively high in both surveys in 1990 and 1997 (Table 11.3). Mussels collected from coastal areas in north and middle of Vietnam contained elevated DDT concentrations (Table 11.3, Monirith et al., 2003). Subsequent surveys conducted by Nhan et al. (1998, 1999) examined OC distribution in clams from different sites along the northern coasts, and results showed a very similar distribution to sediment samples. In particular, residue concentrations of DDTs, HCHs, and PCBs were relatively high in the sites near to the border of China and a decreasing trend was noticed toward southern coastlines (Table 11.3). At the two estuary areas: Hai Phong harbor with extensive human and industrial activities, and Thai Binh province, one of the highest rice production areas in Vietnam, higher concentrations were again observed. In general, the feature of distribution and magnitude of contamination in sediment and biota (fish and bivalves) was very similar in both local and regional scale, which can be characterized by the enhanced

Table 11.3. Concentrations (ng g^{-1} lipid wt) of persistent organochlorines in biological samples from Vietnam

Location	Sample/sampling site description	Year	*N*	Lipid content (%)	DDTs	HCHs	CHLs	PCBs	Reference	Remark
Hanoi	Fish	1990	7	1.9	1900 (680–4000)[a]	120 (47–210)	7.9 (<0.5–17)	580 (270–950)	Kannan et al. (1995)	DDTs: sum of *p,p′*-DDE, *p,p′*-DDD and *p,p′*-DDT; HCHs: sum of α-, β-, and γ-HCH; CHLs: sum of *cis*-chlordane, *trans*-chlordane, *cis*-nonanchor, *trans*-nonanchor, and oxychlordane; PCBs: quantified by an equivalent mixture of Kanechlor preparations (KC-300, KC-400, KC-500, and KC-600)
Phu Da, Hue	Fish	1990	6	1.9	1100 (210–2700)	48 (32–74)	8.9 (<0.5–12)	630 (160–1300)	Kannan et al. (1995)	
Hochiminh City	Fish	1990	6	1.9	1100 (89–4100)	110 (33–200)	3.2 (<0.5–18)	950 (190–3100)	Kannan et al. (1995)	
Con Lu Island, Red River Estuary, Northern Vietnam	Fish (*Mugil sp. and Chlorophthalmus sp.*)	1997	10	3.2	4200 (330–8500)	350 (27–210)	110 (29–210)	110 (81–140)	Minh et al. (2002)	
Con Lu Island, Red River Estuary	Shrimp	1997	20 (pooled as 1 sample)	2.8	160	150	3.9	100	Minh et al. (2002)	
Cat Ba Island, Cai Hai Province	Green mussel, floating habitat	1997	38 (pooled as 1 sample)	1.1	530	3.6	14	86	Monirith et al. (2003)	DDTs: sum of *p,p′*-DDE, *p,p′*-DDD and *p,p′*-DDT; HCHs: sum of α-, β-, and γ-HCH; CHLs: sum of *cis*-chlordane, *trans*-chlordane, *cis*-nonanchor, *trans*-nonanchor, and oxychlordane; PCBs: quantified by an equivalent mixture of
Cat Hai Province	Green mussel, floating habitat	1997	34 (pooled as 1 sample)	0.9	300	12	12	20	Monirith et al. (2003)	
Cat Hai Province	Green mussel, floating habitat	1997	8 (pooled as 1 sample)	0.7	2500	5.7	24	450	Monirith et al. (2003)	
Cat Hai Province	Green mussel, floating habitat	1997	12 (pooled as 1 sample)	2	420	3	5	110	Monirith et al. (2003)	
Lach Truong, Thanh Hoa	Green mussel, aquaculture	1997	33 (pooled as 1 sample)	1.2	610	3.3	13	65	Monirith et al. (2003)	
Ron River Estuary, Ky Anh	Green mussel, fishing village	1997	50 (pooled as 1 sample)	0.6	470	5.5	20	190	Monirith et al. (2003)	
Lang Co, Hue	Green mussel	1997	143 (pooled as 1 sample)	0.9	34000	10	–	380		

Table 11.3. (*Continued*)

Location	Sample/sampling site description	Year	*N*	Lipid content (%)	DDTs	HCHs	CHLs	PCBs	Reference	Remark
Thi Nai, Binh Dinh	Green mussel, urban, shipping traffic, aquaculture	1997	54 (pooled as 1 sample)	1.1	220	6.3	36	26	Monirith et al. (2003)	Kanechlor preparations (KC-300, KC-400, KC-500, and KC-600)
Phan Ri Estuary, Phan Ri	Green mussel, urban, fishing village	1997	30 (pooled as 1 sample)	1.1	240	2.9	11	80	Monirith et al. (2003)	
Hanoi	Clam (*Hyriopsis*), irrigation canal	1996	15 (pooled as 1 sample)	–	7400	97	–	480	Nhan et al. (1998)	DDTs: sum of *p,p′*-DDE, *p,p′*-DDD, and *p,p′*-DDT; HCHs: sum of α-, β-, and γ-HCH; PCBs: sum 13 congeners
Hanoi	Carp (*Cyprinus carpio*), rice field	1996	3 (pooled as 1 sample)	–	22000	370	–	2600	Nhan et al. (1998)	
Balat Estuary, Thai Binh	Shrimp (*Metapenaeus*)	1996	35 (pooled as 1 sample)	–	1000	390	–	490	Nhan et al. (1998)	
Balat Estuary, Thai Binh	Clam (*Meretrix meretrix*)	1996	43 (pooled as 1 sample)	–	830	57	–	220	Nhan et al. (1998)	
Diem Dien Estuary, Thaibinh	Clam (*Mactra quadrangularis*), intertidal mudflat coastal area	1996	13 (pooled as 1 sample)	–	1000	30	–	200	Nhan et al. (1998)	
Tra Co, Mong Cai, northern coast of Vietnam	Clam (*Meretrix meretrix*), intertidal mudflat areas	1997	1 pooled sample	–	1200	2400	–	900	Nhan et al. (1999)	DDTs: sum of *p,p′*-DDE, *p,p′*-DDD, and *p,p′*-DDT; HCHs: sum of α-, β-, and γ-HCH; PCBs: sum 13 congeners
Mong Duong, northern coast of Vietnam	Clam (*Meretrix meretrix*), intertidal mudflat areas	1997	1 pooled sample	–	590	400	–	480	Nhan et al. (1999)	
Ha Long, Quang Ninh, northern coast of Vietnam	Clam (*Meretrix meretrix*), intertidal mudflat areas	1997	1 pooled sample	–	660	93	–	470	Nhan et al. (1999)	
Hai Phong, northern coast of Vietnam	Clam (*Meretrix meretrix*), intertidal mudflat areas	1997	1 pooled sample	–	850	77	–	580	Nhan et al. (1999)	

Ba Lat Estuary, Thai Binh, northern coast of Vietnam	Clam (*Meretrix meretrix*), intertidal mudflat areas	1997	1 pooled sample	–	920	71	–	250	Nhan et al. (1999)	
Cau Dien, Nhue River, Hanoi	Freshwater snails (*Angulyagra sp.*), densely populated industrial area	1997	1 pooled sample	–	23000	29	14	720	Nhan et al. (2001)	DDTs: sum of *p,p′*-DDE, *p,p′*-DDD, *p,p′*-DDT, *o,p′*-DDE, *o,p′*-DDD, *o,p′*-DDT, and DDMU; PCBs: sum 13 congeners; HCHs: sum of α-, β-, and γ-HCH; CHLs: sum *cis*-chlordane, *trans*-chlordane, *trans*-nonachlor, and heptachlor
Cau Dien, Nhue River, Hanoi	Freshwater snails (*Angulyagra sp.*), densely populated industrial area, transformer production	1997	1 pooled sample	–	45000	21	27	2200	Nhan et al. (2001)	
Nhue River, suburb Hanoi	Freshwater snails (*Angulyagra sp.*), rural area	1997	1 pooled sample	–	320	9.8	–	330	Nhan et al. (2001)	
Hanoi downtown	Freshwater snails (*Angulyagra sp.*), densely populated industrial area	1997	1 pooled sample	–	2700	13	1.8	1000	Nhan et al. (2001)	
To Lich River, suburb Hanoi	Freshwater snails (*Angulyagra sp.*), densely populated industrial area	1997	1 pooled sample	–	5300	19	–	3000	Nhan et al. (2001)	
Red River, suburb Hanoi	Freshwater snails (*Angulyagra sp.*), rural area	1997	1 pooled sample	–	910	8.2	2.2	480	Nhan et al. (2001)	
Gia lam, suburb Hanoi	Freshwater snails (*Angulyagra sp.*), rural area	1997	1 pooled sample	–	1000	15	–	340	Nhan et al. (2001)	
Dong Anh, suburb Hanoi	Freshwater snails (*Angulyagra sp.*), rural area	1997	1 pooled sample	–	640	11	1	280	Nhan et al. (2001)	

Table 11.3. (*Continued*)

Location	Sample/sampling site description	Year	*N*	Lipid content (%)	DDTs	HCHs	CHLs	PCBs	Reference	Remark
Mekong River, Can Tho	Catfish (*Pangasianodon hypophthalmus*), common aquaculture	2004	20	3.8 (0.6–7.2)	59 (7.9–150)	0.47 (<0.03–1.5)	0.62 (<0.01–2.6)	7.2 (0.91–27)	Minh et al. (2005)	DDTs: sum of *p,p′*-DDE, *p,p′*-DDD, and *p,p′*-DDT; HCHs: sum of α-, β-, and γ-HCH; CHLs: sum of *cis*-chlordane, *trans*-chlordane, *cis*-nonachlor, *trans*-nonachlor, and oxychlordane; PCBs: quantified by an equivalent mixture of Kanechlor preparations (KC-300, KC-500, and KC-600)
Can Tho	Catfish (*Clarias sp.*), from a pond near municipal dumping site	2004	5	3.6 (3.2–4.1)	390 (330–700)	2.2 (0.86–5.1)	5.7 (4.2–8.2)	50 (37–77)	Minh et al. (2005)	
Con Lu Island, Red River Estuary, northern Vietnam (250–2400)	Resident birds (including 7 species), wetland wintering grounds	1997	16	1.9–16	6200 (1100–	150 13000)[b]	100 (23–310)	780 (5–550)	Minh et al. (2002)	
Con Lu Island, Red River Estuary, northern Vietnam	Migratory birds (including 17 species), wetland wintering grounds	1997	84	4.1–33	2900 (750–6800)	330 (20–1700)	22 (5.3–130)	530 (82–1600)	Minh et al. (2002)	

[a] Mean (range).

[b] Average concentrations of 7 resident and 17 migratory species.

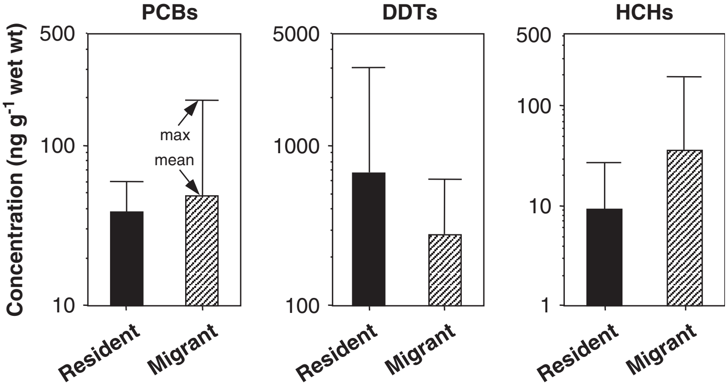

Figure 11.6. Accumulation of persistent organochlorines in birds from Vietnam according to the migratory behavior.

volatilization of semi-volatile organic compounds in high temperature prevailing in tropical ecosystems.

To our knowledge, only few studies have examined OC contamination in higher trophic animals from Vietnam. A survey conducted in 1997 determined OC concentrations in resident and migratory birds from North Vietnam (Minh et al., 2002). Resident birds contained higher concentrations of DDTs than those in migrants (Fig. 11.6). This result indicates recent exposure to DDTs in resident birds from North Vietnam, where elevated DDT contamination is very common as discussed earlier. Interestingly, accumulation of HCHs revealed a contrasting pattern, showing apparently greater concentration in migratory birds (Fig. 11.6). This could be due to accumulation in stopover sites during migration in some polluted areas such as India, southern China, and Japan. The role of these countries as potential sources of HCH accumulation in wintering migratory birds breeding in Lake Baikal, Russia has been also suggested in a recent study (Kunisue et al., 2002). As for PCBs, residue concentrations were similar in residents and migratory species and the levels were relatively low, indicating less prominent sources of PCBs in North Vietnam in recent years. Thus, accumulation pattern of OCs in birds from North Vietnam according to their migratory behavior distinctively reflects the status of contamination of each contaminant. This phenomenon also suggests the suitability of using birds as bioindicators for monitoring POPs in the global environment.

International comparison of OC residues in fish, mussels, and birds from Vietnam indicated relatively higher levels of DDTs in Vietnamese samples (Fig. 11.7). Results of recent surveys in Asia-Pacific Mussel

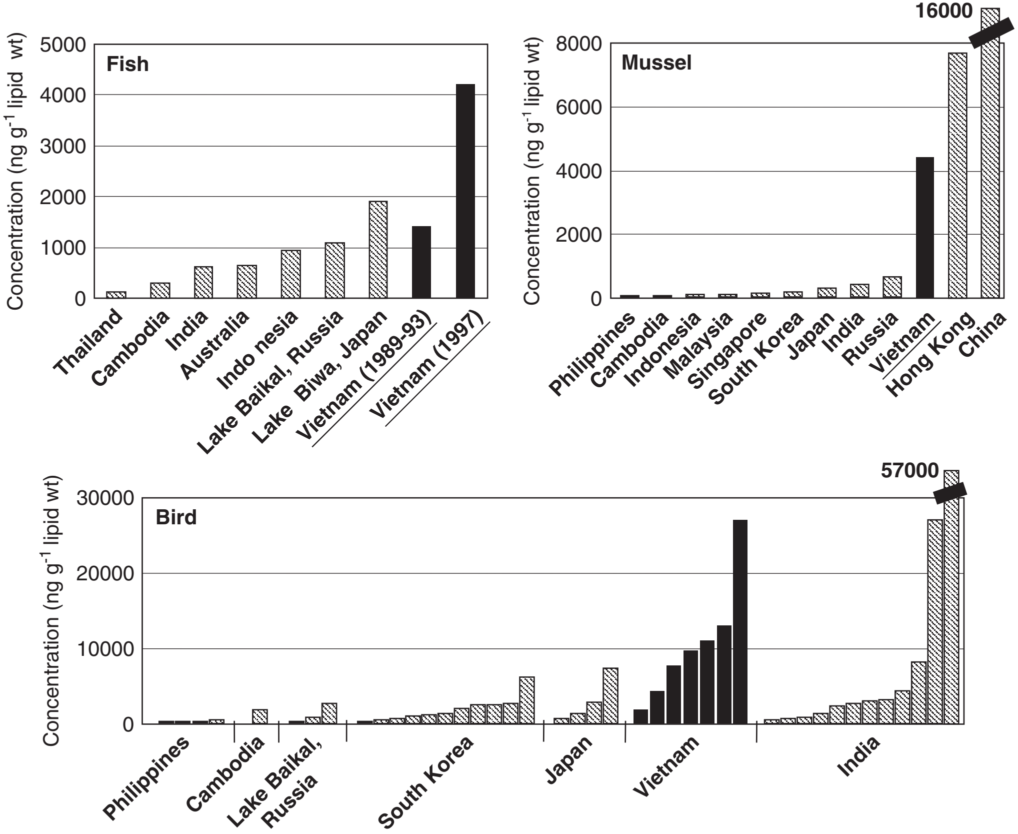

Figure 11.7. Comparison of organochorine residue levels in fish, mussels, and birds in Asia-Pacific countries.

Watch Program showed that DDT levels in Vietnamese mussels were lower than those in mussels from southern China and Hong Kong, but higher than those collected from most of other countries in East Asian region (Fig. 11.7, Monirith et al., 2003). Kannan et al. (1995) reported mean concentration of DDT in fish from Vietnam were higher than India, Thailand, Indonesia, and Australia. Contamination pattern were similar to birds, showing that DDT residue levels in some resident species in Vietnam were among the highest values reported for the Asian countries surveyed (Fig. 11.7, Minh et al., 2002). It is interesting to note that though the recent amounts of DDTs used in Vietnam were lower than those of other countries in the region, the extent of DDT contamination in environmental samples in Vietnam was higher. This observation suggests that the application of DDTs in Vietnam has continued until very recently, resulting in elevated contamination of these compounds in different species occupying low to high trophic levels in food chain.

11.3.3. Human exposure

Available data on human exposure to OC insecticides and PCBs in Vietnamese residents are limited. Preliminary survey by Schecter et al. (1989a) reported very high concentrations of DDTs and HCHs in human breast milk samples from some locations in and around Hochiminh City, southern Vietnam (Table 11.4). DDT levels were higher in both rural and urban areas, ranging from 10,500 to 12,000 $\mathrm{ng\,g^{-1}}$ lipid wt. PCBs levels, however, were relatively low as compared to other countries. A subsequent study conducted in 2000/2001 have provided more extensive data on human exposure and insights into the accumulation kinetics of PCBs and OC insecticides such as DDTs, HCHs, CHLs, HCB, and *tris*(4-chlorophenyl)methane (TCPMe)—a newly detected environmental contaminant which exhibits weak endocrine disrupting properties. Breast milk of 96 nursing women living near the dumping sites of municipal wastes in Hanoi and Hochiminh City, the two biggest metropolitan cities in Vietnam were analyzed for these above contaminants (Table 11.4, Minh et al., 2004). In general, similar degree of exposure to DDTs, CHLs, HCB, and PCBs were observed among samples from Hanoi and Hochiminh City. Interestingly, HCH residues in breast milk of women from Hanoi were significantly greater than those in Hochiminh City, suggesting recent high background levels of HCHs in northern part as compared to southern region. Consistent result was also observed in the survey on sediment and bivalves from various locations along the northern coast of Vietnam, which demonstrated relatively higher residues in sites near the China border (Nhan et al., 1998, 1999). Earlier reports also pointed out similar

Table 11.4. Concentrations of persistent organochlorines in human samples from Vietnam

Locations	Year	Samples/sampling site despcription	Unit	*N*	DDTs	HCHs	CHLs	HCB	PCBs	Reference	Remark
Me Tri and Tu Liem, Hanoi	2000	Breast milk, primiparas women near municipal dumping sites	ng g^{-1} lipid		2400	69	2.5	4.2	76	Minh et al. (2004)	DDTs: sum of *p,p′*-DDE, *p,p′*-DDD, and *p,p′*-DDT; HCHs:β-HCH only; CHLs: sum of oxychlordane, *trans*-nonachlor, and *cis*-nonanchor; PCBs: quantified by an equivalent mixture of Kanechlor; Preparations (KC-300, KC-400, KC-500, and KC-600)
Me Tri and Tu Liem, Hanoi	2000	Breast milk, multiparas women near municipal dumping sites	ng g^{-1} lipid		1700	46	1.4	3.5	72	Minh et al. (2004)	
Me Tri and Tu Liem, Hanoi	2000	Breast milk, overall near municipal dumping sites	ng g^{-1} lipid	42	2100 (480–6900)[a]	58 (11–160)	2.0 (<0.72–13)	3.9 (0.62–9.5)	74 (26–210)	Minh et al. (2004)	
Vinh Loc and Dong Thanh, Hochiminh City	2001	Breast milk, primiparas women near municipal dumping sites	ng g^{-1} lipid		3020	14	7.8	2.8	88	Minh et al. (2004)	
Vinh Loc and Dong Thanh, Hochiminh City	2001	Breast milk, multiparas women near municipal dumping sites	ng g^{-1} lipid		1500	13	6	2.1	70	Minh et al. (2004)	
Vinh Loc and Dong Thanh, Hochiminh City	2001	Breast milk, overall near municipal dumping sites	ng g^{-1} lipid	44	2300 (440–17000)	14 (4.1–35)	6.9 (1.3–26)	2.5 (1.3–10)	79 (29–200)	Minh et al. (2004)	

Tan Than village, suburb Hochiminh City	1985–1987	Breast milk, rural area	ng g^{-1} lipid	2	10500	25	<2.0	<2.0	49	Schecter et al. (1989a)	DDTs: sum of p,p'-DDE and p,p'-DDT; HCHs: sum of α-, β-, and γ-HCH; CHLs: oxychlordane only; PCBs: sum of CB-138, CB-153, and CB-180
Song Be province, southern Vietnam	1985–1987	Breast milk, rural area	ng g^{-1} lipid	3	12000	37	<2.0	10	28	Schecter et al. (1989a)	
Hochiminh City	1985–1987	Breast milk, urban area	ng g^{-1} lipid	7	11400	250	3	3	84	Schecter et al. (1989a)	
Hanoi, rural area	1994	Serum	ng ml^{-1}	30	12 (1.2–59)	–	–	–	–	Schecter et al. (1997)	DDTs: sum of p,p'-DDE and p,p'-DDT
Hanoi, urban area	1994	Serum	ng ml^{-1}	8	32 (12–68)	–	–	–	–	Schecter et al. (1997)	
Hanoi, breast cancer cases	1994	Serum	ng ml^{-1}	21	16 (1.2–52)	–	–	–	–	Schecter et al. (1997)	
Hanoi, control samples for breast cancer cohort survey	1994	Serum	ng ml^{-1}	21	21 (1.5–88)	–	–	–	–	Schecter et al. (1997)	

[a] Mean (range).

spatial distribution in different kinds of environmental samples, showing higher levels of HCHs in Hanoi compared to Hochiminh City (Thao et al., 1993; Iwata et al., 1994; Kannan et al., 1995). In addition to the influence of the possible transport from China, one of the world leading HCH users, the differences in climate between Hanoi (in the northern part) and Hochiminh City (in the southern part) could be an alternative explanation. The Mekong River delta in the southern Vietnam is characterized by the typical tropical climate with high temperature and heavy rainfall. Rapid volatilization of highly volatile HCH isomers may therefore be enhanced in the environment of southern Vietnam, resulting in lower residues in various environmental and human samples.

Similar to those observed for environmental samples, human exposure to DDTs in Vietnam were very high and among the highest ranks for the developing countries and developed nations (Minh et al., 2004). As discussed earlier, high DDT contamination in Vietnam has been apparent in many environmental samples. This is also the case for humans and this fact raises concern over the possible toxic impacts on human health. This result suggests that Vietnam is a potential source of DDTs in the south Asian region.

11.4. Dioxin contamination

Southern Vietnam has been considered as a well-known region where Agent Orange was extensively sprayed during 1961–1971 in the American War, resulting in severe dioxin contamination in various environmental media and food chain including humans. During the last three decades, Schecter and co-workers have been conducting a number of investigations on the dioxin contamination in southern Vietnam, including sediment, foodstuffs, and particularly, human samples living near the “hot spot” of dioxin contamination (e.g., Schecter et al., 1989a, b, c, 1990, 1995, 2001). In general, the dioxin contamination as a result of Agent Orange can be characterized by the predominant of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD), the major contaminants of the herbicide 2,4,5-T, a constituent of Agent Orange. 2,3,7,8-TCDD is one of the most toxic congener and has received wide attention. Researches have shown that this congener can cause adverse health effects in animals (ATSDR, 1998). 2,3,7,8-TCDD was the major component and its concentrations were elevated in foods and human samples including blood, adipose tissues, and breast milk. Recently, Dwernychuk et al. (2002) surveyed soils, sediments, and food items from Aluoi Valley, a “hot spot” of Agent Orange spraying and the former US Army Base sites. The highest concentration of PCDD/Fs in soil were 2200 pg g^{-1} dry wt., which were much higher than those in background levels in many industrialized countries in the world. Of a greater concern, however, are high levels of PCDD/Fs in breast milk, a major dietary intake for breast-fed children. Survey throughout the valley indicates that breast-fed infants of primiparas groups had intake values, 27-fold exceeding the Tolerable Daily Intake proposed by WHO. This fact highlighted a new environmental issue that the first children exposed to high level of contaminants are at higher risk. The breast feeding has been highly recommended by various organizations and scientists due to a number of benefits for children including passing immunological antibody response to the infants, reducing risk of allergic reactions, etc. However, for communities with high exposure to toxic contaminants such as people living near open dumping sites in developing countries, breast feeding has unfortunately become a virtually effective route for the transfer of toxic contaminants to the next generation. Scientific and social efforts are therefore needed to mitigate exposure in order to reduce body burdens of dioxins in both adults and children.

Except for the dioxin problems caused by Agent Orange in southern Vietnam as discussed above, there have been no studies investigating the contamination status, bioaccumulation characteristics, fate and toxic implications of dioxins in a tropical environment in Vietnam until our laboratory reported dioxin contamination in dumping sites for municipal wastes in 2003 (Minh et al., 2003). In recent years, public media have voiced concern regarding the open dumping sites in Asian developing countries where large amount of municipal solid wastes have been dumped. Unfortunately, these open dumping sites are usually located near human habitats; therefore, exposure to various toxic chemicals that originated from dumping sites is of serious concern because of the effects on human health, wildlife and environmental quality. Natural burning for generation of methane gas under anaerobic conditions, combustions by waste pickers scavenging in dumping sites are the favorable factors for the formation of PCDD/Fs in dumping sites. To find an answer for the question of whether open dumping sites are potential source of PCDD/Fs, comprehensive investigations have been conducted to examine residue concentrations of PCDD/Fs in soils and human breast milk from open dumping sites from Philippines, Cambodia, India, and Vietnam (Minh et al., 2003; Kunisue et al., 2004). Concentrations of PCDD/Fs in soils from dumping sites in Hanoi were significantly higher than those in Hochiminh City. Mean and range concentrations in dumping sites from Hanoi were 6100 pg g^{-1} dry wt. (95 pg g^{-1} TEQs), range, 125–50,500 pg g^{-1} dry wt. (0.4–850 pg g^{-1} TEQ) (Minh et al., 2003) (Fig. 11.8).

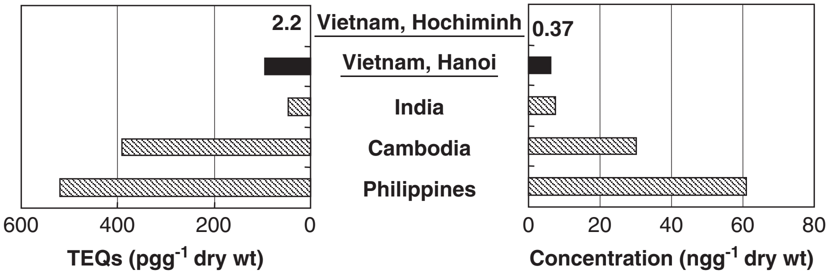

Figure 11.8. Concentrations and TEQs of PCDD/Fs in soils from open dumping sites for municipal wastes in Asian developing countries.

However, in general, dioxin residues in soils from Vietnam were less than those in other Asian countries examined in this study, indicating less dioxin contamination in Vietnam. However, one soil sample contained very high concentration of PCDD/Fs (50 ng g^{-1} dry wt. basis; 850 pg g^{-1} TEQs) (Minh et al., 2003). This level is greater than most of the background levels soils in industrialized countries and even higher than those reported for dioxin-contaminated locations in the world (Minh et al., 2003). In addition, it is interesting to note that PCDD/F levels in soils collected from dumping sites were significantly higher than those in agricultural and resident soils collected far from dumping sites. These results suggest that open dumping sites could be a potential source of dioxins in Vietnam. To understand the degree of human exposure to dioxins in open dumping sites, residue levels of human milk samples were also examined (Kunisue et al., 2004). Mean PCDD/F concentration in breast milk from women living near dumping sites in Hanoi was 52 pg g^{-1} lipid wt. (6.0 pg g^{-1} TEQs), range: 18–120 pg g^{-1} lipid wt. (2.9–9.3 pg g^{-1} TEQs) (Kunisue et al., 2004). These are comparable to those in Philippines and Cambodia, but apparently lower than those in India. Unlike soils, there were no significant differences in PCDD/F residues in milk of women living near dumping sites and far from dumping sites (control sites) (Kunisue et al., 2004).

On the basis of these results, it can be emphasized that the status of dioxin contamination in Vietnam is less pronounced as compared to other countries in East Asian region, but the issue of dioxin pollution in such open dumping site should be considered as one of the priority research in future because of the sporadic evidence of elevated dioxin contamination in dumping sites from Hanoi. Control measures and legislations towards management and mitigation of dioxin emissions in open dumping sites are urgently needed.

11.5. Fate and behavior of dioxins in municipal wastes open dumping sites

Very little information is available regarding the contamination of PCDD/Fs in Asian developing countries. Therefore, fate and behavior of these compounds in developing countries is still obscure. On the basis of the residue concentrations in soils from dumping sites, we estimated the flux of PCDD/Fs to soils to provide insights into the transport and fate of these toxic contaminants (Fig. 11.9, Minh et al., 2003). The estimated fluxes to soils in dumping sites in Asian developing countries including Vietnam were surprisingly higher. Fluxes to soils in Asian dumping sites were higher than those of some other locations in the world, including contaminated areas in the United States and Hong Kong (Fig. 11.9). The loads of PCDD/Fs to the dumping sites were also estimated (Fig. 11.10). Results showed that dumping sites in Philippines and India with a huge area of approximately 23 and 140 ha, could receive the highest annual amount of 3900 and 1400 mg year^{-1} PCDD/Fs (35 and 8.8 mg TEQs year^{-1}), respectively. Dumping site in Hochiminh City, Vietnam, had the lowest loading rate due to the less contamination of PCDD/Fs in soils. As for comparison, total annual fluxes to the Kanto region, Japan, one of the most polluted areas in the world, were estimated and found to range from 50 to 900 g TEQ with a total area of 32,000 km^2 (approximately 3 millions ha) (Ogura et al., 2001). The area of dumping

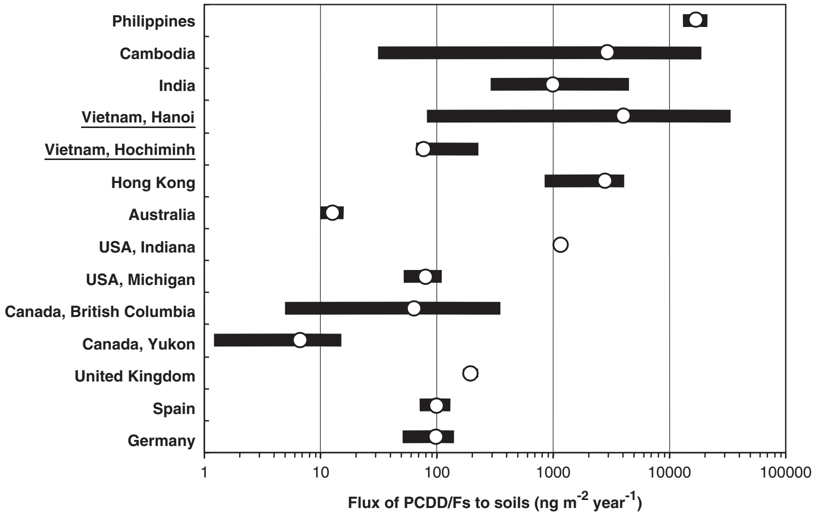

Figure 11.9. Comparison of the fluxes to soils from open dumping sites in Asian countries with those from other locations in the world.

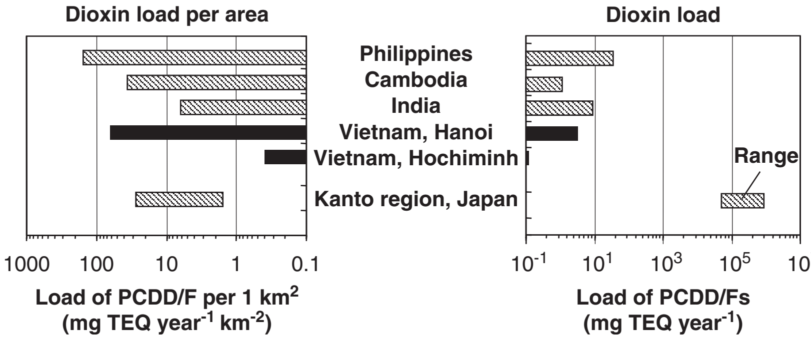

Figure 11.10. Comparison of the load of PCDD/Fs to dumping sites in Asian countries with those in Kanto region, an extensive industrial area in Japan.

sites in India is 140 ha, which is 21,000 times smaller than that of Kanto region, was estimated to receive an amount of 8.8 mg TEQs every year. This data suggest that dumping sites in India and Philippines may be significant reservoirs of PCDD/Fs. Possible impacts on human health and wildlife living near dumping sites are of great concern and warrant further comprehensive studies. On the basis of the results of this study, it is important to note that despite the probable decrease in global pollution by POPs in the future, developing countries may continue to be a potential source of certain compounds, particularly PCDD/Fs.

11.6. Trends of contamination by persistent organic pollutants

Well-designed studies on temporal trends of POP contamination in developing countries are generally limited. This is a common issue in under developed nations, where advanced knowledge, state-of-the-art analytical equipment are still lacking. Therefore, reliable and reproducible data for long-term trends of POP contamination—a key requirement in monitoring program—are limited in these countries, including Vietnam. Nevertheless, studies on temporal trends of contamination are very important, particularly in tropical developing countries. There have been a few reports suggesting the role of the southern Asian region as a possible emission source for the pristine areas such as the Arctic and the Antarctic (Iwata et al., 1993, 1994; Kannan et al., 1995; Kunisue et al., 2002). Despite OCs were banned in most of the developed nations, high consumption of OC insecticides for enhancing food production and eradicating vector-born diseases has been a virtual fact in developing countries. This lends credence that despite rapid decline of OC residues in developed nations, the status of contamination in developing world seemed different with slower rate of decline. Though well-designed studies on the temporal trends of contamination in POP from Vietnam have been limited, trends of OC residues in river water and sediments from Red River estuary and human breast milk from women living in suburb areas of Hanoi and Hochiminh City were investigated along those lines.

Viet et al. (2002) examined residue concentrations of DDTs and γ-HCH (lindane) the two most common insecticides used extensively in Vietnam, in water and sediments from Red River delta. River water and sediments were collected at the same locations annually in both dry and wet season and were examined for the trends of contamination during 1995–2001 (Fig. 11.11). DDT residues in water have declined relatively rapidly during 1995–1998 and remained constant until recent years at the levels below 10 ng L^{-1}. Concentrations in sediments also exhibited a decreasing trend but to a lesser extent. DDT residues in sediments dropped by a factor of 2 during 1997–2000. DDT was officially banned in Vietnam in 1995 (Sinh et al., 1999). The reduction of DDT concentrations in both water and sediments from Red River, northern Vietnam indicate the effect of legislative action in lessening the degree of environmental pollution. Interesting results were observed on the trends of lindane concentrations in sediment, showing peak concentrations in 1997 and lower levels during 1995–1996 and 1999–2001. Recent studies examined HCH residues in sediments from different sites in Red River Delta and estuary showed that HCH concentrations in 1997 survey were higher than in the sampling survey carried out in 1995 (Nhan et al., 1998, 1999). Such a fluctuation of HCH contamination suggests sporadic inputs of this insecticide into the

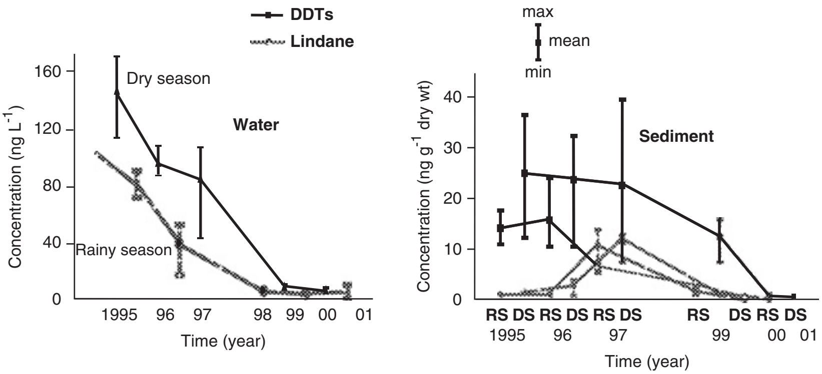

Figure 11.11. Temporal trends of DDTs and lindane in surface water and sediment from Read River Delta, northern Vietnam during 1995–2001.

watershed of Red River. In general, results from water and sediments in recent years indicated a rapid decline of DDTs and HCHs in surface water, but a slow decreasing trend in sediment. There are indeed severe gaps in the monitoring of trends of contamination in biota samples from Vietnam. Temporal monitoring of residue concentrations in biota may provide more realistic hints to understand trends of contamination in the environment. This is because of the fact that the impact of any changes in the environmental input of persistent OCs can be realized relatively slowly in biota samples as compared to those observed for environmental abiotic samples. Similar phenomenon was also seen in the trends of POP pollution in lower and higher trophic animals (Tanabe et al., 2003).

In addition to the studies on the trends of POP levels in the environmental samples, time trends of human exposure is also an important issue for understanding the long-term toxic impacts on general population. Minh et al. (2004) assessed the decline in the rate of human exposure to DDTs and PCBs over the 10 years period (1989 and 2001). A first-order kinetic approach was used to estimate the declining rate of DDTs and PCBs in human breast milk collected from Vietnam. The decrease in the POPs such as DDTs, PCBs, and HCHs in human breast milk was suggested to follow first-order kinetic (Noren & Meironyte, 2000). Another important factor for the assessment is the half-life ($t_{\mathrm{dec}1/2}$) defined as the duration in which initial concentrations decrease to a half. On the basis of the residue concentrations of OCs in 1989 reported by Schecter et al. (1989a) and the levels in 2001 obtained by Minh et al. (2004), the rate constant and $t_{\mathrm{dec}1/2}$ were estimated.

Residue levels of p,p'-DDT have decreased from 4700 to 2700 ng g^{-1} lipid wt. over a period of 10 years with $t_{\mathrm{dec}1/2}$ of around 3 years. On the other hand, p,p'-DDE decreased rather slowly with a $t_{\mathrm{dec}1/2}$ of 6 years. This result is somewhat in agreement with those in Sweden showing half-life of 4 and 6 years for p,p'-DDT and p,p'-DDE, respectively (Noren & Meironyte, 2000). The slightly shorter half-life observed in Vietnam could be due to the tropical climate that exist in Vietnam which might have facilitated the volatilization of p,p'-DDT in the environment leading to its faster decrease in food chains (and thus in humans). Assuming that the decrease in the trend of DDTs remain more or less constant, we can estimate the DDTs levels may reach approximately 700 ng g^{-1} lipid wt. in the year 2011 (Fig. 11.12). However, lower residue levels in future can be expected if the use of DDTs is completely phased out now. The decreasing trend of PCBs was lower compared to those of DDTs (11–18 years for some major congeners such as CB-138, -153, and -180). This result is somewhat in agreement with those reported in Sweden showing the half-life for some PCB congeners varying from 11 to 17 years (Noren & Meironyte, 2000).

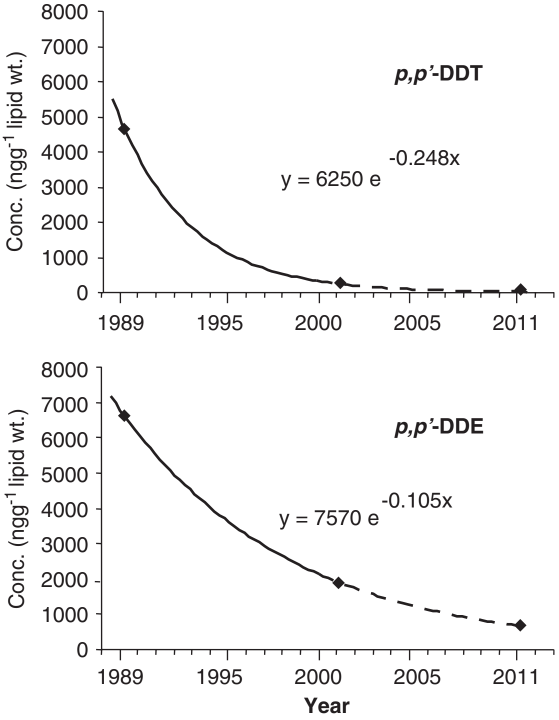

Figure 11.12. Estimation of time-trend curve of *p,p'*-DDT and *p,p'*-DDE residues in human breast milk in Vietnam.

11.7. Environmental and human health implications

Widespread contamination by OC insecticides, particularly DDTs in different environmental samples of Vietnam has been apparent as indicated in our survey in early 1990s. In a survey of estuarine sediments collected from various locations from the northern to southern part of the country, higher concentrations of DDTs were observed (Iwata et al., 1994). The Environment Canada has recently updated the sediment quality guidelines for protection of the aquatic life. The Interim Fresh water Sediment Quality Guidelines (ISQG) and the Probable Effect Levels (PEL) for *p,p'*-DDE are 1.42 and 6.75 ng g^{-1} dry wt., respectively, while these values for *p,p'*-DDT are 1.19 and 4.77 ng g^{-1} dry wt. (Canadian Council of the Ministers of the Environment, 2002). Among the 18 locations examined throughout Vietnam during the survey in early 1990s (Iwata et al., 1994), about half of the sediment samples contained *p,p'*-DDE and *p,p'*-DDT greater than the ISQG values. Some samples collected from the municipal sewage canals contained elevated levels of DDTs, far exceeding the PEL. PCB concentrations in Vietnamese sediments in these locations were also beyond the PEL level for PCBs. Likewise, residue concentrations of DDTs in many soil samples collected from some locations from north, middle, and south Vietnam (Thao et al., 1993) approached or exceeded the guideline level of 700 ng g^{-1} dry wt. proposed by Environment Canada and the level of 1000 ng g^{-1} dry wt. recommended by Japanese Government. Taking into account all these facts, it is important to note that the magnitude of contamination by DDTs in Vietnam is of concern and warrant further studies.

As for PCDD/Fs, the formation of these contaminants in open dumping sites in Asian developing countries raised a considerable human health concern for not only communities living near the dumping sites, but also for people who live far away because PCDD/Fs may undergo atmospheric transport and deposit in distant areas. For risk assessment of soils contaminated by dioxins and related compounds, The Agency for Toxic Substances and Disease Registry (ATSDR) proposed guidelines recommending that areas having soil concentrations within the range from 50 to 1000 pg TEQ g^{-1} should be evaluated for bioavailability, ingestion rates, community concerns, etc., and soils with the concentrations over 1000 pg TEQs g^{-1} should be considered for stronger actions like health studies, exposure investigations, etc. (ATSDR, 1997). Japanese Government recently issued new standards for dioxins in soil, establishing 1000 pg TEQ g^{-1} as the maximum acceptable level and those within 250–1000 pg TEQ g^{-1} be kept under surveillance. Many soil samples in dumping sites contained TEQ concentrations exceeding 250 pg g^{-1} TEQs (Fig. 11.13, Minh et al., 2003), suggesting the necessity of continuous monitoring. Particularly, some soils from dumping sites in Cambodia and Hanoi, Vietnam contained TEQ concentrations beyond the level of 1000 pg g^{-1}, suggesting their potential for causing adverse health risk for humans and wildlife.

In the perspective of human health implications, surveys conducted in early 1990s on OCs in foodstuffs provided useful information regarding the dietary intake of these compounds by Vietnamese population (Kanan et al., 1992). Interestingly, the estimated average daily intakes based on the exposure through foodstuff to PCBs in Vietnam were higher than India, Thailand and comparable to those reported for developed nations like USA and Germany. Particularly, average daily intake of DDTs by Vietnamese was estimated to be 19 μg person^{-1} day^{-1}; and this value was the highest as compared to the countries in the region and in developed nations (Kanan et al., 1992). Although the data used for estimation have been reported a decade before, this fact clearly suggests elevated exposure to DDTs and PCBs by Vietnamese population during the past 10 years.

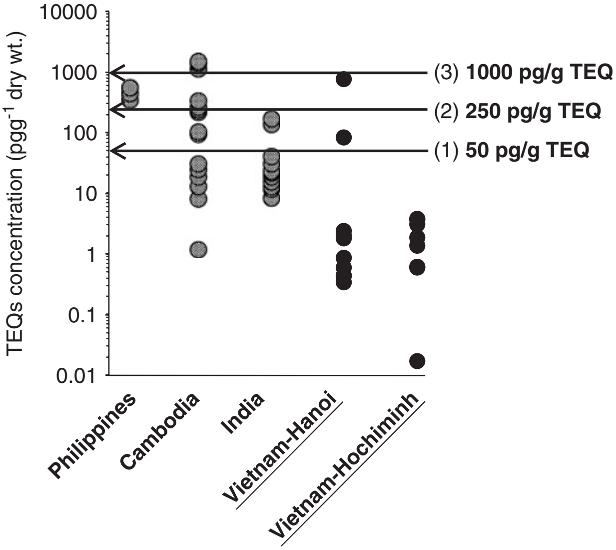

Figure 11.13. Concentrations of PCDD/Fs in soils from dumping sites in Asian developing countries in comparison with various environmental guideline values.

Surveys in the framework of recent Asia-Pacific Mussel Watch Program indicated that dietary intake of DDTs and PCBs from fish in Vietnam were higher than those in Cambodia and Thailand, but still lower than those in industrialized nations such as Australia, Japan, and Hong Kong (Monirith et al., 2000). On the basis of the recent data of average seafood consumption reported by Food and Agriculture Organization of the United Nations, the average daily intake of PCBs and DDTs from seafood for different countries in Asia-Pacific region were estimated (Monirith et al., 2003) (Table 11.5). Interestingly, results again showed that intakes of DDTs by Vietnamese population were apparently higher than those reported in other countries examined.

In addition to the elevated exposure of DDT via seafood to Vietnamese general population, certain cohorts living near the municipal dumping sites may be at a higher risk by toxic substances: dioxins and dibenzofurans. A methodical approach has been developed to evaluate the risk of exposure to PCDD/Fs via soil ingestion and dermal absorption (Minh et al., 2003). Human exposure to PCDD/Fs in soil is considered to be different for children and adults due to the differences in the ingestion rate as well as body weight of children and adult. Intakes of dioxins were estimated to be the highest in people of Philippines, followed by Cambodia, India, Hanoi (North Vietnam), and Hochiminh City (South Vietnam). Intakes of

Table 11.5. Estimated daily intakes of persistent organochlorines via mussels by different populations in Asia-Pacific region

Country	Survey year	Seafood consumption[a] (g $person^{-1}$ day^{-1})	Intake of PCBs[b] (ng $person^{-1}$ day^{-1})	Intake of DDTs (ng $person^{-1}$ day^{-1})	Intake of HCHs (ng $person^{-1}$ day^{-1})
Cambodia	1998	20	15	6.6	<0.2
China	1999–2001	71	180	17000	57
Hong Kong	1998–1999	69	260	8300	14
India	1998	13	49	55	26
Indonesia	1998	52	68	52	2.1
Japan	1994	196	5900	690	63
South Korea	1998	114	420	400	30
Malaysia	1998	156	160	220	<1.6
Philippines	1998	77	440	31	2.3
Russia	1999	54	3400	650	54
Vietnam	1997	47	66	1900	2.8

[a] Seafood consumption data were cited from FAO Food Balance Sheets, FAO Statistics Division, FAO 2006.

[b] Intakes were estimated on the basis of residue concentrations in mussels (Asia-Pacific Mussel Watch Program) reported by Monirith et al. (2003).

PCDD/Fs by the people living near dumping sites in Vietnam were ~2200-fold greater than those for the people in control sites, and thus emphasizing the greater health risk, threatening those people. In addition, it is important to note that the estimated intakes of dioxins via soil ingestion and dermal exposure for children were higher than those for adults, suggesting greater risk of dioxin exposure for children in dumping sites (Minh et al., 2003). Further investigations should be focused on children and infants as they are the most susceptible group and have higher exposure levels to dioxins. The breast-fed children intakes of PCDD/Fs estimated on the basis of residues in breast milk of women living in open dumping sites in Asian countries were given in Fig. 11.14. The intake estimated for Vietnamese were comparable to those in Cambodia but lower than in the Philippines and India. In addition, it is important to note that intakes estimated for children living near the hot spot of dioxin contamination due to Agent Orange in southern Vietnam were still very high even after the Agent spraying ended almost three decades (Fig. 11.14, Dwernychuk et al., 2002). Thus, Vietnam could serve as suitable location for future research on possible toxic effects of dioxins on wildlife and humans due to the unique situation where both current and historical dioxin contamination exists.

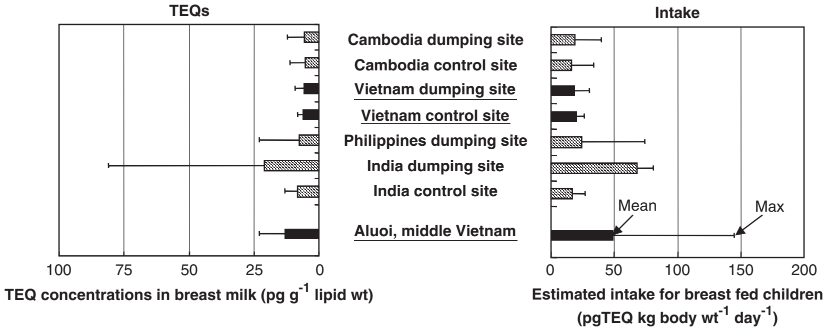

Figure 11.14. TEQs concentrations and estimated intakes of PCDD/Fs for breast-fed children from open dumping sites and control sites in Asian countries and Aluoi Valley, a former Agent Orange spraying during Vietnam War.

11.8. Conclusions and recommendations for future research

Multimedia monitoring studies conducted during the last decade on POPs in Asia-Pacific region including Vietnam indicated that contamination by OC insecticides, particularly DDTs, has been apparent. As a consequence, high degree of exposure of general populations to DDTs via foodstuff, particularly fish and other seafood has been of concern over the last several years. In addition, a certain group of people living near the dumping sites of municipal wastes are exposed to elevated concentrations of PCDD/Fs and other toxic chemicals in dumping sites, and may be at higher risk. It is important to note that despite the decrease in global contamination by POPs in the future, developing countries in Asia-Pacific region may continue to be a potential source for certain contaminants such as DDTs and PCDD/Fs. Systematic temporal trend studies are therefore needed for developing countries. Possible toxic effects on human health and wildlife should be investigated. Capacity building on advanced technologies and providing laboratory facilities to developing countries through international cooperative research programs is indispensable.

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Chapter 12

Persistent Toxic Substances in the Philippine Environment

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Abstract

This chapter provides a comprehensive review of the studies on persistent toxic substances (PTS) in the Philippines environment. Many of these persistent organic pollutants (POPs) including pesticides and industrial chemicals, which were either banned or restricted for use in most northern industrialized countries, are still in use in some developing countries. This review focuses on organochlorine compounds (OCs) such as dichlorodiphenyltrichloroethane and its metabolites (DDTs), hexachlorocyclohexane isomers (HCHs), chlordane compounds (CHLs) and hexachlorobenzene (HCB) in the Philippines environment and biota. It also includes a review of residue levels of industrial chemicals such as polychlorinated biphenyls (PCBs), unintentional contaminants such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and also the new candidates of POPs, polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs). Environmental monitoring of POPs in the Asia-Pacific region, including the Philippines, revealed apparent POPs contamination particularly of PCBs and dioxins. Consequently, these studies suggest higher risk and exposure of the general populace to these toxic contaminants, more so for people residing near dumping site areas, where elevated concentrations of PCDD/Fs have been noted. PBDEs and HBCDs in human breast milk samples are widely present in general population of the Philippines as that of OCs. It can be presumed that PBDEs may become a major environmental concern in the Philippines as they were found at elevated levels in our work and were higher than in Japan, an industrially developed country. HBCDs were also higher than those reported in other available reports. Although decrease in POPs contamination may have been observed recently on a global scale, developing countries, such as the Philippines, may act as

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potential sources for certain contaminants for many more years. Therefore, a more systematic and continuous multi-media monitoring of these toxic substances in the Philippines seem imperative. Human health implications and toxic effects to wildlife must likewise be investigated.

12.1. Introduction

The hazards associated with persistent organic pollutants (POPs) have been known for years and the knowledge on the extent of harm they cause has increased. The POPs chemicals are highly toxic, remain in the environment for long periods, become more concentrated as they go up the food chain, and can spread thousands of kilometers from the point of emission. The weight of scientific evidence strongly suggests that overexposure to certain POPs can cause serious immune and metabolic effects, neurological defects, reproductive anomalies, cancer and other abnormalities in both humans and animals. Bioaccumulation of these compounds has been related to serious toxic threats. The continued production and consumption of pesticides in several countries have also brought unprecedented awareness that these toxic chemicals may elicit impact on animal health and the environment. These chemicals may disrupt the delicate balance of the environment's various interdependent components (Hoekstra et al., 2003). It is well recognized, however, that characterization of the potential adverse effects of exposure, including but not limited to monitoring of the distribution, fate, interaction, effects, and/or impact of pesticides on population dynamics within the ecosystem, is one of the complex fields in risk management activities. Its complexity is further aggravated by such limitations as lack of technical expertise, limited laboratory facilities, inadequate funding, and weak regulations and enforcement programs, particularly in developing countries.

Apart from POPs, several other toxic halogenated chemicals also exist in the environment as a result of their use in many industrial processes. Among these, polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs), commonly used as flame retardants, have routinely been added to consumer products for several decades in a successful effort to reduce fire-related injury and property damage. Recently, concern for this emerging class of chemicals has risen because of the occurrence of several classes of brominated flame retardants (BFRs) in the environment and biota. PBDEs are additive flame retardants and the highest production group of BFRs currently in use. The structure of PBDEs is similar to that of polychlorinated biphenyls (PCBs). PBDEs are however, typically produced at three different degrees of bromination, i.e., Penta-BDE, Octa-BDE and Deca-BDE, and classified according to their average bromine content. HBCDs are white crystalline powder, with 74.7% bromine produced from bromination of cyclododecatriene (a butadiene trimer), resulting in the formation of three isomers (α, β, and γ), with the γ isomer being the predominant product. HBCDs are susceptible to thermal degradation.

In May 1995, the UNEP Governing Council decided that an international assessment be undertaken on an initial list of 12 POPs (known as the dirty dozen), which included: aldrin, chlordanes, dichlorodiphenyltrichloroethane and its metabolites (DDTs), dieldrin, dioxins, endrins, furans, hexachlorobenzene (HCB), heptachlor, mirex, PCBs, and toxaphene. In February 1997, UNEP convened an Intergovernmental Negotiating Committee (INC) to prepare a legally binding instrument for implementing international action, initially focused on the 12 POPs. Subsequently, on May 21–23, 2001, diplomats from around the world gathered in Stockholm, Sweden and signed the Stockholm Convention Treaty on Persistent Organic Pollutants, which represents the efforts by the global community to restrict and ultimately ban the use of these chemicals. The treaty also aims to ensure environmentally sound management and chemical transformation of POPs waste and prevent the emergence of chemicals with POPs-like characteristics. As of April 2006, 151 countries have signed the treaty and 121 States including the Philippines and one regional economic integration organization had ratified, accepted, and approved it to signify their intentions for the global actions to reduce POPs and their release to the environment (UNEP, 2006).

The Philippines is one of the archipelagic countries of the Southeast Asian region, which has a land area of approximately 300,000 km^2 and a coastline that extends to ~36,289 km. Its estimated population is ~85 million, where 39 million occupy the coastal areas. Its main industries include agriculture and fisheries. With its strategic geographical position, agricultural and industrial development, the Philippines has become an important site for studies dealing with environmental pollution monitoring during the last decade.

This chapter provides a comprehensive review of the studies on persistent toxic substances (PTS) in the Philippines environment. Available information on PTS in the Philippines was compiled on the basis of investigations conducted within the framework of multilateral cooperative research between Japan and the Philippines through the Core University Program of the Japan Society for the Promotion of Science (JSPS) and the Asia-Pacific Mussel Watch Program. Results from other laboratories were likewise included to derive greater insights into the transport, fate and distribution and bioaccumulation features of PTS and its possible implications on human health in particular, and the quality of the environment in general. This paper focuses on organochlorine compounds (OCs) such as DDT and its metabolites, hexachlorocyclohexane isomers (HCHs), chlordane compounds (CHLs), and HCB. It also includes a review of residue levels of industrial chemicals such as PCBs, polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and also the new candidates for POPs, PBDEs and HBCDs. The cited values of residual concentrations from various literatures were rounded off to two significant digits for comparison purposes.

Overall, the toxicology database of OCs and BFRs in the Philippines are very limited; the current literature is incomplete and often conflicting. Many animals—including whales, dolphins, seals, birds, and humans—have already been found to be contaminated with these substances, and the levels appear to be increasing in the developed countries, whereas in the developing countries such as the Philippines not much studies has been carried out and needs detailed studies on the present scenario.

12.2. Characteristics of the Philippines agricultural sector

The Philippines is a predominantly agricultural country, with more than half of the population living in the rural areas. Rice and corn are the main staple crops for the majority of the farming population while the major cash crops include coconut, sugarcane, banana, and pineapple. The country being an archipelago, fish and other marine products, particularly prawns and seaweeds, are also significant elements of the agricultural economy. Another factor to note is the role of women in agricultural production. Official figures show that women compose 35% of the agricultural labor force in the Philippines. Their role has affected not only their economic productivity but also their health and that of their children. Women in the Philippines, like their Asian counterparts, have been assigned menial tasks like transplanting, weeding, spraying, and harvesting, which could expose them to unreasonable levels of chemicals. Some agrochemicals have been known to cause infertility, spontaneous abortion, stillbirths, and birth defects; toxic properties may also be passed on to the infant through breast milk. In spite of the UN Resolution calling for countries to prohibit the exposure of women of childbearing potential to hazardous chemicals, the socio-economic conditions prevailing in the Philippines are significant setbacks as far as enforcement is concerned.

12.3. Pesticide industry and usage profiles

The pesticide industry in the Philippines is entirely in the hands of the private sector, dominated by transnational companies. There are ~200 agricultural pesticide companies, including ~30 formulation plants, operating in the country. They include manufacturers, formulators, repackers, importers, distributors, traders, and suppliers. Pesticide companies in the Philippines, as in most countries, include most of the big transnational corporations—engaged in selling a wide range of agricultural, industrial, and consumer products—with assets that are larger than the gross national product of many developing countries, including the Philippines. For example, many chemical companies produce pharmaceuticals, dyes, surfactants, paints, and resins as well as pesticides and some produce photocopying papers, films for magnetic recording tapes, and facsimile transceivers and are involved in chromate mining operations. Giant transnationals like Hoechst, Bayer, Monsanto, Dow, American Cyanamid, Ciba-Giegy, Rhone-Poulenc, and Sandoz are diversified and are continuously growing through mergers and acquisitions.

Pesticides sale in the Philippines grew tremendously over the years until the introduction of the integrated pest management (IPM) concept. From 1987 to 1989, the major pesticide companies in the Philippines put on the market 20,100 tons of pesticides. In the 1990s, the pesticide industry grew at an annual average of ~17.5%. In certain regions of the country, the annual increase in pesticide usage was as high as 500%.

In recent years, however, a pattern of reduction is seen with the continuous popular support for sustainable agriculture initiatives. Among the pesticides that are considered as POPs, endosulfan was most widely used over the last three decades. Endosulfan was misused as a molluscicide for golden snail control when organotin compounds became scarce due to regulation. Despite being banned for use in rice and being severely restricted in 1993, endosulfan is in continues use illegally due to inadequacies in the implementation of regulatory decisions (The Philippines, 1996).

12.4. National inventory of POPs in the Philippines

To meet its obligations under the Stockholm Convention on POPs, the Philippine government, through the Environmental Management Bureau of the Department of Environment and Natural Resources under a GEF-UNDP Grant, conducted an initial National Inventory of POPs (Factora et al., 2004). It was reported that 5 of the 12 POPs—aldrin, dieldrin, endrin, heptachlor, and toxaphene—have been banned in the Philippines since 1989. Although HCB and mirex have no reported use, importation, or production control in the country, and the provisions of Presidential Decree 1144 (National Pesticides Safety Program) will apply for these two pesticides also (Zosa, 1978). On the other hand, DDT is the only restricted pesticide and only the Department of Health is allowed to import the chemical in very small amounts for malaria control. The use of DDT started even before the 1960s and lasted until 1992, when permethrin, an alternative for DDT, was introduced. While chlordane was reported to be the most popular chemical for the control of termites, the inventory further revealed that until its prohibition in 1999, the chemical has been used in many projects and it is even utilized in the treatment of residential structures. Moreover, the survey found that significant quantities of PCBs were evidently present in the Philippines, mainly in electrical equipments. Approximately 8027 equipments were surveyed, of which 1.78% were positively identified as containing PCBs. Based on the inventory, there were 2,089,000 kg of PCB oils in the country contained in electric transformers, capacitors, and circuit breakers (Bravante and Moreno, 2005). It was further revealed that there is approximately 498 tons of PCB oil in the country and 1903 tons of oil are assumed to contain PCBs. PCBs in closed applications still exists in all the priority facilities covered by the survey (Factora et al., 2004).

On the other hand, the Environmental Division of the Industrial Technology Development Institute (ITDI) of the Department of Science and Technology (DOST) conducted a National Inventory of Dioxins and Furans (Pablo et al., 2004) using the UNEP Standardized Toolkit. It was found that the PCDD/Fs of each main source category and sub-category yielded 534.06 g toxic equivalents (TEQ) per annum as the total annual release to all environment compartments. Combustion processes emitted the highest levels of PCDD/Fs with 187.05 g TEQ yr^{-1} or 35% of the total annual releases, followed by power generation and cooking at 157.23 g TEQ yr^{-1}, and production of chemicals and consumer goods at 91.56 g TEQ yr^{-1}. It was further reported that uncontrolled combustion processes was found to be contributing to releases to three environmental media—air, land, and residues (Factora et al., 2004).

12.5. Contamination levels

In developing countries where food supply problems brought about by a growing population prevails, usage of OCs seems unlikely to decline or discontinue. Their usage is considered inevitable partly in tropical agro-ecosystems and public health programs to control pests and vector-borne diseases (Mowbray, 1988; Forget, 1991; Tanabe and Tatsukawa, 1991), respectively. Further, the use of these chemicals has been found to be less costly and therefore economically unavoidable for developing countries (Thao et al., 1993). As most developing countries are located in the tropical belt, where high temperature and heavy rainfall are very common, such climatic factors facilitate the specific distribution, behavior, and fate of these contaminants that will have far-reaching complications and ultimately contribute to global contamination (Tanabe, 1994). On the other hand, PCDDs, PCDFs, and coplanar PCBs are lipophilic-stable contaminants of great concern with respect to their toxic effects on humans and wildlife (Kunisue et al., 2004). In developed countries, the residue levels of these contaminants in various environmental media and biota have generally decreased (Alcock and Jones, 1996; Bradley, 2000; Noren and Meironyte, 2000). In contrast, a few studies have reported contamination status of these chemicals in developing countries, especially regarding human exposure (LaKind et al., 2001). Massive amounts of waste electric products (television, computer, etc.) used in the developed countries such as U.S.A, Japan, Canada, and Europe were exported as trash to Asian developing countries (Ueno et al., 2004). This fact was prominent in the case of PBDEs and HBCDs by the large quantity and increased usage in Asia. Their rapidly rising concentrations in the environment (Ueno et al., 2004; Kajiwara et al., 2006) may have potential effects on global terms in future.

12.5.1. Soils and sediments

Organochlorine (OC) residues in soils of the agriculture site of the Philippines were examined and found that DDT and HCH residue levels were comparable with the values reported from other countries (Lee et al., 1997) in the world (Table 12.1). Analysis of the composition of DDT and its metabolites in most of the soil samples showed higher percentages of p,p'-DDE than p,p'-DDT, which seem suggestive of the reducing usage of OCs such as DDT for agricultural purposes in the Philippines. HCH residue levels were also not high, suggesting partly their rapid dissipation through volatilization in tropical agro-ecosystem as pointed out in previous studies (Takeoka et al., 1991; Tanabe et al., 1991). These findings were further reflective of the decline in the usage of OCs for agricultural purposes in the country. This downward trend is likely to continue as the government has imposed strict ban on the usage, production, importation, and marketing of these chemicals for agricultural purposes from the

Table 12.1. PCB, DDT, and HCH concentrations (ng g^{-1} dry wt.) in soils from various countries

Location	Soil type	Year	PCBs	DDTs	HCHs	Reference
Philippines	Agriculture	1994	<1.0	1.2–200	0.1–5.2	Lee et al., 1997
Philippines	Dumping site	1994	30–200	50–1100	10–190	Lee et al., 1997
Indonesia (Jakarta)	Urban soil	2002–2003	NA	25	29	EMC, 2003
India (Chennai)	Dumping site	2000	180	24	30	Minh et al., 2006
India (Chennai)	Rural soil	2000	0.052	0.079	0.048	Minh et al., 2006
China (Pearl River Delta)	Non Agriculture	2000	NA	6.7	8.2	Fu et al., 2003
China (Pearl River Delta)	Agriculture	2000	NA	68	16	Fu et al., 2003
Cambodia (Phnom Penh)	Dumping site	1999/2000	140	350	1.7	Minh et al., 2006
Cambodia (Phnom Penh)	Rural soil	1999/2000	0.85	1.1	<0.01	Minh et al., 2006
South Korea	Urban soil	1996	NA	0.4	0.4–2.9[a]	Kim and Smith, 2001
Vietnam (Hanoi)	Rural soil	2000	0.73	3.2	0.14	Minh et al., 2006
Vietnam (Hochiminh)	Rural soil	2001	3.6	3.8	0.36	Minh et al., 2006
Vietnam (Hanoi)	Dumping site	2000	12	20	0.83	Minh et al., 2006
Vietnam (Hochiminh)	Dumping site	2001	22	23	0.37	Minh et al., 2006
Vietnam (Hanoi)	Various soils	1992	12	35	2.1	Thao et al., 1993
Egypt	Urban soil	1996	NA	1.4	2.3[b]	Ahmed et al., 1998
Ireland	Agriculture	1992	3.49	12	1.16	Grath, 1995
Ireland	Urban soil	1992	2.97	1.8	1.14	Grath, 1995
Russia	Agriculture	1992	1.4–92	0.34–28	0.04–16	Iwata et al., 1995
Slovak Republic	Waste site	1996	NA	11	12	Marta et al., 1997
Argentina	Agriculture	1996	NA	30	21	Miglioranza et al., 1999
United States	General soil	1998	5.9	NA	NA	Meijer et al., 2003
United States (Alabama)	Agriculture	1996	NA	50	0.23	Harner et al., 2001

Note: NA—Not available.

[a] Range is given when mean value is not available.

[b] Median value.

year 1977, as embodied in the National Pesticide Safety Program and mandated by Presidential Decree 1144 (Zosa, 1978). Although, HCB was officially banned from agricultural use in the country from 1972, other pesticides containing HCB as impurities might pose as one of the pollution sources. CHL residue levels were comparable with values of HCB found, while PCB residues were low in all the samples (Lee et al., 1997).

As for the dumpsite soils collected from Smokey Mountain, a 29 hectare former dumpsite area within metropolitan Manila, highly significant DDT, HCH, and PCB residue levels were found, which could be attributed to the extensive usage of these chemicals for public health and the industries from where the wastes were dumped in the area (Lee et al., 1997). The high levels of DDT residues and marked proportion of *p,p′*-DDT found could be attributed to its recent usage for the control of vector-borne diseases such as malaria. Smokey Mountain was used as an open dumpsite until its closure in 1994 and this area has been reported to be home to ~3000 families and 14,000 individuals, which translates to a population density of ~463 persons per hectare (Abad, 1991). With no provisions for community health care, Smokey Mountain may be considered a malarial area. As such, the Government's Department of Health through its Malaria Eradication Service Division, conducts residual spraying of DDT, for malaria control purposes until its phase-out, all over the country by virtue of a memorandum issued by the Secretary of the Department of Health (Flavier, 1992). Moreover, mean concentrations of CHLs detected and the proportions of CHL compound found suggest that technical mixture of CHLs is still in use for public health purposes, for example as termiticides, in urban and industrialized areas.

Significant levels of PCBs were also detected and attributing to the fact that Smokey Mountain could be a dumping ground for PCB contaminated wastes. This observation lends support to results of a study conducted by Thao et al. (1993), which suggested that soil contamination of PCBs could likely to occur at some point sources for PCB storage and usage especially on cases where facilities for the proper use and disposal of PCBs may be lacking as in Smokey Mountain. HCB residues in Smokey Mountain (dumping site soils) were found much higher when compared to those in agricultural soils (Lee et al., 1997). It was suspected that the main source of HCB residues at the dumpsite soil could be fungicide application and its release as an impurity of several industrial and chemical products and as a byproduct in various chlorination processes and combustion system of wastes.

In another study conducted by Minh et al. (2003), concentrations of PCDD/Fs and coplanar PCBs were determined in soils from dumping sites in the Philippines, Cambodia, India, and Vietnam. Residue levels in dumpsite soils were apparently greater than those soils collected in agricultural or urban areas far from dumping sites, suggesting that dumpsites are potential sources of PCDD/Fs and related compounds. Mean concentrations of PCDD/Fs and coplanar PCBs in soils from dumping sites were the highest in the Philippines, followed by soils from Vietnam, Cambodia, and India. Further, observed PCDD/F concentrations in soils from dumpsites in the Philippines and Cambodia were found to be comparable or even higher than those reported for dioxin-contaminated locations in the world (Minh et al., 2003). Homologue profiles of PCDD/Fs in dumping site soils in the Philippines reflected patterns of samples representing typical emissions. Uncontrolled burning of solid wastes by waste pickers and low-temperature burning with the formation of methane gas are plausible explanations for the formation of dioxins in dumping sites. Estimated flux of PCDD/Fs to dumpsite soils from the Philippines was the highest and was found to be even greater than those from other locations in the world (Table 12.2). Considerable loading rate at 3900 mg yr^{-1} (35 mg TEQ yr^{-1}) of PCDD/Fs in the Payatas dumpsite in the Philippines suggest that Payatas dumpsite is a potential reservoir for PCDD/Fs. Possible implications on human health and wildlife living near dumping sites are of great concern and deserve further comprehensive studies.

Table 12.2. Estimated flux of PCDD/Fs to soils in dumping sites in various countries

Country	Flux (ng m^{-2} yr^{-1})	
	Mean	Range
Philippines[a]	17,000	13,000–21,000
India[a]	990	290–4500
Cambodia[a]	2900	31–19,000
Vietnam—Hanoi[a]	4100	83–34,000
Vietnam—Hochi Minh[a]	67	3.8–160
Hongkong[b]	2800	840–4030
Australia[b]	13	10–16
Germany[b]	97	51–140
Spain[b]	100	72–130
United Kingdom[b]	180	170–220
Yukon Territory, Canada[b]	6.6	1.2–15
British Columbia, Canada[b]	64	4.2–350
Michigan, USA[b]	80	52–110
Indiana, USA[b]	1280	1260–1290

[a] Data from Minh et al., 2003.

[b] Data from Wagrowski and Hites, 2000 (as cited in Minh et al., 2003).

Lee et al. (1997) also found high residue levels of CHLs, PCBs, and DDTs in sediments from Manila Bay and its inflowing rivers, which could imply recent usage of these contaminants for public health purposes as the bank of Pasig River is full of residential shanties, where water and vector-borne diseases are more likely to occur. HCH and DDT levels in Pasig River sediments were comparable with those found in similar areas in other tropical countries. HCB concentrations in Pasig River sediments was low, which affirmed the findings of our previous study (Iwata et al., 1994), attributing the trend to the rapid evaporation from water phase to atmosphere because of the prevailing high temperature in this tropical area. However, the mean DDTs concentration in the sediments from Pasig River was found to be higher than those reported from Taiwan, Thailand, Malaysia, and India. The relatively high DDT concentrations suggest that DDT has been used until recently for public health purposes as discussed earlier. Interestingly, highest range of PCB concentrations were found in sediments from Pasig River among the samples analyzed and the principal source of PCB contamination is still unclear, but industrial effluents along the river coat is possible considered.

12.5.2. Biological samples (bivalves, waders, cetaceans and fish)

The green mussels (*Perna viridis*), being filter feeders, are considered to be highly suitable for culture in the coastal areas. These mussels have become one of the most valuable mariculture organisms produced in Asia (Goldberg et al., 1978). The Philippines is one of those countries that have ventured into large-scale exploitation of green mussel. As early as the 1950s, the Philippines was one of the countries outside Europe to have explored the possibilities of intensive mussel culture. Thus, in 1955, the first commercial mussels farm started its operation, marking the beginning of a mussel industry that has proved to be as lucrative as the oyster industry (Yap et al., 1979; Guerrero et al., 1983). Despite the fact that mussels are part of the nation's diet, monitoring studies on the residues of toxic contaminants in this seafood is rather limited.

Monirith et al. (2003), conducted a study to assess the levels of toxic contaminants in green mussels collected from Philippines' coastal waters, particularly in the major mussel culture areas within the framework of the Asia-Pacific Mussel Watch program. Among the OCs, PCBs were observed to be generally prominent in green mussels analyzed. Relatively higher PCB levels were measured in green mussels collected around Manila Bay area, which may imply that PCB contamination could be from the highly populated and industrialized cities. Based among the Asian countries the PCB levels reported in bivalve mollusks (Table 12.3),

Table 12.3. Mean concentrations of OCs (ng g^{-1} lipid wt.) in mussels from Asian countries

Countries	Lipid (%)	PCBs	DDTs	HCHs	CHLs	HCB
Philippines	1.8	290	21	1.8	54	<0.80
Cambodia	1.3	35	23	<0.30	<0.30	1.2
China	2.0	120	16,000	44	190	56
Hong Hong	1.2	310	7700	18	240	<1.5
India	1.7	340	380	120	35	4.0
Indonesia	1.5	87	70	3.0	7.3	0.70
Japan	1.3	3000	270	28	550	8.2
South Korea	2.4	170	150	14	25	2.3
Malaysia	1.3	56	90	3.7	140	0.80
Vietnam	1.1	160	4400	5.8	17	1.0
Russia	2.0	3200	630	45	56	4.5
Singapore	2.7	90	110	12	28	<0.40

Note: Data from Monirith et al. (2003).

values found in green mussels from the Philippines were similar to those found in Hong Kong, but higher than those found in mussels from South Korea, Vietnam, and China. However, PCB levels in mussels from the Philippines were lower than those in mussels from Russia, Japan, and India. CHL concentrations in green mussels from the Philippines' coastal waters proximal to urbanized and industrialized areas were observed to be a magnitude higher than the levels in mussels collected from the coasts of rural areas. Similar to PCBs, this spatial difference is suggestive that CHL contamination may be coming from thickly populated and industrialized areas. On an international basis, monitoring data on CHL residues in bivalves is rather scarce. Nevertheless, comparable levels of CHLs were found in green mussels from the Philippines' coastal waters (Prudente et al., 1999). On the other hand, DDT and HCH concentrations obtained for green mussels in the Philippines were lower than those found in mussels from all the other Asian countries (Table 12.3). HCB concentrations were the lowest and the uniform HCB concentrations found in green mussels from the various study sites were within the same range as the levels detected in green mussels from the coastal waters of Thailand (Prudente et al., 1999). It has been reported that HCB contamination may have originated from usage of fungicides or as an impurity in pesticide formulations, a byproduct of various chlorination processes, and the combustion of industrial and municipal wastes (Kannan et al., 1994).

Concentrations of BFRs (PBDEs and HBCDs) and OCs in the muscle and liver of skipjack tuna collected from the offshore waters of various regions in the world, including the Philippines were recently conducted

Table 12.4. Concentrations of PBDEs, HBCDs and OCs (ng g^{-1} fat wt.) in the liver of skipjack tuna collected from offshore waters and open seas

Location	*N*	BL (cm)	BW (kg)	PBDEs	HBCDs	PCBs	DDTs	CHLs	HCHs	HCB
Off-Philippines	5	42	1.5	14	0.86	190	98	17	<0.13	1.7
North Pacific-1	5	44	1.8	5.8	25	110	30	43	28	9.4
North Pacific-2	10	47	2.2	16	29	250	96	60	1.2	6.1
North Pacific-3	5	79	11	6.4	1.1	530	93	25	0.82	3.8
Off-Japan-1	5	49	2.6	7.7	32	170	48	35	11	7.2
Off-Japan-2	5	52	3.3	11	45	800	180	150	6.7	7.6
Japan Sea	5	63	5.6	20	6.5	900	510	110	2.5	5.1
East China Sea-1	5	58	3.9	34	44	620	630	85	13	1.4
East China Sea-2	5	61	5.2	23	28	580	290	57	4.4	2.7
Off-Taiwan-1	4	61	4.9	53	27	980	420	100	8.1	3.9
South China Sea	1	31	0.5	21	3.2	140	670	38	6.7	2.2
Bay of Bengal	2	47	2.0	1.8	0.27	120	410	13	7.8	1.5
Off-Indonesia	2	47	2.0	3.1	0.41	50	31	7.8	1.4	1.3
Off-Seychelles	3	55	3.6	ND	ND	14	39	33	<0.29	1.7
Off-Brazil	4	55	3.7	13	0.28	460	92	63	2.7	2.4

Note: Data from Ueno et al., 2003, 2004, 2006.
PBDEs and HBCDs – Muscle; OCs – Liver samples; ND – Not detected.

(Ueno et al., 2003, 2004, 2006). PBDEs, HBCDs, and OCs were detected in all the samples off the Philippines suggesting widespread contamination of these compounds in the Philippines environment (Table 12.4). Among the organohalogen compounds, PBDE levels in the Philippines were found to be higher than those in Japan, India, Indonesia, and Brazil and lower than China and Taiwan. In the case of HBCDs the levels were found almost equal to India and Indonesia and one magnitude lower than Japan, China, and Taiwan. The observed ranges of this compound seemed to indicate a spatial variability that might be due to exposure to different background residue levels in the environment. PCBs and DDTs were the predominantly identified compounds in the case of OCs. PCBs were higher in tunas from the offshore waters of temperate regions in Asia. DDTs were the predominant compounds in tuna samples from tropical regions, including the Philippines, which could be reflective of continued use of DDT until recently in the region. Such patterns of PCB and DDT contaminations were also observed in a previous monitoring survey of cetaceans in the Asia-Pacific region (Prudente et al., 1997).

To our knowledge, there are very few studies that examined OCs contamination in higher trophic animals from the Philippines. A survey on migrant and resident waders collected from Calatagan Bay, Philippines was conducted (Kunisue et al., 2003) and among the OCs measured in the resident waders, PCBs were the prominent compounds followed by DDTs, CHLs, HCHs, and HCB. This pattern was found to be similar to

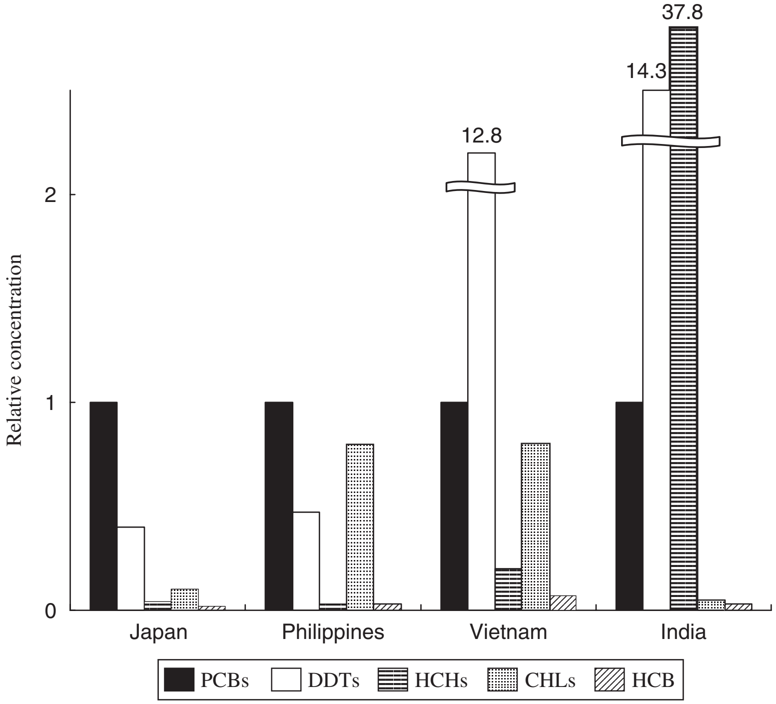

Figure 12.1. Mean relative concentrations of OCs to PCBs in resident waders from various Asian countries (Kunisue et al., 2003).

those waders collected from Japan, suggesting that notable PCB contamination of biota in these countries is still occurring (Fig. 12.1) (Kunisue et al., 2003). It can be gleaned further that the relative concentrations of CHLs in waders from Calatagan was higher than that from other countries, while the residue levels of other OCs were generally low. As for the migrant species, the composition of OCs followed the order of DDTs > PCBs > HCHs > CHLs > HCB, which also holds true with the waders collected from Vietnam (Fig. 12.2). This result seem to indicate that on their migratory routes, wader species collected from Calatagan Bay could be wintering and feeding in areas of high DDT usage. These observations confirm the notion that DDTs and PCBs are highly persistent, less biodegradable, and are retained in the animal's body for a long time (Tanabe and Tatsukawa, 1991). This suggests that the accumulation features of OCs in migratory waders reflect not only the pollution status in the area of collection, but also in stopover sites, breeding and wintering grounds. DDTs and PCBs were the dominant

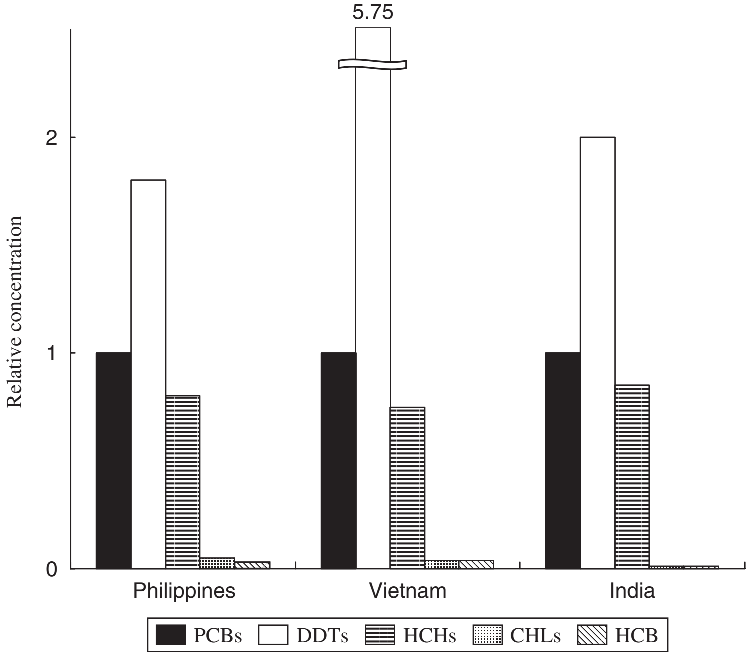

Figure 12.2. Organochlorine residue patterns in migratory migrant waders from the Philippines, Vietnam, and India (Kunisue et al., 2003).

contaminants in short-distance migrants from the Philippines. It is known that many species from the Philippines have their breeding grounds around Persian Gulf, Red Sea, and Caspian Sea (Hoyo et al., 1996). High concentrations of PCBs were also detected in Caspian seals and fishes from Caspian Sea and PCBs' release into this environment could be continuing (Kajiwara et al., 2002). Moreover, the accumulation pattern in short-distance migrants from Calatagan Bay was almost similar to those from Vietnam. In both countries, the relative concentrations of HCHs in short-distance migrants were slightly higher than those found in resident birds. These results are indicative that short-distance migrants from Calatagan Bay and Vietnam may have their breeding grounds or stopover sites in China, since China is known to have widely used HCHs and DDTs (Wu et al., 1982; Li et al., 1996; Zhu et al., 1999). While long-distance migrants from Calatagan Bay showed similar trends to short-distance migrants, indicating that the long-distance migrant waders might have been exposed to high levels of DDTs in their stopover sites and breeding grounds. In addition, relative concentrations of HCHs in long-distance migrants from the Philippines and Vietnam were slightly higher than those found in short-distance migrants. This finding could be suggesting that these long-distance migrant birds might have been exposed to HCHs in the Arctic regions, which are known to be polluted by HCHs due to the long-range atmospheric transport from the southern hemisphere (Muir et al., 1999).

Recent scientific studies on marine mammals in the Philippines revealed that at least 18 and possibly 27 species of cetaceans are found in the Philippine seas (Tan, 1995). This apparent diversity however, is threatened by the ongoing destruction of their ecological support systems and increasing competition for food, as well as whale and dolphin fisheries that are reportedly being practiced in the southern part of the country. Numerous investigations have emphasized that the seas and oceans should be considered as significant sinks for toxic and bioaccumulate contaminants. In particular, marine mammals, such as whales, dolphins, and seals, living in these areas are at the top of the food chain, and are known to have extremely high rates of contaminant accumulation, hence are believed to be facing high risk in the ecotoxicological context (Tanabe et al., 1994). In this perspective, Kajiwara et al. (2006) studied the accumulation of these contaminants in the lipid-rich blubber tissues of one spinner dolphin (*Stenella longirostris)* collected from the tropical waters of northeastern Sulu Sea in the Philippines.

The mean concentration of PBDEs, DDTs, and PCBs detected in these cetaceans from Sulu Sea, Philippines were lower than those reported in the other Asian countries (Table 12.5). DDTs and PCBs levels in these cetaceans were found to be considerably higher than other OCs. However, PBDE, DDT and PCB residue levels in the Philippines were very much lower than those in Hong Kong and Japan. These observations showing relatively significant DDT residue levels in tropical species reflect DDT origination from the tropics. Apparently higher DDT residue levels found in air and water samples from tropical and subtropical coastal waters than those from the temperate ones (Iwata et al., 1994) confirm this notion. Moreover, as evidenced by Iwata et al. (1993, 1994), less movable nature of DDTs through long-range atmospheric transport might have led to the significant contamination of tropical surface seawater as well as tropical species. Meanwhile, mean CHL levels detected in the cetaceans in this study were found to be higher than those in India and an order of magnitude lower than those in other Asian countries (Table 12.5). The mean concentration of HCHs and HCB levels in the Philippines were similar to the levels found in Indian dolphins, but one or two magnitude lower than those of other Asian countries.

Table 12.5. Mean concentrations (ng g^{-1} lipid wt.) of PBDEs and OCs in the blubber of cetaceans collected from Asian waters

Species	n	Lipid (%)	PBDEs	PCBs	DDTs	CHLs	HCHs	HCB
Phillippines								
1996 Spinner dolphin	3	38	36	3600	16,000	540	110	220
Japan								
1998–2000 Finless porpoise								
Seto Inland Sea	5	61	730	120,000	76,000	21,000	3300	280
Pacific Coast	2	47	620	29,000	32,000	4800	950	690
1999 Harbour porpoise	3	87	73	2200	3300	1000	730	710
2000 Dall's porpoise								
truei-type	5	87	57	9000	11,000	4200	1200	860
dalli-type	5	86	530	18,000	31,000	5200	1900	580
2001 Melon-headed whale	5	68	320	24,000	27,000	4100	210	270
1999 Pacific white-sided dolphin	5	69	690	8700	14,000	3300	900	460
2000–2001 Stejneger's beaked whale	5	71	530	19,000	110,000	4500	2700	690
Hong Kong								
2000–2001 Finless porpoise	6	46	600	13,000	120,000	740	250	160
1997–2001 Indo-Pacific humpback dolphin	7	31	1900	45,000	190,000	2200	720	280
India								
1992 Indo-Pacific humpback dolphin	2	57	11	2000	75,000	160	110	16
1990–1992 Spinner dolphin	3	47	6.8	1600	48,000	160	220	28

Note: Data from Kajiwara et al. (2006).

12.5.3. Human exposure

Limited data are available on human exposure to organohalogen compounds in the Philippine environment. A survey conducted by our group (Prudente et al., 2004) reported considerably lower levels of OC residues in breast milk samples from Payatas, an open dumpsite area in the suburbs of Metropolitan Manila area, compared with those found in human breast milk samples collected from other countries in Asia. DDT residues were found to range from 35–570 ng g^{-1} lipid wt., while PCB residues ranged between 39–160 ng g^{-1} lipid wt. It was further revealed that the contamination pattern of OCs in human breast milk resembled those observed among marine mammals (Prudente et al., 1997). The bioaccumulation pattern of OCs in human breast milk from the Philippines (DDTs $>$ PCBs $>$ CHLs $>$ HCHs $>$ HCB) were reported by Kunisue et al. (2002). In a most recent study on the measurement of OCs such as DDTs, PCBs, CHLs, HCHs, HCB, TCPMe, and BFRs including PBDEs and HBCDs in 33 human breast milk samples from the Philippines carried out in our laboratory (Malarvannan et al., 2007), all the compounds were detected in all the samples, indicating their widespread contamination in the Philippines. DDTs were the predominantly identified compounds in all the samples at an average of 170 ng g^{-1} lipid wt., followed by other compounds in the order of PCBs (70 ng g^{-1} lipid wt.), CHLs (12 ng g^{-1} lipid wt.), PBDEs (7.2 ng g^{-1} lipid wt.), HCHs (5.5 ng g^{-1} lipid wt.), HCB (2.4 ng g^{-1} lipid wt.), TCPMe (2.2 ng g^{-1} lipid wt.), and HBCDs (0.84 ng g^{-1} lipid wt.). The concentrations of other organohalogen compounds were 1–3 orders of magnitude less than those of DDTs and PCBs. The observed residue level pattern (DDTs > PCBs > CHLs > PBDEs > HCHs > HCB > TCPMe > HBCDs), is different from other Asian developed and developing countries (DDTs > PCBs > HCHs > CHLs > HCB > PBDEs) (Sudaryanto et al., 2005), indicating different exposure patterns to organohalogen compounds in the general population of the Philippines. Interestingly, PBDEs may become a major environmental concern in the Philippines as they were found at elevated levels in our work and were higher than in Japan, an industrially developed nation (Hites, 2004, Sudaryanto et al., 2005). HBCDs were also higher than those reported in other available reports (Covaci et al., 2006).

However, the accumulation pattern of OCs in human milk was different from that found in mussels from the Philippines coastal environment (Monirith et al., 2003), which showed higher levels of PCBs and CHLs, probably because of the difference in exposure routes. However, DDTs were consistently the prevalent OCs in both samples, indicating that DDTs are the major environmental contaminants in the Philippines environment.

In a subsequent study conducted by Kunisue et al., (2004), it was reported that dioxins and related compounds (DRCs) were detected in all the human breast milk collected from dumpsite areas. The concentrations of PCDDs in human breast milk from the Payatas dumpsite in the Philippines ranged from 29 to 730 pg g^{-1} lipid wt. It was also noted that the level of TEQ in human breast milk from the Philippines (12 pg TEQ g^{-1} lipid wt.) was lower than that from developed countries but comparable with that from other developing countries (Schecter et al., 1990; Paumgartten et al., 2000) (Fig. 12.3). Similarly, in the third round of WHO-coordinated dioxin exposure study on levels of dioxin-related compounds in human milk of Filipino mothers (Pablo et al., 2005), it was found that contamination in Filipino breast milk was among the lowest when compared to other countries. To understand the magnitude of exposure to DRCs by infants, daily intake (DI) from human breast milk observed in this study were estimated based on the assumption that an infant ingests 700 ml milk perday and that the weight of an infant is 5 kg (Hooper et al., 1997). Daily intake from human breast milk from the Philippines was in a range of 1.9–130 pg TEQ kg^{-1} d^{-1} (mean: 39 pg TEQ kg^{-1} d^{-1}), which exceeded the tolerable daily intake (TDI) set by WHO at 1–4 TEQ kg^{-1} d^{-1}.

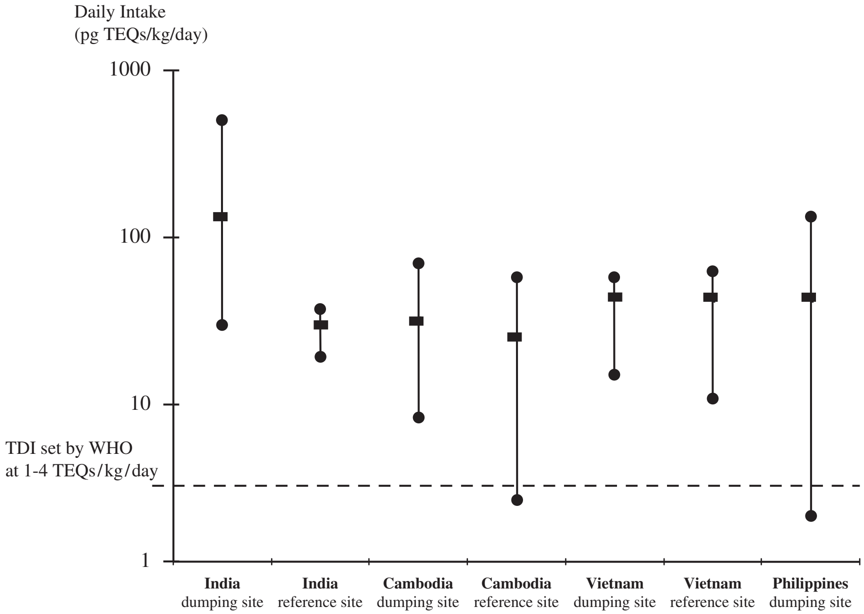

Figure 12.3. Estimated daily intakes of TEQs from human breast milk based on the assumption that an infant ingests 700 ml milk per day and that the weight of an infant is 5 kg (Hooper et al., 1997).

In a related study conducted by Minh et al. (2003), PCDD/F concentrations in some soil samples from the Philippines, Cambodia, India, and Vietnam exceeded environmental guideline values, suggesting potential health effects on humans and wildlife living near the dumpsites. Human intakes of dioxins via soil ingestion and absorption by dermal exposure were estimated to be highest in people of the Philippines followed by Cambodia, India, and Vietnam. The estimated intakes of dioxins via soil ingestion and dermal exposure for children were higher than those for adults, suggesting greater risk of dioxin exposure for children in dumpsites. Findings in this study underscored the serious health risk on people living near dumpsite areas considering the hundreds of people scavenging in the dumpsite area and even living there (as in the case of Payatas dumpsite in the Philippines). Moreover, the study addressed the issue that open dumping sites are potential sources of PCDD/Fs and related compounds, and dioxin contamination in dumpsites may become a key environmental problem in developing countries, particularly in the Philippines.

12.6. Management and regulation of POPs in the Philippines

The Philippine Senate ratified the Stockholm Convention in 2004 making the Philippines the 51st party to the Stockholm Convention. Further, the Philippine government through its Environmental Management Bureau (EMB) of the Department of Environment and Natural Resources (DENR) has conducted enabling activities as part of its obligation to the Convention. This enabling activity project was conducted through the support of the Global Environment Facility (GEF) channeled through the United Nations Development Program (UNDP) (Bravante and Medina, 2004). Among the activities that have been conducted were: establishment of a coordination mechanism, which includes the formation of a Technical Working Group on POPs management, a Project Steering Committee, and the Regional Interagency Committee (RIAC) on POPs; capacity building activities; conduct of capacity and needs assessment; conduct of an Initial National Inventory and Public Awareness; and information campaign activities.

To articulate the country's commitment to the Convention, Philippine POPs Environmental Policy has been drafted (Madrazo and Ang, 2005). This policy was formulated upon agreement and acceptance by the stakeholders and stated as follows:

> *Consistent with the policy of the State to protect the environment and promote the general welfare and health of the people and their right to a balanced and healthful*

> *ecology, the Philippines commits itself to implement policies, strategies and actions designed to eliminate the production and use of Persistent Organic Pollutants (POPs) and minimize the release of unintentional POPs by-products covered by the Stockholm Convention. The Philippines shall execute the National Implementation Plan to meet its obligations under this Convention.*

The Philippines is in its final stages in the process of formulating a National Implementation Plan (NIP) that aims toward identifying national actions and programs parallel to the objectives of the Stockholm Convention (Madrazo and Ang, 2005). The development of a national document such as NIP in the Philippines is a relatively long process as it was necessary to have core-enabling activities be completed so as to provide the baseline information needed in formulating the NIP. Workshops and focus group discussions were frequently held among the stakeholders (government and non-government agencies) to ensure their extensive involvement, as the actual development of the NIP is a consultative process. With the results of the enabling activities, the Philippine NIP aims to present the current status of POPs in the country, set the priorities for future activities to protect human health and the environment, and to indicate and formulate procedures for implementing any necessary policy and regulatory reforms, capacity building and other programs (Madrazo and Ang, 2005).

Based on the activities that were initially conducted for the enabling activity project (Bravante and Medina, 2004), it was reported that little is known about POPs in the country and that even the users have minimal understanding of their hazards. As no comprehensive data on POPs is available for use as baseline information, a more comprehensive inventory is needed for the Philippines to have an actual measure of the risks that must be managed and addressed in the NIP. The Initial National Inventory conducted showed that POPs have already been banned in the country except HCB and mirex, which have no recorded use, importation or production in the country. Significant amounts of PCBs mainly come from electric transformers and capacitors. Dioxins and Source Inventory by DOST showed that there are numerous sources of dioxins and furans in the country, which emit significant quantities of dioxins and furans into the environment. No treatment facility in the country that deals with the destruction of POPs and other toxic hazardous wastes are present in the country (Bravante and Moreno, 2005).

There are existing legal mandates that cover the management of POPs and other toxic and hazardous substances in the country. In June 1999, the Philippine Congress enacted the Philippine Clean Air Act (Republic Act 8749), wherein Section 32 addresses POPs and Section 20 incorporates a provision calling for a ban on incineration. Furthermore, pursuant to the provisions of the Republic Act 6969 otherwise known as Toxic Substances and Hazardous and Nuclear wastes Control Act of 1990, DENR Administrative Order No. 29, Series of 1992, otherwise known as the "Implementing Rules and regulations of RA6969" and other applicable laws, rules and regulations, Chemical Control Order for PCBs was promulgated and took effect on March 19, 2004. Furthermore, DENR developed a list of Priority Chemical List (PCL) and the Philippines Inventory of Chemicals and Chemical Substances (PICCS), which are scheduled for updating every five years. To date, the Philippine Congress has yet to ratify House Bill 5429 otherwise known as the "Philippine Hazardous and Nuclear Wastes Management Act of 2003", that aims to protect human health and the environment from the potential risks of hazardous and radioactive wastes within the framework of sustainable development through the formulation and implementation of integrated and comprehensive waste management systems. This act when passed into law can help pave the way for a real solution to the country's hazardous waste management problems from collection, treatment, storage and disposal (Madrazo, 2004).

12.7. Conclusion and recommendations for future research

During the last decade, environmental monitoring of persistent organic pollutants in the Asia-Pacific region, including the Philippines, revealed apparent POPs contamination particularly of PCBs and dioxins. Consequently, these studies suggest higher risk and exposure of the general populace to these toxic contaminants, more so for people residing near dumping site areas, where elevated concentrations of PCDD/Fs have been noted. Although decrease in POPs contamination may have been observed globally, developing countries, such as the Philippines, could be potential sources for certain contaminants. Therefore, a more systematic and continuous multi-media monitoring of these toxic substances seem imperative. Human health implications and toxic effects to wildlife must likewise be investigated. Lack of data in terms of measured concentrations and threshold values may require the conduct of systematic appraisal using data on BFRs and POPs releases and ecotoxicological properties to measure environmental risks. Active participation in international cooperative research programs would help the Philippines in its need for capacity building on appropriate advanced technologies and laboratory facilities to carry out these studies.

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Chapter 13

Persistent Toxic Substances in the Environment of Indonesia

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Abstract

Although Indonesia has been using vast amounts of chemicals for accelerating its economic development as well as for combating various vector borne diseases, the state of knowledge on toxic pollutants in the country is not much understood, due to lack of information, limited financial resources etc. Regional and nationwide monitoring studies indicate that the levels of most studied compounds, including classical organochlorines and butyltins in the environment of Indonesia are generally low when compared to global contamination levels and guideline standards. However, there is also a concern on wildlife and human health due to elevated levels of DDTs (the major contaminants) and tributyltin, particularly in the locations which are close to human activities such as ports and harbors, urban centers and areas of intensive agriculture. There is limited information on temporal trends for most contaminants, however, it was found that DDTs and PCBs exhibited declining levels in Indonesian environment with time. New environmental challenges are also emerging in Indonesia, such as contamination of coastal and terrestrial ecosystems by brominated flame retardants (BFRs). Recent investigations on BFRs revealed that PDBEs and HBCDs are widespread in the environment and concentrations may increase in future. Overall, this chapter provides an overview of the levels, occurrences and distributions of PCBs, organochlorine pesticides, BFRs and organotins, and their possible impacts on the environment of Indonesia.

13.1. Introduction

Growth in industrial, agricultural and many other activities caused by increasing human population has resulted in a rapid increase in inputs of anthropogenic chemicals into the environment, including the chemicals that are generally referred to as "persistent toxic substances" (PTS).

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Substances in this category are diverse. Many of the substances of greatest interest are organic compounds characterized by persistence in the environment, resistance to degradation, and acute and chronic toxicity. In addition, many are subject to atmospheric, aquatic or biological transport over long distances and are, thus, globally distributed, and detectable even in the areas where they have never been used. The lipophilic properties of these compounds cause their bioaccumulation in tissues of living organisms leading to body burdens that pose potential risks of adverse health effects. The persistence and bioaccumulation of PTS may also result in increase over time of concentrations in consumers at higher trophic levels, including humans. Several groups of chemicals are having such properties, including the chemicals traditionally referred to as persistent organic pollutants (POPs), organometalics, heavy metals, and other substances. For several decades, these PTS have been found in a range of environmental media and biota, and their toxic impacts on wildlife and humans is a major issue that gives rise to concerns at local, national, regional, and global scales.

Indonesia is an archipelago located in Asian tropical belt between the Pacific and Indian oceans, and two continents, Asia and Australia. The whole territory consists of 17,508 islands of which ~6000 are uninhabited. The population was around 240 million in 2004 making it the fourth most populous country in the world (after China, India, and the United States). About 60% of the total population live in Java, the fifth largest island of the territory. Presently, Indonesia is experiencing rapid industrialization and high annual economic growth rates, and as a result many chemicals are produced and used for industrial, agricultural, and health purposes. In the last decade there were many evidences on the declining environmental quality resulting in decreasing or even disappearing populations of wildlife and adverse effects on humans (Untung, 1999). In this situation, it seems that the accelerating development of Indonesian economy may have been primarily achieved at the expense of the environment. However, little information exists on levels of toxic contaminants as well as assessment of their potential toxicity to wildlife and human. The aims of this chapter are to overview the levels of selected PTS in the environment of Indonesia comprising areas of various land-based activities from urban to rural areas, the potential sources of contaminants, and the toxicological consequences on the wildlife and human. In this chapter, occurrence and distributions of certain groups of PTS such as organotins (OTs), organochlorines (OCs) including polychlorinated biphenyls (PCBs) and OC pesticides, such as dichlorodiphenyltrichloroethane and its metabolites (DDTs), hexachlorocyclohexane isomers (HCHs), chlordane compounds (CHLs), hexachlorobenzene (HCB), *tris*

(4-chlorophenyl) methane (TCPMe) and new candidates of POPs, polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) in the water, sediment, soil, air, mussel, fish, and human milk in Indonesia are reviewed.

13.2. Historical use, production, and management of POPs

As an agriculture-based tropical country, use of pesticide in Indonesia is very much needed for the national development. The use of pesticides has been increasing very rapidly because of the expansion of area cultivated under food crops and vegetables. In 1979–1980, ~6500 tons of pesticides were used and it became 15,000 tons in 1981–1982 (Soekarna and Sundaru, 1983). The first group of insecticides that were introduced by the government for agriculture was DDT and other OCs in early 1950s, followed by organophosphates and carbamates in the late 1960s (Untung, 1999). According to the reports (UNIDO, 1984; Untung, 1999; Suroso et al., 2000; EMC, 2003), no data on the total amount of DDT used for agricultural are now available. However, information is available for some other OC pesticides. For example, in 1974, total imports and production of aldrin was 30,000 kg, chlordane 20,902 kg, and toxaphene 144 kg. In 1979, 3000 kg of dieldrin and 3720 kg of chlordane were imported and used. The latest recorded data on the use of dieldrin was in 1990 when a total of 3492 kg was imported. Total import and consumption of chlordane in 1990, 1991, and 1992, were 21,072, 25,984, and 37,871 kg, respectively.

Under the laws and regulations of pesticide registration, since 1974, some of the OC pesticides, including aldrin, DDT, endrin, and heptachlor were prohibited for agricultural purposes. However, owing to the unavailability of alternative insecticides, dieldrin, and chlordane remain registered and are allowed restrictedly for use in termite control. Toxaphene 70 EC was specially registered and permitted for use on cotton, but finally was banned in 1980. In 1992, dieldrin 20 EC and chlordane 960 EC were the last group of OCs that were prohibited by the government for agricultural use. Among the POPs, HCB and mirex were never registered; however they were used in Indonesia for agricultural purposes. No data are available on HCHs usage. Currently, the pesticides used in Indonesia belong to different groups, such as organophosphates, carbamates, synthetic pyrethroids, insect growth regulators, and biological pesticides. In efforts to limit and terminate the use of hazardous and persistent pesticides, including chemicals in the POPs list, since 1986 the Government has adopted the Integrated Pest Management (IPM) approach.

By implementing IPM, Indonesia is now reducing the national consumption of pesticides.

Although the use of DDT in agriculture was banned in 1974, this pesticide was officially used until the mid-1990s for eradication of *Culex sp.* and *Anopheles sp.*, the main vector of malaria. In 1952, the government through the Department of Health introduced DDT and dieldrin for malaria control in Java Island. The formulation of DDT used was 75% WDP (Water Dispersable Powder) and it was applied two times a year at a dose of $2\,\mathrm{g\,m^{-2}}$. From 1969 to 1974, 8,900,000 houses were sprayed with 5,250,000 kg of DDT 75% WDP. In 1975–1979, the number of house sprayed in Java and Bali increased significantly up to 18,600,000 houses and 13,300,000 kg of DDT was used. At the same time, a total number of 3,400,000 houses in outer islands of Java and Bali were sprayed with 1,600,000 kg of DDT. In the period of 1984–1989, the number of houses sprayed in Java and Bali reduced drastically, down to 1,900,000 houses that were sprayed with 1,200,000 kg DDT, but in outer Java and Bali the number of houses sprayed increased up to 6,200,000 and 2,600,000 kg DDT was applied. The extensive use of DDT for malaria control program was at the period from 1974 to 1982, with annual consumption accounting on an average of 2565.4 tons DDT. In 1992–1993, by the decree of the Ministry of Health, the use of DDT for malaria control was terminated in Java and Bali, and subsequently for the whole country in 1993–1994.

Indonesia is also one of the few countries that produced DDT. In 1984, formulation plant of DDT was built with an annual capacity as much as 7000 tons $\mathrm{year^{-1}}$, and the main task was to supply all the DDT of needed by the Department of Health for malaria control program. The rest of the production only was permitted for export aimed to the countries that were using DDT for eradication of diseases, such as Latin America, and other Asian countries. The production was stopped in 1994, after the Department of Health banned the usage of DDT for health purposes. Currently, there is not enough information on the stockpile of these compounds available.

With regard to other POPs, PCBs have not been imported to Indonesia for the last 5 years, and they have been prohibited for use in industrial activities. According to Untung (1999), the Department of Mining and Energy which manage the supply of electrical power for the whole country, and also National Electrical Company, none had any concern or put forth any special instruction on the use of PCBs in electrical appliances including use of PCBs in the insulators, capacitors, and generators. Therefore, PCBs are still present in many electrical appliances, which have been used and distributed widely in the country.

The usage of toxic chemicals such as POPs was generally based on government regulations on environmental management. For example, according to Government Regulation No. 73 of 1973 on the control, distribution, storage, and use of pesticides, every pesticide must be registered at the Ministry of Agriculture through National Pesticide Committee. Based on Presidential Decree No. III/1986, 57 pesticides consisting of 28 active ingredients, including POPs pesticide were banned for controlling targeted organisms in rice fields. In other regulation, Agency for the Environmental Impact Management (BAPEDAL) under Ministry of Environment is responsible for the national management of environmental problems. In accordance with international efforts to reduce and eliminate POPs gradually, which are released either intentionally or unintentionally into environment, Indonesia has signed the Stockholm Convention in 2001 along with 176 countries. Following this, the Government of Indonesia responded to the need for the management of hazardous and toxic substances by passing Regulation Number 74 in 2001, which banned ten chemicals included in the Stockholm Convention list of POPs, i.e. eight chemical pesticides (Aldrin, Dieldrin, Chlordane, DDT, Endrin, Heptachlor, Mirex, and Toxapene) and two industrial chemicals (HCB and PCBs). While Dioxins and Furans are not currently regulated, Decree Number 03/BAPEDAL/09/1995 addresses the technical requirements for hazardous waste management by identifying emission standards for the incinerator process. The Governmental Regulation Number 85/1999 controls the air emission standard and the destruction removal efficiency (DRE) of incineration process for dioxins and furans. Some other related regulations also were stated by Ministry of Agriculture and Ministry of Health. Although some regulations have been stipulated, Indonesia until now does not have set standards for all POPs chemicals, either for human or the environment.

In order to better protect human health and the environment from the hazards of POPs, the Government of Indonesia has developed the National Implementation Plan (NIP). The objective of developing the NIP was not only to adhere to Indonesia's commitment as a signatory of the Stockholm Convention (Article 7) but also to unify the existing POP management strategies and achieve cooperation among all national stakeholders.

In this context, environmental monitoring and inventory study are important as the basis for formulating and development of NIP. Several scientists of the region may have been dealing with POPs monitoring, however not much of the results could be accessed widely. Comprehensive monitoring researches since 1990s to date from the Department of Environment Conservation (currently Center for Marine Environmental

Studies), Ehime University (Japan), contributed much valuable information on the occurrence, fate, and behaviour of POPs in tropical Asian developing countries, including Indonesia. The Ministry of Environment of the Republic of Indonesia is now responsible for carrying out the inventory to determine the actual state of environmental pollution caused by POPs. To strengthen the national capability and to enhance knowledge and understanding among decision makers, managers, industries, and public, to meet the obligations of the Stockholm Convention and implement the elimination of POPs, several international collaboration studies have been conducted. During 1996–1999, under the Asia Pacific Mussel Watch Project coordinated by Professor Shinsuke Tanabe from Ehime University (Japan), cooperative research efforts with scientists from respective developing countries succeeded in ascertaining the status of marine pollution by toxic contaminants in the Asia-Pacific region, including Indonesia. The Ministry of the Environment has also taken an inventory program on POPs under the Global Environment Facility (GEF) project enabling activities to facilitate early action on the implementation of the Stockholm Convention on POPs in Indonesia. Further to this, in 2001, Environmental Management Centre (PUSARPEDAL), Ministry of Environment, Indonesia, in collaboration with United Nations University (UNU), Japan,and Japan International Cooperation Agency (JICA), conducted POPs residues monitoring in the river, seawater, sediments, and soil from several locations that have been considered as hot spots of contamination. All of these efforts, however, are still far from clarifying the status of POPs in Indonesia as much of these data are not published.

13.3. Environmental contamination by organochlorine compounds (OCs)

13.3.1. Contamination by OCs in abiotic compartment (water, sediment, soil, and air)

Available information on concentrations of OCs, particularly OC pesticides in water, sediment, soil, and air has been summarized in Table 13.1. In most cases, larger data sets on OC concentrations in abiotic compartment are from the surveys conducted in recent years (1990s to the middle of 2000s), with particular concern on water and sediment (Table 13.1). A nationwide occurrence of OC pesticides in water and sediment indicate that the two major contaminants in the Indonesian environment are DDTs and HCHs (Table 13.1). Although, there is no report on the usage of HCHs, elevated levels of this compound in water and sediment confirm

Table 13.1. Residue levels of OCs in water, sediment, soil, and air from various locations in Indonesia

Location	Year	*n*	α-HCH	β-HCH	γ-HCH	HCHs	*p,p′*-DDE	*p,p′*-DDD	*p,p′*-DDT	DDTs	PCBs	CHLs	References
River water (ng L^{-1})													
Rungkut River, Surabaya, East Java	2001	2	4.0 (3.3–4.7)	na	4.3 (3.8–4.8)	8.3 (8.0–8.5)	nd	1.9 (0.86–2.9)	2.6 (1.6–3.5)	8.3 (6.9–9.7)	na	na	Ratnaningsih et al., 2002
Rungkut River, Surabaya, East Java	2002–2003	2	8.0 (nd–16)	4.1 (nd–8.1)	6.5 (nd–13)	19 (nd–37)	nd	nd	nd	nd	na	nd	EMC, 2003
Surabaya River, Surabaya, East Java	2001	6	0.73 (nd–2.2)	na	3.4 (2.2–5.6)	4.1 (2.2–7.8)	16 (nd–98)	5.0 (0.75–22)	22 (1.3–120)	71 (7.1–390)	na	na	Ratnaningsih et al., 2002
Surabaya River, Surabaya, East Java	2002–2003	13	120 (nd–390)	4.2 (nd–19)	6.2 (nd–23)	130 (nd–480)	0.19 (nd–2.0)	0.11 (nd–1.1)	0.11 (nd–1.3)	0.54 (nd–4.7)	na	28 (nd–360)	EMC, 2003
Banjir Kanal T, Semarang, Central Java	2001	4	7.9 (7.0–12)	na	10 (2.3–18)	19 (14–23)	0.02 (nd–0.08)	2.3 (0.75–3.9)	nd	5.0 (2.2–8.0)	na	na	Ratnaningsih et al., 2002
Banjir Kanal T, Semarang, Central Java	2002–2003	4	13 (nd–35)	4.3 (nd–17)	25 (nd–76)	43 (nd–110)	nd	nd	0.24 (nd–0.96)	0.41 (nd–0.96)	na	0.63 (nd–1.4)	EMC, 2003
Banjir Kanal B, Semarang, Central Java	2001	4	1.1 (0.38–1.6)	na	3.5 (2.5–4.7)	4.6 (3.0–6.2)	nd	2.2 (0.73–2.8)	1.7 (nd–3.1)	4.7 (3.2–6.3)	na	na	Ratnaningsih et al., 2002
Banjir Kanal B, Semarang, Central Java	2002–2003	4	1.7 (nd–4.0)	0.46 (nd–1.6)	1.6 (nd–4.9)	3.9 (nd–9.2)	nd	nd	nd	nd	na	nd	EMC, 2003
Ciliwung River, Bogor, West Java	1991	1	14	4.2	3.7	22.0	0.073	0.038	0.071	0.19	1.3	0.24	Iwata et al., 1994
Ciliwung River, Bogor, West Java	2001	6	1.4 (nd–4.3)	na	4.1 (1.3–7.3)	5.5 (1.3–12)	0.11 (nd–0.57)	2.0 (0.70–3.3)	1.9 (nd–3.8)	6.8 (3.0–10)	na	na	Ratnaningsih et al., 2002
Ciliwung River, Bogor, West Java	2002–2003	8	2.7 (nd–7.7)	2.2 (nd–11)	1.6 (nd–7.1)	6.6 (nd–22)	0.025 (nd–0.20)	0.20 (nd–1.6)	0.054 (nd–0.43)	0.46 (nd–3.3)	na	1.1 (nd–3.2)	EMC, 2003
Ciliwung River, Jakarta, West Java	1991	2	2.4 (1.7–3.2)	0.66 (0.53–0.78)	1.0 (0.84–1.2)	4.2 (3.1–5.2)	0.65 (0.094–0.12)	0.076 (0.064–0.087)	0.052 (0.016–0.087)	0.24 (0.22–0.27)	2.5 (0.38–2.1)	0.17 (0.071–0.26)	Iwata et al., 1994
Ciliwung River, Jakarta, West Java	2001	4	12 (3.0–23)	na	5.2 (nd–14)	19 (6.9–27)	0.22 (nd–0.68)	1.9 (0.68–3.1)	2.4 (nd–6.2)	8.3 (1.8–14)	na	na	Ratnaningsih et al., 2002

Table 13.1. (*Continued*)

Location	Year	*n*	α-HCH	β-HCH	γ-HCH	HCHs	*p,p*′-DDE	*p,p*′-DDD	*p,p*′-DDT	DDTs	PCBs	CHLs	References
Ciliwung River, Jakarta, West Java	2002–2003	6	13 (nd–59)	1.2 (nd–7.3)	3.2 (nd–12)	17 (nd–78)	0.25 (nd–0.84)	0.26 (nd–1.6)	1.5 (nd–4.2)	2.0 (nd–4.3)	na	0.73 (nd–2.8)	EMC, 2003
Upper Citarum, West Java	na	21	na	na	400 (nd–910)	na	na	na	180 (nd–750)	na	na	na	Parikesit et al., 2005
Coastal water (ng L^{-1})													
Siak, Riau	1997	na	nd–0.86	nd–0.098	nd–2.1	na	nd–0.24	nd–3.0	nd–0.70	na	na	na	Hutagalung et al., 1997
Kuala Tungkal, Jambi	1997	na	nd–0.24	0.071–0.95	nd–0.020	na	nd–0.34	nd–0.70	0.071–0.42	na	na	na	Munawir, 1997
Musi, Palembang, South Sumatra	1998	na	nd–0.013	nd–0.16	nd–0.20	na	nd–0.13	nd–0.11	nd–0.070	na	na	na	Munawir, 1998
Kuala Jambi, Jambi	1999	na	nd–0.31	nd–1.2	nd–1.2	na	nd–0.49	nd–0.43	nd–0.15	na	na	na	Munawir, 1999
Asahan, North Sumatra	2001	na	nd	nd–0.38	nd–1.3	na	nd–6.7	nd–2.5	nd–3.5	nd	na	na	Munawir, 2001a
Way Kambas, Lampung	2001	na	nd–0.12	nd–0.62	nd–0.93	na	nd	nd–1.2	nd–8.3	na	na	na	Munawir, 2001b
Way Sekampung, Lampung	2001	na	nd–0.16	nd–2.0	0.21–2.7	na	nd–0.97	nd–0.88	nd–5.6	na	na	na	Munawir, 2001b
Coastal, Surabaya, East Java	2001	4	0.33 (nd–1.3)	na	2.7 (1.3–3.9)	3.0 (1.3–5.2)	0.12 (nd–0.48)	1.8 (0.65–3.2)	2.5 (1.3–3.5)	6.3 (2.7–9.6)	na	na	Ratnaningsih et al., 2002
Coastal, Surabaya, East Java	2001	4	0.58 (nd–1.2)	na	3.0 (nd–6.2)	3.4 (nd–7.4)	nd	1.1 (nd–2.8)	1.2 (nd–3.2)	2.9 (nd–6.4)	na	na	Ratnaningsih et al., 2002
Coastal, Semarang, Central Java	2002–2003	1	7.0	8.7	2.0	19	nd	nd	nd	nd	na	nd	EMC, 2003
Coastal, Semarang,, Central Java	2001	4	0.71 (0.09–1.5)	na	4.2 (1.8–7.4)	4.9 (1.9–8.8)	nd	1.9 (0.65–3.3)	2.4 (1.3–3.5)	6.7 (3.2–10)	na	na	Ratnaningsih et al., 2002
Coastal, Jakarta Bay	2002–2003	3	1.3 (nd–4.0)	0.75 (nd–2.2)	3.0 (nd–9.0)	5.3 (nd–16)	nd	nd	0.25 (nd–0.76)	0.73 (nd–2.2)	na	nd	EMC, 2003
Coastal, Jakarta Bay	1994	na	nd–0.015	nd	nd	na	nd–3.5	nd–0.049	nd	nd	na	na	Razak and Munawir, 1994
Arafura, West Papua	2002	na	nd	0.027–0.046	0.006–0.031	na	0.015–0.038	nd–0.009	0.021–0.032	na	na	na	Munawir, 2002
Memberamo, West Papua	2003	12	nd	nd	nd	na	nd	nd	nd	na	na	na	Munawar, 2005

River sediment (ng g^{-1})												
Surabaya River, Surabaya, East Java	2002–2003	12	140 (nd–430)	10 (nd–51)	7.3 (nd–61)	150 (nd–480)	2.3 (nd–12)	2.1 (nd–7.4)	7.0 (nd–51)	12 (nd–51)	na	0.89 (nd–8.7)	EMC, 2003
Bajir Kanal T, Semarang, Central Java	2002–2003	4	7.0 (nd–16)	2.5 (nd–6.2)	5.1 (nd–11)	15 (nd–31)	0.025 (nd–0.10)	nd	6.3 (1.4–8.7)	8.0 (2.7–11)	na	0.20 (nd–0.78)	EMC, 2003
Bajir Kanal B, Semarang, Central Java	2002–2003	4	0.64 (nd–1.8)	1.0 (nd–4.0)	1.4 (nd–2.9)	3.0 (nd–7.4)	0.32 (nd–0.81)	0.042 (0.17)	1.6 (nd–3.0)	2.0 (nd–3.8)	na	0.055 (nd–0.22)	EMC, 2003
Ciliwung River, Bogor, West Java	1991	2	0.001 (nd–0.002)	0.019 (0.018–0.020)	0.033 (0.015–0.051)	0.053 (0.035–0.071)	20 (19–21)	10 (5.5–15)	2.0 (0.86–3.2)	34 (26–42)	180 (140–220)	23 (8.0–38)	Iwata et al., 1994
Ciliwung River, Bogor, West Java	2002–2003	7	35 (nd–210)	0.20 (nd–1.2)	2.1 (nd–6.8)	37 (nd–220)	0.26 (nd–0.86)	0.24 (nd–1.0)	2.1 (0.25–4.3)	2.6 (0.29–5.5)	na	0.36 (nd–1.2)	EMC, 2003
Ciliwung River, Jakarta	1991	2	nd	026 (0.013–0.040)	0.052 (0.045–0.059)	0.078 (0.058–0.099)	2.5 (0.95–4.1)	2.3 (0.94–3.6)	2.8 (1.3–4.4)	8.2 (3.4–13)	42 (5.9–79)	0.32 (0.16–0.49)	Iwata et al., 1994
Ciliwung River, Jakarta	2002–2003	6	51 (nd–200)	10 (nd–54)	7.6 (nd–26)	68 (nd–260)	2.0 (nd–7.6)	0.81 (nd–1.9)	4.1 (nd–14)	6.8 (nd–22)	na	1.5 (nd–7.5)	EMC, 2003
Coastal sediment (ng g^{-1})												
Jakarta Bay	1994	na	nd–0.62	nd–0.21	nd	na	nd–1.5	nd–3.6	nd	na	na	na	Razak and Munawir, 1994
Siak, Riau	1997	na	nd–0.006	nd–2.8	nd–1.4	na	nd–1.2	nd–2.9	nd–5.4	na	na	na	Hutagalung et al., 1997
Kuala Tungkal, Jambi	1997	na	nd–0.18	nd–0.056	nd–1.8	na	nd–0.27	nd–1.2	nd–5.5	na	na	na	Munawir, 1997
Musi, Palembang, South Sumatra	1998	na	nd	nd–0.30	nd–0.064	na	nd–0.61	nd–0.004	nd–0.076	na	na	na	Munawir, 1998
Kuala Jambi, Jambi	1999	na	nd–0.027	nd–0.087	nd–0.52	na	nd–0.59	nd–0.009	nd–2.2	na	na	na	Munawir, 1999
Asahan, North Sumatra	2001	na	nd–1.7	nd–5.5	nd–2.0	na	nd–0.11	nd	nd–0.15	na	na	na	Munawir, 2001a
Way Kambas, Lampung	2001	na	nd–0.075	nd–0.40	0.14—3.0	na	nd–0.16	nd	nd	na	na	na	Munawir, 2001b
Way Sekampung, Lampung	2001	na	nd	nd	0.48–3.1	na	nd	nd	0.56–1.6	na	na	na	Munawir, 2001b
Arafura, West Papua	2002	na	0.009–0.11	0.017–0.051	0.005–0.025	na	0.006–0.022	nd	nd	na	na	na	Munawir, 2002
Mamberamo, West Papua	2003	12	nd	nd	nd	na	nd	nd	nd	na	na	na	Munawar, 2005

Table 13.1. (*Continued*)

Location	Year	*n*	α-HCH	β-HCH	γ-HCH	HCHs	*p,p′*-DDE	*p,p′*-DDD	*p,p′*-DDT	DDTs	PCBs	CHLs	References
Soil (ng g^{-1})													
Surabaya, East Java	2002–2003	11	140 (nd–1300)	1.9 (nd–12)	41 (nd–430)	190 (nd–1700)	3.8 (0.81–7.6)	3.2 (nd–13)	8.8 (nd–39)	16 (1.8–42)	na	0.82 (nd–5.1)	EMC, 2003
Semarang, Central Java	2002–2003	8	1.8 (nd–5.3)	4.2 (nd–26)	1.1 (nd–3.9)	7.2 (nd–30)	1.9 (nd–8.8)	0.24 (nd–1.3)	7.3 (nd–18)	9.5 (nd–21)	na	0.17 (nd–0.68)	EMC, 2003
Bogor, West Java	2002–2003	8	1.3 (nd–2.8)	0.86 (nd–3.0)	0.57 (nd–2.2)	2.7 (nd–6.7)	0.30 (nd–2.0)	0.31 (nd–2.3)	3.9 (nd–6.2)	4.5 (nd–15)	na	0.76 (nd–4.8)	EMC, 2003
Jakarta	2002–2003	6	24 (nd–110)	3.8 (nd–15)	1.5 (nd–5.9)	29 (nd–130)	0.56 (nd–1.4)	1.1 (nd–3.7)	23 (nd–120)	25 (nd–120)	na	1.2 (nd–5.7)	EMC, 2003
Air (pg m^{-3})													
Java Sea	1989–1990	1	56	na	19	75	1.5	na	23	39	36	3.9	Iwata et al., 1993
Celebes Sea	1989–1990	1	95	na	23	120	0.70	na	23	37	22	7.9	Iwata et al., 1993
Indian Ocean	2004	2	0.30–0.50	na	2.8–5.6	3.1–6.1	na	na	18–28	27–33	28–51	1.1–3.8	Wurl et al., 2006

Note: Data of OCs from various literatures were selected based on the similar target compounds; all values of concentrations were normalized into similar unit and rounded to two digits for comparison; nd = not detected; na = no data available.

their usage in Indonesia. DDT has been intensively used in the past for almost three decades in agriculture as well as for health purposes. Geographical distributions of OCs indicate spatial variability of DDTs and HCHs in water from Indonesia. DDT and HCHs were highly present in the aquatic environment from several rivers and coastal areas in Java Island such as Surabaya, Semarang, Bogor, Jakarta, and Citarum than in other parts of Indonesia (Table 13.1). For instance, the occurrence of HCHs and DDTs in western (Sumatra Island) and eastern parts of Indonesia (West Papua) were much lower. DDTs and HCHs were not detected in remote areas such as Memberamo River at West Papua Province (Munawar, 2005). Higher concentration of HCHs and DDTs in several river and coastal areas in Java Island indicate their intensive usage in this island. *p,p′*-DDT was still found as the predominant compound both in river and coastal waters of these areas with concentration around 780 ng L^{-1} in upstream Citarum River. In most cases, higher concentrations of DDTs were found in rivers than those in coastal areas, indicating considerable use of this compound in inland rather than coastal areas.

The profiling of HCHs was also similar to those of DDTs (Table 13.1). Higher proportion of both α-HCH and γ-HCH were observed in various studies that indicate the use of technical HCHs and lindane (purified γ-HCH) in this country. Likewise, there were differences in use of different formulations of HCH among the locations. Higher α-HCH levels in water from some locations in Java may have been due to preferential use of technical HCHs, whereas high concentration of γ-HCH in several rivers and coastal areas in Sumatra Island may indicate the considerable usage of lindane. It has been reported that lindane is commonly used on palm oil tree plantations (Othman and Balasubramanian, 2001). It is plausible that this pesticide is intensively applied on palm oil tree, a common plantation crop in Sumatra Island.

PCBs have been reported only by Iwata et al. (1994) in water from Ciliwung River, West Java. Although there was no considerable variation among the locations in this river, higher concentrations of PCBs were found in river waters across Jakarta City than upstream rural area in Bogor, indicating elevated contribution from urbanized area.

Unlike contamination patterns in water, the OCs residue levels in coastal and riverine sediments revealed less variation between locations nationwide (Table 13.1). Similar pattern has been reported by a larger study in sediments from northern and southern countries in Asia (Iwata et al., 1994). Likewise, this is due to the prevailing high temperatures in these countries including Indonesia throughout the year and hence volatile compounds such as HCHs and DDTs remain for shorter time in the water. Tanabe et al. (1991) in their field study indicated that, more than

90% of HCH applied in a paddy field of tropical India evaporated into atmosphere. Although little variability of OCs was observed in sediment samples, sediments from rivers and coastal areas in Java Island, such as Surabaya, Jakarta, and Semarang seems to accumulate DDT and HCH higher than those in Sumatra Island (Table 13.1). The data obtained from sediment reflects the long-term use of these compounds in Java Island than in Sumatra Island. In the case of PCBs (Table 13.1), similar to those found in water, river sediment in Ciliwung River located in Jakarta City was relatively higher than that in upper stream at Bogor rural area (Iwata et al., 1994), again indicating higher contribution of this compound from the industrialized and urban areas. Furthermore, preliminary results also indicated widespread contamination by PBDEs and HBCDs, relatively new compounds which are commonly used as flame retardants, in sediments along coastal areas of Indonesia (Sudaryanto et al., 2006a). Relatively higher residue levels of these brominated flame retardants (BFRs) were found in sediments collected from Jakarta Bay, indicating similar pattern generally found for PCBs that are higher in populated and industrialized areas.

In contrast to water and sediment, very little information is available on the contamination of soil. OCs were found to be present in soils from river banks in four major cities on Java Island such as Jakarta, Bogor, Semarang, and Surabaya (EMC, 2003). Again, DDTs and HCHs were higher when compared to other target OCs such as CHLs and HCB (Table 13.1). Higher DDTs in soil was observed in riverbank of Ciliwung River located in Jakarta and Surabaya (up to 120 ppb and 42 ppb, respectively). Although, DDT for controlling malaria has been legally banned in 1994, high proportions of *p,p′*-DDT observed in soil collected from these locations, indicate persistency and/or the recent usage of this compound. The higher concentration of DDTs in soil from populated areas such as Surabaya and Jakarta may be due to intensive use of this compound for malaria eradication in these locations as well as for agricultural purposes. Elevated α-HCH was found in soil collected from riverbank in Surabaya (up to 1300 ppb) and Jakarta (up to 110 ppb) indicating favored use of technical mixture of HCHs in these locations. The profile of HCHs in soils and sediments indicate high use of technical HCH in Java Island. However, γ-HCH was also found to be dominant in the soil, particularly in samples from Semarang, suggesting also the use of lindane in this area. As for water and sediment, the profiles of HCHs and DDTs in soil also reflect the intensive and recent use of these two pesticides in Indonesia.

Among the abiotic compartment, atmosphere is known to be an important media for the distribution of volatile compounds in the global environment; however very few studies have reported the contamination of OCs in air in Indonesia (Table 13.1). The atmosphere can be considered as a mobile phase for the long-range transport of POPs towards final sink including the polar regions, where cold condensation of POPs to the ocean occurs. In addition to primary sources, the atmosphere receives input of POPs via evaporation processes from soil and the oceans, which occur intensively in tropical regions. There were two reports indicating the occurrence of POPs in the atmosphere of Indonesia, concerning the oceanic atmosphere (Iwata et al., 1993; Wurl et al., 2006) and/or semi continental (Wurl et al., 2006). In 1990s, Iwata et al. (1993) provided information on the concentrations of PCBs, DDTs, HCHs, and CHLs in air of seas and oceans along southern to northern hemisphere including two locations of Indonesian seas, Java Sea and Celebes Sea, the inland sea located at center and northern parts of this country. Based on available data from this study, distribution of OCs between these two seas was found to be quite similar (Table 13.1). In a subsequent study in 2004, Wurl et al. (2006) carried out studies on regional oceanic atmospheric levels of POPs in Indian Ocean and adjacent areas (Table 13.1). Although, HCHs concentration was lower in the latest study, there has been no change in concentrations of DDT between these two studies. Similar magnitude of pollution was observed more than ten years ago (1989–2004, see Table 13.1), indicating that emission of DDT is still taking place in Indonesia.

13.3.2. Contamination by OCs in biotic environment (mussel and fish)

Information on the occurrence of POPs in biota samples from Indonesia is very scarce and the available data are generally from studies in Asia-Pacific region dealing with low trophic aquatic wildlife such as mussel and fish (Kannan et al., 1995b; Monirith et al., 2003; Ueno et al., 2003b, 2004; Sudaryanto et al., 2005b, 2006a, 2007b), and no data has been reported for higher trophic animals. Table 13.2 shows compiled data of OCs including PCBs, DDTs, HCHs, CHLs, and HCB in biological samples from Indonesia, whereas Fig. 13.1 illustrates the distribution of some OCs. As a part of Asia-Pacific Mussel Watch Project organized by Ehime University, Japan (Tanabe, 2000), a comprehensive monitoring study using mussel as bioindicator reported spatial variability of OCs in coastal environment of Indonesia (Monirith et al., 2003). Similarly, an extended monitoring study, using fish and other aquatic and terrestrial animals also revealed the same distribution pattern (Sudaryanto et al., 2005b, 2006a, 2007b, Fig. 13.1). In all these studies, among OCs, DDTs and PCBs were the predominant compounds in aquatic wildlife (Table 13.2).

Table 13.2. Concentrations of OCs (ng g^{-1} lipid wt.) in mussels and fish from various locations in Indonesia

Location	Year	*n*	Fat (%)	PCBs	DDTs	CHLs	HCHs	HCB	Remark
Mussel[a]									
Belawan, North Sumatra	1998	48	1.4	13	15	5.3	5.3	0.80	Rural
Hurun Bay, Lampung	1998	40	1.1	14	65	15	4.1	<0.90	Rural, mariculture
Lada Bay, Banten	1998	56	1.1	85	110	<0.90	2.4	1.1	Rural, mariculture
Kamal, Jakarta	1998	54	1.3	210	45	13	<0.80	<0.80	Urban, fishing port
Ancol, Jakarta	1998	51	1.9	96	48	7.5	4.9	<0.50	Urban, marina
Cilincing, Jakarta	1998	49	1.7	140	58	7.4	4.7	<0.60	Urban, fishing port
Cirebon, West Java	1998	51	2.0	30	160	16	2.1	1.5	Rural, fishing village
Surabaya, East Java	1998	50	1.2	190	120	<0.80	<0.80	1.2	Urban, industrialized
Maros, South Sulawesi	1998	24	1.8	5.6	6.5	<0.60	<0.60	0.80	Rural, fishing village
Fish[b,c]									
Bogor, West Java	1991	5	3.0	86	930	15	24	1.7	Rural/suburban
Bogor, West Java	2003	8	7.6 (5.3–11)	110 (21–150)	640 (37–1100)	10 (2.0–21)	11 (3.4–24)	1.3 (0.26–2.6)	Rural/suburban
Jakarta Bay	1998	105	2.7 (1.4–5.8)	1400 (530–2700)	340 (73–750)	46 (11–80)	1.5 (0.40–2.6)	1.6 (0.70–1.9)	Urban, industrialized
Jakarta Bay	2003	13	5.3 (2.9–8.0)	690 (260–1100)	190 (110–350)	44 (23–81)	1.8 (1.0–3.7)	8.3 (0.44–28)	Urban, industrialized
Cirebon, West Java	1998	10	2.6 (1.2–5.1)	260 (27–560)	450 (70–880)	5.1 (nd–8.4)	16 (nd–77)	0.90 (0.30–1.5)	Rural, agriculture
Lada Bay, Banten	1998	10	5.0 (4.0–7.1)	170 (32–360)	310 (19–810)	5.9 (4.2–7.1)	2.4 (1.7–3.2)	5.1 (0.90–16)	Rural, agriculture
Lampung Bay, Lampung	2003	10	2.5 (1.1–5.5)	33 (9.7–94)	39 (12–120)	8.5 (0.73–30)	2.6 (0.78–4.2)	1.0 (0.22–2.1)	Rural, marine culture
West Sumatra	1998	5	2.5 (1.1–5.5)	33 (9.7–94)	39 (12–120)	8.5 (0.73–30)	2.6 (0.78–4.2)	1.0 (0.22–2.1)	Offshore (tuna)

Notes: nd = not detected; DDTs = *p,p′*-DDE + *p,p′*-DDD + *p,p′*-DDT; HCHs = α-HCH + β-HCH + γ-HCH; CHLs = *oxy*-CA + *cis*-CA + *trans*-CA + *trans*-nona + *cis*-nona.

[a] Data on mussels were reported by Monirith et al. (2003).

[b] Fish on 1991 by Kannan et al. (1995b).

[c] Fish on 1998 and 2003 by Sudaryanto et al. (2007b).

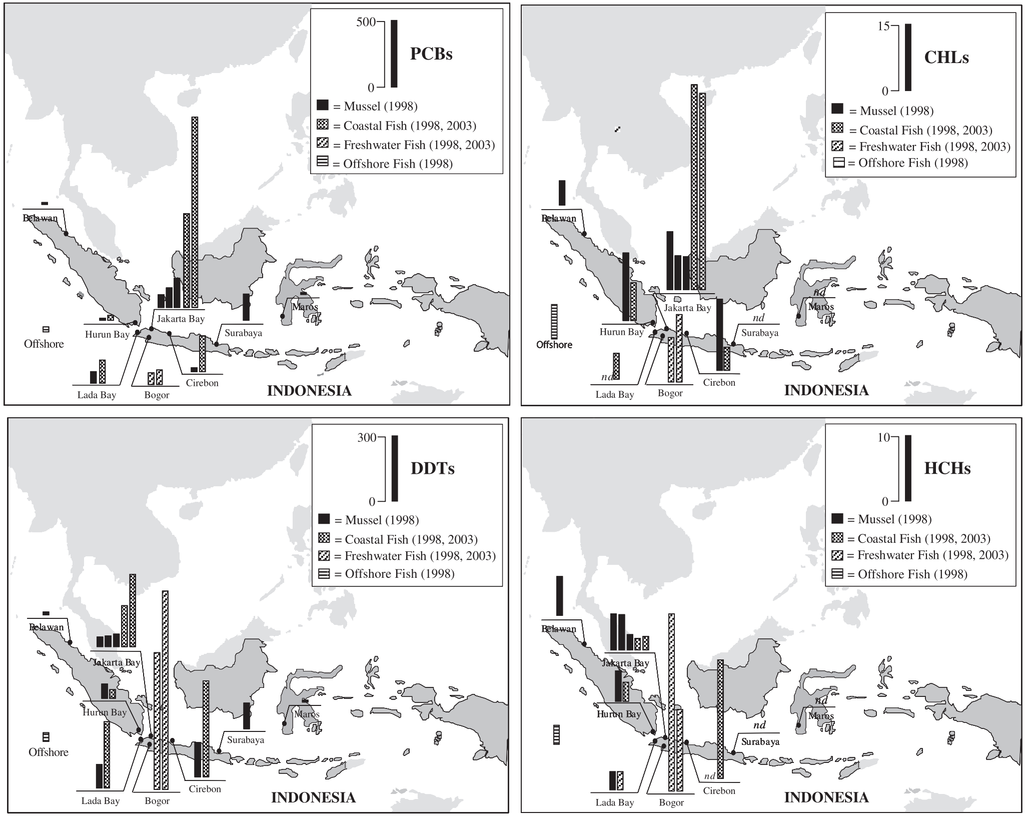

Figure 13.1. Distribution of OCs in mussels and fish from Indonesia.

So far, on lipid weight basis, the maximum concentrations of PCBs and DDTs reported were 210 ng g^{-1} and 160 ng g^{-1} in mussels, and 2700 ng g^{-1} and 1100 ng g^{-1} in fish, respectively (Monirith et al., 2003; Sudaryanto et al., 2005b, 2007b), while HCHs, CHL, compounds, and HCB were one or two order magnitude lower. Concentration patterns of OCs in mussels and fish were generally in the order DDTs > PCBs > CHLs > HCHs > HCB (Kannan et al., 1995b; Monirith et al., 2003; Sudaryanto et al., 2005b, 2007b). Higher concentrations of PCBs and DDTs in biological samples have been suggested as due to the higher bioaccumulative properties of these compounds and continuous discharge into aquatic environment; particularly in the case of DDTs which has been intensively used in agriculture as well as malaria eradication program (Untung, 1999).

A nationwide comparison indicates that elevated levels of OCs were found in the samples collected from Java Island than Sumatra and Sulawesi Islands (Table 13.2; Fig. 13.1). In Belawan (North Sumatra), Hurun Bay (Lampung), and Maros (South Sulawesi) residue levels of OCs were low. Such a pattern is understandable because Java Island is the most populated and industrialized island with intense agricultural activities, and the results could reflect the usage status of OCs in this island. Levels of OCs are still low in remote areas of Sumatra offshore waters as exemplified by less contamination in tuna (Ueno et al., 2003b).

Study conducted by Kannan et al. (1995b) showed the presence of DDT at higher concentration (960 ng g^{-1} lipid wt.) in fish collected in 1991 from Bogor, a rural area located 60 km away from Jakarta. In a survey conducted more than ten years later, DDT was still found to be high in this area (640 ng g^{-1} lipid wt.). Considerable levels of DDTs were also found in fish and mussels from Cirebon and Lada Bay (Monirith et al., 2003, Sudaryanto et al., 2007b). While comparing inland and coastal species, DDTs were apparently higher in freshwater fish (Ciliwung River, Bogor) than in marine fish species (Sudaryanto et al., 2005b, 2007b), indicating higher pollution by DDT in the terrestrial environment. All these results indicate considerable exposure to DDTs in the farming areas in Java Island. This is probably because of their intensive usage in both agricultural activities and malaria control program at those sites. DDTs have been banned since 1974 for agricultural application; however the country used the chemical until very recently for health purposes. Information on the amount of DDT usage in agriculture is not available; however, for disease eradication, Indonesia used DDT as much as 2565.7 ton year^{-1} during 1974–1982 (UNIDO, 1984). For this program, DDT was formulated in Indonesia since 1984 with an annual capacity of as much as 7000 tons year^{-1} (UNIDO, 1984; Untung, 1999).

Interestingly, although DDTs were low in rural areas in Sumatra Island (Lampung Bay), *p,p′*-DDT was relatively prevalent, suggesting recent application of DDT in this region (Sudaryanto et al., 2005b, 2007b). Profiles in abiotic samples also support this hypothesis. Recent monitoring study using human breast milk also indicated that there was possible recent input in specific rural agricultural areas (Burke et al., 2003; Sudaryanto et al., 2006b).

Although, there is little variability of HCHs in mussels, their distribution pattern in fish is relatively similar to DDTs. In fish, higher concentrations of HCHs were found in Ciliwung River (Bogor) and Cirebon coastal area than other locations. Higher levels of HCHs in fish from rural area also indicate their particular usage pattern and reflect recent input of HCH in agricultural sites. While, concentrations of HCHs were relatively low in all the samples, there was difference in the isomer patterns among the locations. Survey in 1991 indicated that γ-HCH was in higher proportion in rural area of Bogor (Kannan et al., 1995b). Similarly, study during 1998–2003 also found γ-HCH as the major contributor to total HCHs in fish from rural areas in Bogor and Lampung Bay (Sudaryanto et al., 2005b, 2007b). Despite lack of available information on their usage, the results in fish also reinforce the finding from abiotic samples and suggest the usage of lindane in Indonesia.

PCBs were particularly higher in the samples from urban sites (Table 13.2; Fig. 13.1). In Jakarta Bay, mussels collected from three locations contained PCBs from 96 to 210 $\mathrm{ng\,g^{-1}}$ lipid wt., that are one or two orders of magnitude higher than other locations. Similarly, an urban area of Surabaya also had elevated levels of PCBs (190 $\mathrm{ng\,g^{-1}}$ lipid wt.) within the range found in mussels from Jakarta Bay. In the samples collected at the same time of sampling as those of mussels, concentrations of PCBs in fish from Jakarta Bay (530–2700 $\mathrm{ng\,g^{-1}}$ lipid wt.) were also one or two orders of magnitude higher than other locations (Sudaryanto et al., 2007b). Survey of fish in 2003 also revealed similar distribution pattern, although PCBs decreased to 260–1100 $\mathrm{ng\,g^{-1}}$ lipid wt. in Jakarta Bay (Sudaryanto et al., 2005b, 2007b). No information is available on PCBs usage and production in Indonesia (Untung, 1999); however, the results indicate that notable contamination by PCBs is associated with a highly industrialized and populated area.

In case of CHLs, although elevated levels in mussel appeared in agricultural sites, notable contamination was also found in fish from Jakarta Bay (Table 13.2; Fig. 13.1). Besides being used as agricultural pesticides, CHLs are also generally used for killing termites in wood building materials and thus it could be a suitable explanation for higher CHLs in populated cities like Jakarta. According to regulation of OC pesticides, CHLs and dieldrin were the last group of OC pesticides that were prohibited by government for agricultural use in 1992 (Untung, 1999). During the period from 1974 to 1991, the amount of usage of CHLs increased from 20,902 to 37,871 tons. Thus, higher CHLs in fish from Jakarta Bay indicate higher usage of these compounds for termite control in urbanized area and reflect continuous input of CHLs in Indonesia.

Distribution of HCB concentrations in fish from Indonesia was rather uniform and the levels were much lower than other OCs (Table 13.2). However, relatively higher concentrations of HCB were observed in fish from Jakarta Bay. Higher concentrations of HCB in fish of the populated city in Jakarta Bay may be because HCB is not only used as a fungicide for crops and in industries, but also generated as a by-product during the production of several agrochemical and industrial chemicals. Furthermore HCB has been released into the environment by waste incineration (van Birgelen, 1998; Bailey, 2001). Therefore, various sources of HCB might be present in the areas that have been populated and industrialized.

To understand the magnitude of contamination in biotic samples from Indonesia, an extensive study on regional comparison of OCs in mussels (Monirith et al., 2003), fish (Kannan et al., 1995b), and tuna (Ueno et al., 2003b) are presented in Fig. 13.2. International comparison of OCs in mussels and fish from Indonesia revealed lower levels in Indonesian samples similar to those in other Southeast Asian countries such as Malaysia, Philippines, Cambodia, and Oceanian countries (Papua New Guinea and Solomon Island). The spatial variability of OC levels in multimedia biological samples suggested the presence of elevated levels of PCBs in Japan and Australia, and HCHs in India and China, which may reflect the high usage of the respective compounds in these countries (Kannan et al., 1995b). PCBs are discharged from Japan, which is a highly developed and industrialized country (Ueno et al., 2004). In case of HCHs, it was estimated that ~575,000 tons was used in India until 1985 (Kannan et al., 1995b). Although, it is believed that DDTs were intensively used in Indonesia for longer periods, global comparison indicates low levels of DDTs in biological samples. Apart from differences in sampling time, this result may suggest a lower accumulation in tropical fish, which could be due to the rapid volatilization of DDTs in the tropical environment (Kannan et al., 1995b). Kannan et al. (1995b) also noted that DDTs levels in tropical fish were ~1–2 orders of magnitude lower than those of United States.

With regard to brominated flame retardants, PBDEs were also reported in various samples including sediment, mussel, freshwater fish, coastal fish, and offshore marine fish (Ueno et al., 2004; Sudaryanto

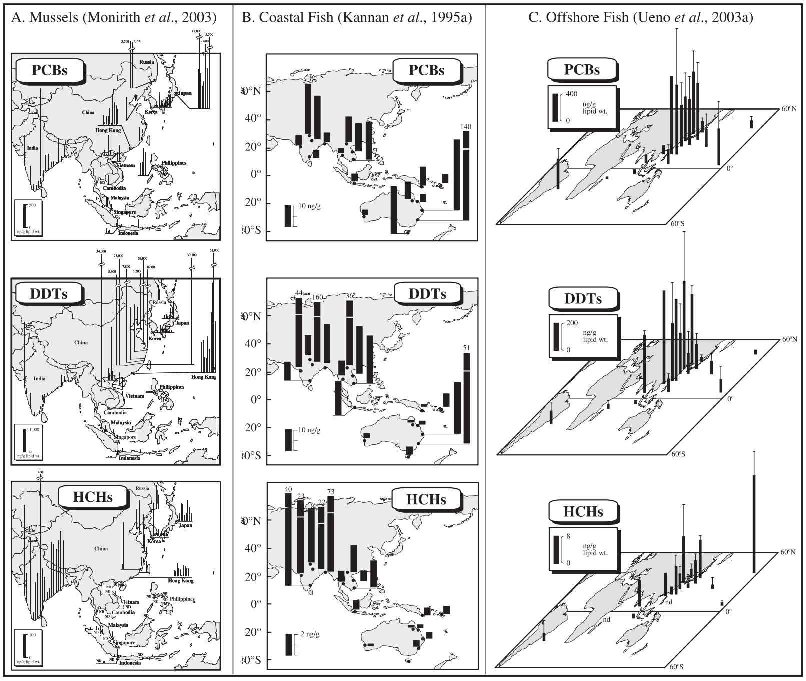

Figure 13.2. Regional distribution of OCs in mussels, fish and tuna in Asia-Pacific region.

et al., 2005b, 2006a; Fig. 13.3), and HBCDs was found in sediment and mussels from coastal waters (Sudaryanto et al., 2006a), suggesting their occurrence in the environment of Indonesia. Concentrations of PBDEs in fish also varied within species and locations. As those in sediment samples, relatively higher residue level of these brominated flame retardants were found in biological samples from urban areas in Jakarta Bay and Surabaya (Fig. 13.3), indicating similar pattern generally found for PCBs which are normally higher in populated and industrialized areas. Low levels of PBDEs and HBCDs were found in samples from remote areas including offshore waters. In comparison with OCs, the levels of PBDEs was the third most abundant pollutant class after DDTs and PCBs followed by CHLs, HCHs, and HCB in freshwater fish, whereas PBDEs ranked fourth in marine fish both from Jakarta Bay and Lampung Bay (Sudaryanto et al., 2005b). This result indicates that PBDEs are becoming chemicals of environmental concern as they frequently occur and are ubiquitous in the environment, similar to OCs, the classical contaminants routinely detected in the environment.

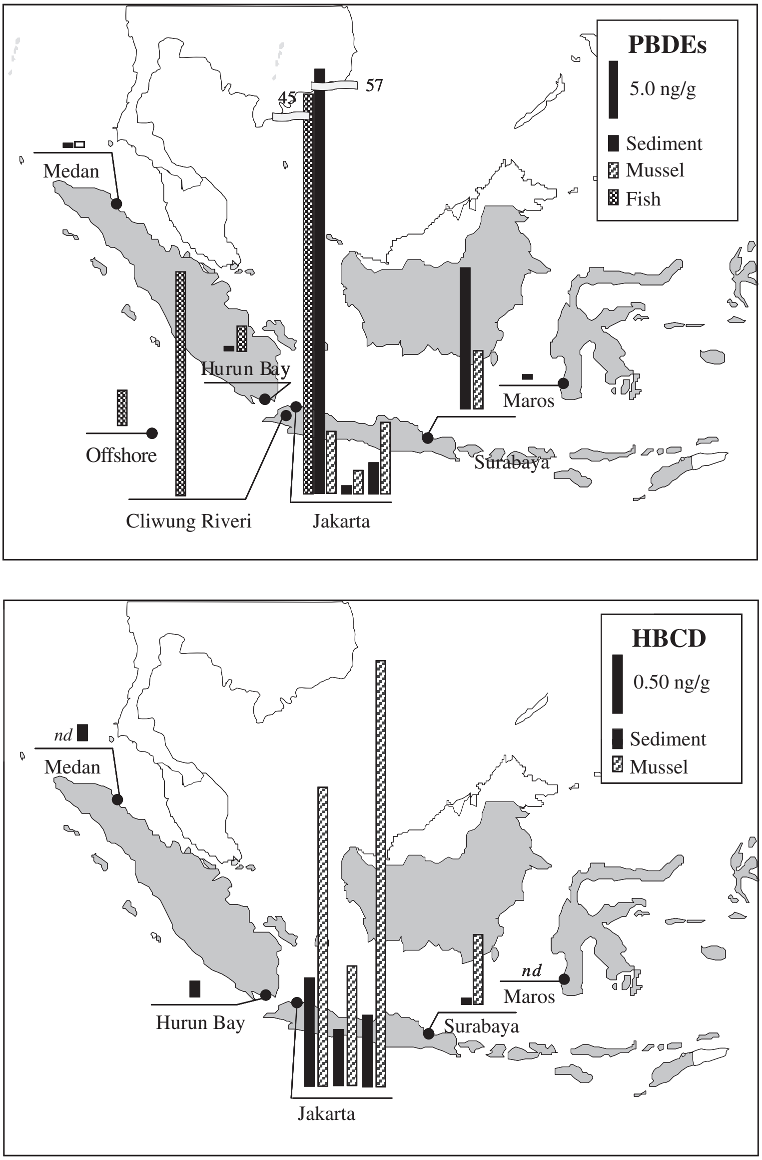

Figure 13.3. Spatial distribution of PBDEs and HBCDs in the environment of Indonesia.

Generally, levels of BFRs in Indonesian samples were considered low when compared worldwide. Ueno et al. (2004) showed regional differences in concentrations of PBDEs in tuna from several Asian countries and revealed low levels in Indonesian samples. The levels in fish were also much lower as compared to fish in North America (Dodder et al., 2002; Rayne et al., 2003) and European countries (Zennegg et al., 2002; Sellstrom et al., 1998; Erdogrul et al., 2005). Various species of fish in North America accumulated PBDEs that ranged from few hundred ppb to ppm level on lipid wt. basis, both in freshwater and marine fish. For example, Hale et al. (2001) reported maximum concentration of total PBDEs in carp from Virginian watershed up to 48,000 ng g^{-1} lipid wt., which is much higher than in carp from Indonesia (24 ng g^{-1} lipid wt.). In European studies, PBDEs were reported in levels ranging from few tens of ppb to ppm levels in various fish species, such as Whitefish and Pike. In Viskin River, Sweden close to several plastics and textile facilities, Sellstrom et al. (1993) found high concentrations of PBDEs in perch (37,000 ng g^{-1} lipid wt.).

13.3.3. Contamination by OCs in foodstuffs

Four studies have indicated the food contamination by OCs in Indonesia (Table 13.3). DDT was detected in vegetables (14–4400 ng g^{-1} wet wt.), chicken muscle (7.1–4000 ng g^{-1} wet wt.), egg (8800 ng g^{-1}), pork (47 ng g^{-1}), and fish (29–700 ng g^{-1}). DDT in chicken tissue and eggs from sprayed villages in Central Java exceeded the MRL of FAO/WHO

Table 13.3. Mean concentrations (ng g^{-1} wet wt.) of OCs in certain foodstuffs from Indonesia[a]

Food item	Location	Year	PCBs	HCHs	DDTs	References
Vegetables	Central Java	1984	na	12	14	Kuwatsuka et al., 1986
Vegetables	Central Java	1987	na	na	4400	Sulistiyono, 2004
Chicken muscle	Central Java	1989	na	na	4000	Noegrohoati et al., 1992
Egg	Central Java	1989	na	na	870	Noegrohoati et al., 1992
Carp fish	Central Java	1989	na	na	700	Noegrohoati et al., 1992
Rice	Bogor	1991	0.34	0.12	0.10	Kannan et al., 1994
Chicken muscle	Bogor	1991	4.5	4.4	7.1	Kannan et al., 1994
Pork fat	Bogor	1991	2.9	0.88	47	Kannan et al., 1994
Squid	Bogor	1991	2.0	0.06	0.66	Kannan et al., 1994
Fish	Bogor	1991	3.9	1.4	29	Kannan et al., 1994

Note: na = no data available.

[a] Values are from pooled individuals of several samples; all values of concentrations were normalized into similar unit and rounded to two digits for comparison.

(Noegrohoati et al., 1992). A greater proportion of *p,p′*-DDT was found in most food samples of animal origin, suggesting possible usage of DDT for malaria vector control. HCH, HCB, and PCB in Indonesian foods were relatively low, as observed in Thailand and other countries. As it has been shown in various abiotic samples and some fish from Bogor (Kannan et al., 1995b) and Lampung (Sudaryanto et al., 2005b, 2007b), levels of γ-HCH were greater than those of other HCH isomers, underlining the use of lindane rather than technical HCH (Kannan et al., 1994). These results indicate that Indonesians are exposed to high levels of DDT via their diet, particularly of animal origin.

13.3.4. Human exposure to OCs

As those in wildlife samples, only very few studies have addressed the accumulation of OCs in human from Indonesia and many of them focused on human breast milk particularly from women living in Java, the most populated island (Noegrohoati et al., 1992; Burke et al., 2003; Sudaryanto et al., 2006b). Except in a study by Sudaryanto et al. (2005a, 2006b) which included PCBs, TCPMe/OH, and PBDEs as target compounds, all the available data from this country are related to OCs pesticides (Noegrohoati et al., 1992; Burke et al., 2003). In an earlier study, Noegrohoati et al. (1992) investigated concentration of DDTs in human breast milk from single population of women who had lived in huts sprayed with DDTs during the malaria control in Central Java Province in 1982. In this study, very high concentrations of the parent compound *p,p′*-DDT (mean = 12,000 ng g^{-1} lipid wt., max = 42,000 ng g^{-1} lipid wt.) and recalcitrant metabolite, *p,p′*-DDE (mean = 16,000 ng g^{-1} lipid wt., max = 55,000 ng g^{-1} lipid wt.) were reported. This information provides an evidence on considerable usage of DDTs during the mid-1980s. A greater proportion of *p,p′*-DDT was also found in chicken muscle, egg, carp fish, and vegetables in this village, suggesting the recent usage of DDT for malaria control. Further study by Burke et al. (2003) attempted to understand spatial variability of OC pesticides by analyzing DDTs, HCHs, and HCB in human milk from women living in two different locations in urban (Jakarta) and rural areas (Puncak, Bogor). In this study, they found no significant difference in concentrations of DDTs, β-HCHs, and HCB between the cohorts, in which mean concentrations ranged between 200 and 460 ng g^{-1} lipid wt., 80–100 ng g^{-1} lipid wt., and 30–40 ng g^{-1} lipid wt., respectively. A more comprehensive data on human exposure conducted by Sudaryanto et al. (2006b) found variable sources and specific exposure routes to these contaminants in the general population of Indonesia. In particular, DDTs were significantly higher

($p < 0.05$) in breast milk from mothers living in suburban (Bogor), rural agriculture (Purwakarta), and rural fisheries (Lampung) than in urban area (Jakarta). Interestingly, based on these two recent studies, it can be concluded that until the early 2000s, some residents were exposed to relatively high levels and/or fresh input of DDTs, particularly in specific areas that have intensive agriculture and malaria eradication program (Burke et al., 2003; Sudaryanto et al., 2006b). For example, elevated level of DDTs (15,000 ng g^{-1} lipid wt.) was found in a woman living in an agricultural area (Purwakarta) located 70 km away from the capital city, Jakarta (Sudaryanto et al., 2006b). Furthermore, a woman, also with a farming background accumulated high level of *p,p′*-DDT (2400 ng g^{-1} lipid wt.) with a low ratio (0.56) of *p,p′*-DDE/*p,p′*-DDT (Sudaryanto et al., 2006b). Similarly, Burke et al. (2003) also reported a considerable proportion of *p,p′*-DDT in some donors from urban (Jakarta) and rural areas (Bogor) with a ratio of *p,p′*-DDE/*p,p′*-DDT as low as 0.20 and 0.50, respectively. Although, according to the regulation, the use of DDT in Indonesia has been totally banned since 1990s, the ratio and residue levels in some specific donors indicate ongoing usage of DDTs. Similar finding in abiotic compartments and fish also reflect the continuous fresh input of DDT. It was reported that after the peak usage from 1986 to 1991, the cumulative factory stock of DDT at the end of 1991 was around 4121 kg. It is possible that the stock of this obsolete DDTs may still be illegally distributed and used in recent years.

Unlike DDTs, Sudaryanto et al. (2006b) found only little spatial variation of PCBs, HCHs, CHLs, and HCB contamination among the above locations. A similar finding was made by Burke et al. (2003) for HCHs and HCB. However, it seems that PCBs were slightly higher in human milk samples from urban area (Jakarta = 33 ng g^{-1} lipid wt.) than suburban and rural areas (Lampung = 27 ng g^{-1} lipid wt., Purwakarta = 24 ng g^{-1} lipid wt., and Bogor = 21 ng g^{-1} lipid wt.), but no such trend was observed for HCHs, CHLs, and HCB, which might be due to the low levels of their accumulation in Indonesian breast milk as well as other environmental matrices. Residue levels of PCBs, HCHs, CHLs, and HCB were reported to be 1–3 orders of magnitude less than those of DDTs.

The bioaccumulation pattern of OCs in human breast milk from Indonesia (DDTs > HCHs > PCBs > CHLs > HCB; Sudaryanto et al., 2006b) was reported to be different with those in mussels and fish (Monirith et al., 2003; Sudaryanto et al., 2005b, 2007b), which showed higher level of PCBs and CHLs compared to HCHs. This may probably be because of differences in exposure route(s), and/or because the intakes of these compounds via seafood by the Indonesian population are not significant. In fact, there is no correlation between OCs levels in breast milk and frequency of seafood consumption either in the studies of Burke et al. (2003) or by Sudaryanto et al. (2006b). These results imply that other foodstuffs may also be responsible for exposure of the Indonesian general population. Indeed, the occurrence of OCs has been reported in vegetables (Kuwatsuka et al., 1986), rice, chicken, egg, pork, pork fat, and squid (Kannan et al., 1995b; Noegrohoati et al., 1992). Further studies using large number of samples and various foodstuffs are needed to clarify human exposure, accumulation levels, and sources of OCs in Indonesia.

With regard to compounds recently identified as endocrine disrupters, TCPMe/TCPMOH, and PBDEs were first reported by Sudaryanto et al. (2005a, c, 2006b, 2007a). Of the total 55 human milk samples, TCPMe was detected in almost all the donors but TCPMOH was found only in 10% of the samples (Sudaryanto et al., 2006b), similar to that seen in some other populations (Kunisue et al., 2003; Minh et al., 2004). The low bioavailability of TCPMOH has been suggested as it is rapidly metabolized and eliminated by humans (Minh et al., 2001). The average concentrations of TCPMe in breast milk from the four locations in Indonesia ranged from 2.8 to 9.3 ng g^{-1} lipid wt., comparable to other populations from Asian developing countries (Kunisue et al., 2003; Minh et al., 2004). Though a variety of sources could be possible (Jarman et al., 1992), accumulation of TCPMe in general population of Indonesia can be suggested to be from technical DDT, as a significant ($p<0.05$) positive correlation between concentrations of DDTs and TCPMe was observed (Sudaryanto et al., 2006b).

Further to this, using a subset of samples ($n = 30$), a study by the same authors also found ubiquitous contamination by PBDEs in general population of Indonesia (Sudaryanto et al., 2007a). Among the four locations mentioned above, there were no significant differences ($p>0.05$) in PBDEs concentrations (Sudaryanto et al., 2007a). Because of the short usage history, levels of PBDEs in human breast milk from Indonesia were still 1–3 orders of magnitude lower than PCBs, DDTs, HCHs, and CHLs, but comparable with TCPMe and HCB. PBDEs in breast milk from Indonesia did not correlate with age of mother and parity (number of children of the respective mother), an accumulation kinetics that showed different picture from those of PCBs and DDTs (Sudaryanto et al., 2005a, 2006b, 2007a), the group of compounds having similar properties and structure as PBDEs. Another report by Sudaryanto et al. (2005c) on widespread contamination of PBDEs in human breast milk from Asian countries, such as Japan, Korea, China, Vietnam, Philippines, Cambodia, and India, provided a regional comparison of this compound in general population of Asia. Concentrations of PBDEs in human milk from Indonesia are relatively similar to those in other Asian countries, a distribution pattern different from those of OCs that shows specific regional contamination status. The level of PBDEs in Indonesia was also comparable with some European countries, but still much lower than North America (Schecter et al., 2003), a region with largest consumption of PBDEs in the world.

Among 14 congeners (mono- to deca-BDE) analyzed by Sudaryanto et al. (2007a), BDE-47 and BDE-153 were generally the predominant congeners. However, some higher brominated congeners such as BDE-183 and BDE-209 were also prevalent, and equal to or even higher than BDE-47 in some donors. This is an important observation because it has been hypothesized that these compounds are less bioaccumulative due to their relatively high molecular weight. This study reveals the exposure of certain human population to higher brominated PBDEs, which is different to those observed in fish from Indonesia. The exposure routes are different for BDE-47 and higher brominated congener like BDE-183, i.e., food is the important source for BDE-47 because it is the major contaminant in wildlife, whereas airborne uptake seems to be more noticeable for BDE-183. The results of this study indicate that Indonesian people have been exposed to multiple source(s) and pathways of PBDEs.

13.4. Environmental contamination by OTs

Development of ports, ship construction, increasing shipping, and fishing activities in Indonesia (Soegiarto and Stel, 1998) has become an important issue with possible contamination of OTs in the marine waters (Sudaryanto et al., 2005d). OTs assessment in the environment of Indonesia was a main part of the comprehensive monitoring surveys in Asia–Oceania conducted by Ehime University, Japan (Kannan et al., 1995a; Ueno et al., 2003a; Sudaryanto et al., 2002, 2005d). In an earlier report, Kannan et al. (1995a) provided information on butyltins (BTs) residues in muscle of two species of fish purchased at market from Bogor, but could not give information on from where they were caught. Subsequently, Ueno et al. (2003a) found BTs contamination in liver of five individuals of tuna collected in 1998 from Western Sumatra open sea waters. In the same period on the above study, under the framework of Asia-Pacific Mussel Watch Project (Tanabe, 2000), Sudaryanto et al. (2002) revealed the occurrence of BTs in mussel along the coastal waters of Indonesia and other Asian developing countries. In a large scale survey covering various matrices (sediment, mussel, and fish) and locations, representing different land-based activities such as commercial ports, fishing ports, marinas, mariculture, as well as rural areas, widespread contamination by BTs was made clear in the marine environment of Indonesia (Sudaryanto et al., 2005d).

Figure 13.4 illustrates widespread contamination by BTs in the environment of Indonesia from available references. Concentrations of BTs in mussels, fish, and sediments from coastal waters were reported to be in the range of 3.7 to 64 ng g^{-1} wet wt., 3.3–84 ng g^{-1} wet wt., and 0.51–320 ng g^{-1} dry wt., respectively (Sudaryanto et al., 2005d), whereas in tuna from offshore waters, the values ranged from 13 to 150 ng g^{-1} wet wt. (Ueno et al., 2003a). In this study, it was indicated that maritime activities play a major role as sources of BTs. Usage of BTs on fish culture nets seems to be minimal in Indonesia. Indeed, almost all the mussels, fish and sediments showing higher concentration of BTs were from the areas with intensive maritime activities (Fig. 13.4) such as large commercial harbors or marina and fishing ports (Jakarta Bay, Surabaya, and Belawan). In Tanjung Priok Port, Jakarta, high concentrations (0.022–0.204 ppm) of tributyltin (TBT) were reported in seawater (Budianto, 2000). Nevertheless, concentrations of BTs found in the major marine culture areas (Hurun Bay and Lada Bay) are still low (Sudaryanto et al., 2005d). Among BTs, TBT was substantially higher than the metabolites di- (DBT) and monobutyltin (MBT) in almost all the samples (Fig. 13.5), suggesting recent input of BTs into marine environment. The

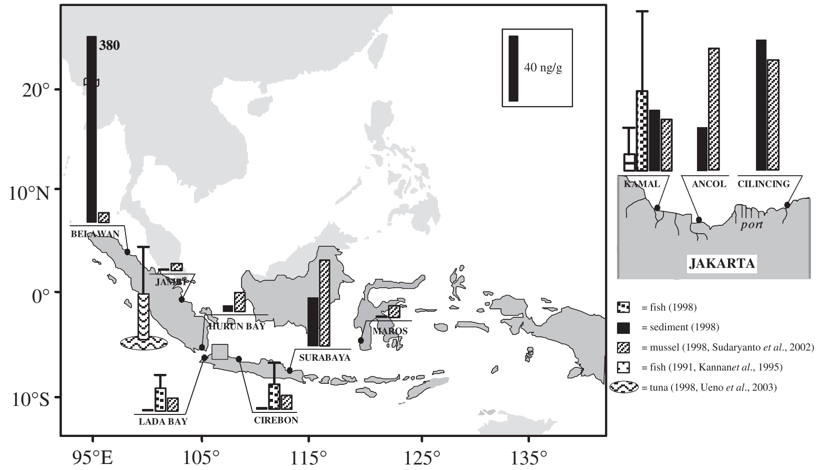

Figure 13.4. Levels and distribution of BTs in the environment of Indonesia.

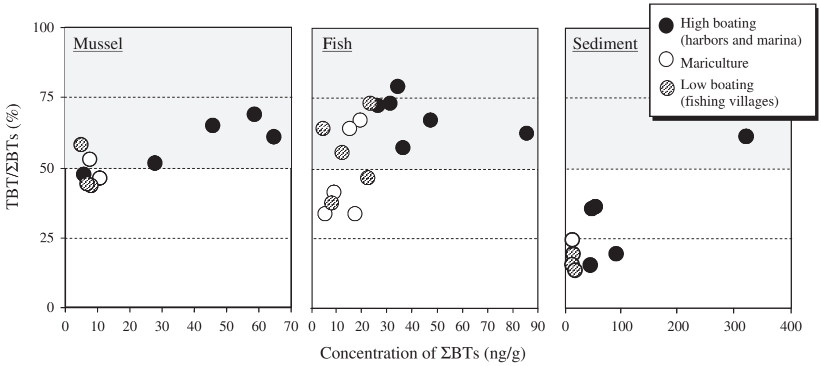

Figure 13.5. Concentrations of BTs and their relation with the proportion of TBT/ΣBTs according to various maritime activities.

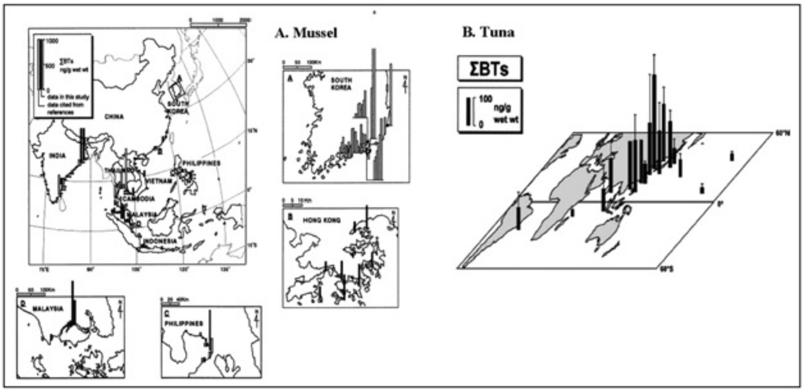

Figure 13.6. Regional distribution of ΣBTs in mussels (A) and tuna (B) from Asia-Pacific region.

composition pattern was similar to those in surrounding Asian developing countries (Sudaryanto et al., 2002), suggesting similar status of TBT usage in this region.

An appropriate regional comparison using similar species and analytical methods (Fig. 13.6) revealed that mussels and tuna from Indonesia contained lower levels of BTs when compared to certain other Asian countries (Sudaryanto et al., 2002; Ueno et al., 2003a). In the study of Sudaryanto et al. (2002), it was reported that, among Asian developing countries, mussel samples from Hong Kong, South Korea, Malaysia, and Thailand showed relatively high levels of BTs. Similarly, Ueno et al. (2003a) using liver of skipjack tuna (*Katsuwonus pelamis*) collected from

Asian offshore waters (off-Japan, the Japan Sea, off-Taiwan, the East China Sea, the South China Sea, off-Philippines, off-Indonesia, the Bay of Bengal, off-Seychelles, off-Brazil) and open seas (the North Pacific) also pointed out a similar pattern found in mussels (Fig. 13.6). Interestingly, the orders of mean and 90th-percentile values of concentrations in mussel agreed well with the per capita gross national product (GNP) of each country (Sudaryanto et al., 2002). Since per capita GNP is an indicator of economic status, butyltin contamination seems to be related to the industrial and human activities. The contamination of BTs may increase in those countries with increasing economic growth rates. Considering the high economic growth rate and the unregulated usage of TBT in many Asian developing countries, including Indonesia and the increasing demand for antifouling paints in Asia and Oceania (Layman, 1995), contamination by BTs in Asian aquatic environments may be expected to become more serious in the future. Thus, continuous monitoring and investigations on BTs contamination are required in Indonesia as well as other Asian developing countries.

Worldwide comparison of BTs in sediment and fish from Indonesia also revealed lower levels in Indonesian samples. The residue levels of BTs found in sediment (0.96–380 $\mathrm{ng\,g^{-1}}$ dry wt.) were lower than those reported in many coastal and harbor areas of various countries including several Asian developing countries, such as Malaysia and Thailand, as well as urbanized industrial nations such as the USA, Europe, Australia, and Japan (see Sudaryanto et al., 2004 and references therein). A similar case was also for fish (Fig. 13.7). Concentrations of BTs in fish from Indonesia were obviously lower than those reported in urbanized developed regions, such as the USA, Japan, Australia, Italy, and Netherland (See Takahashi et al., 1999 and references therein). The levels were also lower than those of the polluted areas of Asian developing countries, including the Malacca Strait, Malaysia (Sudaryanto et al., 2004).

13.5. Temporal variation of contaminations

It has been well known through intensive monitoring efforts that decreasing trends of classical OCs in the environment of developed countries occurred as a consequence of their regulation on use and waste treatment. However, considerably little information is available on their temporal trend in developing countries. In Indonesia, there are only few studies dealing with PTS in the environment (see review above) and no data series from temporal monitoring study are available, thus making it difficult to provide reliable long term trends. However, some findings on

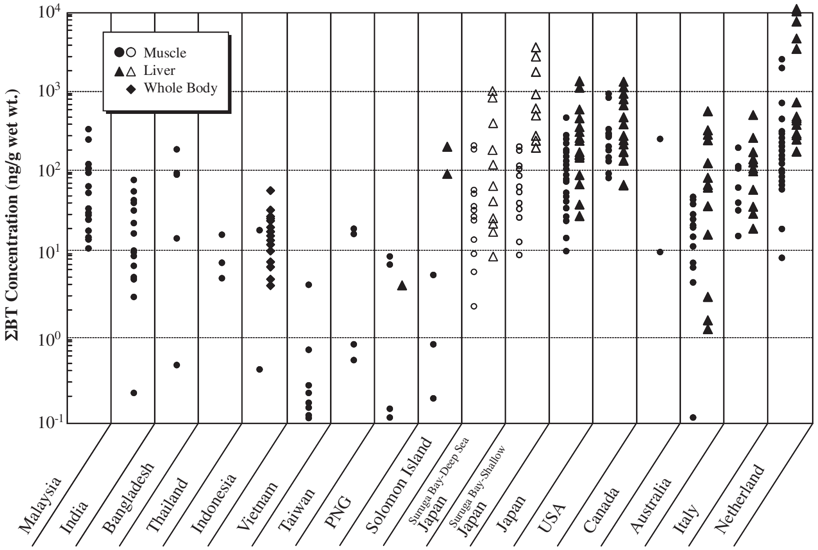

Figure 13.7. Worldwide comparison of ΣBTs in fish.

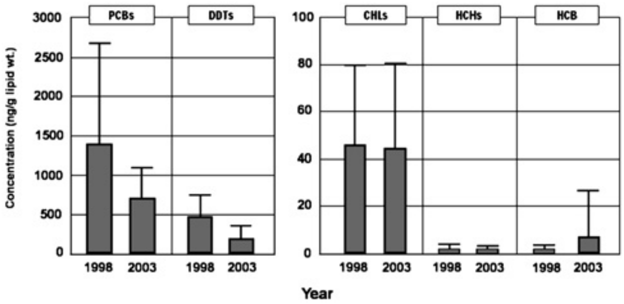

Figure 13.8. Comparison of OCs in fish caught at Jakarta Bay between 1998 and 2003.

PTS in the same sample matrices (mostly OCs in fish) and locations in different years of sampling are available that can explain temporal variation in the environment of Indonesia. Comparing data of OCs in fish caught from Jakarta Bay in 1998 and 2003 (Sudaryanto et al., 2007b) showed that concentrations of PCBs and DDTs have decreased significantly (Fig. 13.8). Similarly, levels of DDTs in freshwater fish collected in 2003 (Sudaryanto et al., 2007b) from Bogor were also significantly lower than those in fish collected in 1991 (Kannan et al., 1995b). DDTs in human breast milk collected during recent years around 2000–2003

(Burke et al., 2003; Sudaryanto et al., 2006b) were also much lower than those in 1991 (Noegrohoati et al., 1992). Based on these data, PCBs and DDT levels may appear to have declined with time in Indonesia. However, there was less temporal variation for other OCs, which could be due to lower background levels in the environment.

In case of BTs, a reduction of TBT contamination was also recorded in many developed countries after the regulation (Champ, 2000). In Indonesia, contamination status of BTs did not seem to improve during 1991 (Kannan et al., 1995a) to 1998 (Sudaryanto et al., 2005d); on the other hand, the contamination relatively increased in the later period, at least in the case of fish. This implies continuous pollution by BTs derived from heavy ship traffic in the busiest ports such as in Jakarta, coming from the countries having no TBT usage regulation. Declining trend of the contamination of TBT were not found in other countries in Asia also, such as India (comparing the data between 1994–1995 and 1998) and South Korea (between 1994 and 1997–1999) (Sudaryanto et al., 2002).

13.6. Ecological and human health risk

Risk of OCs and PBDEs has been estimated based on human dietary intake of OCs via seafood. The average dietary intake of PCBs and DDTs by an Indonesian as well as the data for other countries reported elsewhere are presented for comparison in Table 13.4. The FAO/WHO and Health Canada acceptable daily intake (ADI) as well as dose-response variable for target analytes (US-EPA, 2000) are listed for reference. None of the daily intake values of OCs reached the ADIs recommended by various agencies, indicating minimum risk caused by these pollutants. In case of PCBs, the mean daily intake of 1.2 μg person^{-1} day^{-1} and 0.81 μg person^{-1} day^{-1} via fish in 1998 and 2003, respectively, was only around 2% of the FAO/WHO and Health Canada-suggested maximum of 60 μg person^{-1} day^{-1} (FAO/WHO, 1986; Oostdam et al., 1999) or 10% of the conservative oral reference dose (RfD) proposed by US-EPA (2000). Although, PCBs were reported to be declining during several years before, the present value is higher than the dietary intake of PCBs during the 1991 survey conducted by Kannan et al. (1995b) as average seafood consumption has increased in recent years from 40 ng day^{-1} in 1991 to 57 ng day^{-1} in 2003. Comparing with other countries, the dietary intake of PCBs in Indonesia was lower than in developed countries such as Japan (17 μg person^{-1} day^{-1}) and Australia (3.0 μg person^{-1} day^{-1}) but higher than Cambodia, Thailand, India, and Solomon Island (Table 13.4). In case of DDTs, intake by an Indonesian in 1998 and 2003 was

Table 13.4. Estimated average daily intake (μg $person^{-1}$ day^{-1}) of OCs and PBDEs from fish in Indonesia in comparison with other countries

Country	Fish consumption	PCBs	DDT	HCHs	CHLs	HCB	PBDEs	References
Cambodia (1998)	20	0.007	0.16	0.002	0.002	0.002	na	Monirith et al., 1999
Thailand (1990)	57	0.091	0.35	0.047	0.15	0.014	na	Kannan et al., 1995b
Vietnam (1990)	36	0.36	0.94	0.065	0.004	0.002	na	Kannan et al., 1995b
Australia (1992)	55	3.0	1.2	0.019	2.8	0.23	na	Kannan et al., 1995b
SI (1990)	121	0.44	0.58	0.064	0.069	0.002	na	Kannan et al., 1995b
India (1990)	10	0.036	0.16	0.29	0.025	0.001	na	Kannan et al., 1995b
Japan	90	17	1.4	na	na	na	na	EAJ, 1997
Hong Kong	160	na	2.7	na	na	na	na	Dickman and Leung, 1998
Indonesia (1991)	40	0.11	1.1	0.030	0.018	na	na	Kannan et al., 1995b
Indonesia (1998)	51	1.2	0.54	0.006	0.004	0.004	na	Sudaryanto et al., 2007b
Indonesia (2003)	57	0.81	1.1	0.018	0.010	0.010	0.037	Sudaryanto et al., 2007b
Acceptable daily intake by FAO/WHO		60	1200	na	na	na	na	FAO/WHO, 1986
Acceptable daily intake by Health Canada		60	1200	18	3	17	na	Oostdam et al., 1999
Oral reference dose (RfD)		12	30	18	30	na	na	US-EPA, 2000
LOEL (reduce male fertility & T4 in rat)							60	Kuriyama et al., 2005
LOEL (behavior alteration in mouse)							400	Viberg et al., 2003

Note: na = no data available.

0.54 μg $person^{-1}$ day^{-1} and 1.1 μg $person^{-1}$ day^{-1}, respectively, and accounted less than 1% of FAO/WHO and Health Canada guideline standard. The Indonesian daily intake of DDTs via seafood in recent years is similar to those ten years ago reported in a study conducted by Kannan et al. (1995b), but lower than those for Chinese (Dickman and Leung, 1998). However, the levels were relatively higher than those for other Asian countries (Table 13.4). The dietary intake of CHLs and HCHs was much lower than those of PCBs and DDTs (Table 13.4).

In case of PBDEs, based on data obtained from Sudaryanto et al. (2005b), average Indonesian daily intake via fish was 0.037 μg $person^{-1}$ day^{-1}, which corresponds to the lower end of the estimate for the total PBDE intake by the Nordic consumer (0.2–0.7 μg $person^{-1}$ day^{-1}) (Darnerud et al., 2001) and the maximum daily intake in Switzerland

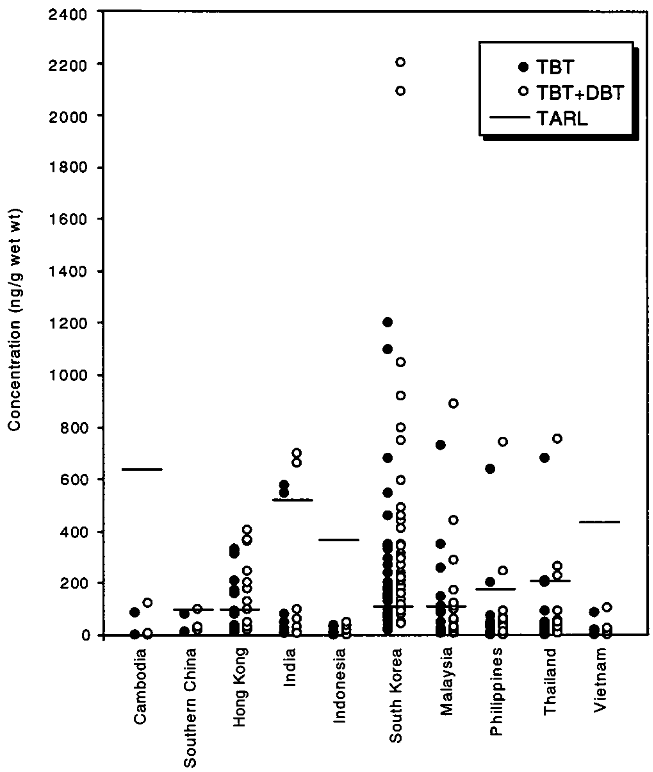

Figure 13.9. Residue levels of TBT and sum of TBT and DBT (TBT + DBT) detected in mussels from coastal waters of Indonesia and some other Asian countries compared with the tolerable average residue levels (TARLs) for seafood in each country.

(0.15 μg person^{-1} day^{-1}) (Zennegg et al., 2002). This value is still well below the experimental body burden associated with various developmental effects in neonatal mice and rats (Kuriyama et al., 2005; Viberg et al., 2003), such as reduced male fertility and T4 in rat (60 μg kg^{-1} day^{-1}) and behavior alteration in mouse (400 μg kg^{-1} day^{-1}). Although a number of limitations are involved in the estimation and interpretation of dietary intake values of OCs and PBDEs, including small number of samples, the use of whole body tissue (instead of fillets), and also not much availability of information on fish consumption pattern and fish dietary intake on each location, this result provide some useful indication of the approximate exposure levels and the need to conduct further studies to determine and/or to control excessive human exposure. Further studies toward clarifying current contribution from various food items to organohalogens intake by an Indonesian are also important. Moreover, in the light of continued use of PBDE in large quantities, monitoring levels of these compounds will continue to be an important issue.

With regard to BTs, the residue levels of TBT in mussels and fish were lower than the levels causing growth retardation in bivalves (Page and Widdows, 1991) and sublethal effect in fish (Rice et al., 1995). However, TBT residues found in some fish, particularly from hot spot areas such as Jakarta Bay (9.7–52 ng g^{-1} wet wt.), and mussels from Jakarta Bay (13–38 ng g^{-1} wet wt.) and Surabaya (28 ng g^{-1} wet wt.) were close to the threshold levels observed in several animals based on laboratory and field studies. For example, Horiguchi et al. (1994) estimated that *Thais clavigera* developed imposex when exposed to a threshold concentration of 10–20 ng TBT g^{-1} wet wt. In the tropical muricid *Thais distinguenda,* the development of imposex was observed when the body burden exceeded 20.4 ng TBT g^{-1} (Bech et al., 2002).

For instance, an extrapolated water TBT concentration (0.21–5.9 ng L^{-1}) based on concentrations of TBT and its bioconcentration factors (5000–10,400 for TBT in mussel and 9400–11,000 in marine fish) (Sudaryanto et al., 2005d) were also close to or above the threshold levels of toxic implications, such as imposex in mollusks and immunotoxicity in mussel (St-Jean et al., 2002). The levels were also near to the criteria established by US-EPA (2003) to protect saltwater aquatic life from chronic toxic effects of TBT (0.0074 μg L^{-1}). Indeed, high incidence of imposex in gastropods has been shown to occur in Indonesia, such as the Ambon coastal area (Ellis and Pattisina, 1990). An evidence of ecotoxicological impact of TBT, imposex incidence is also a usual phenomenon in gastropods in coastal waters of some other Asian countries

(Swennen et al., 1997). These observations suggest that TBT levels in some polluted areas of Indonesia and other Asian countries pose a toxic threat to susceptible mollusks and other marine organisms.

Human health risk assessment by BTs has also been estimated by using tolerable average residue levels (TARLs) for TBT in seafood products (Sudaryanto et al., 2002). TARLs value for seafood in Indonesia was estimated to be 360 ng g^{-1} wet wt. for an average person weighing 60 kg. When compared to TARL value, concentrations of TBT or the sum of TBT and DBT (TBT + DBT) in mussels from Indonesia were below this value (Fig. 13.9), suggesting no immediate public health risk. This situation was similar to those in Cambodia (TARL: 630 ng g^{-1} wet wt.) and Vietnam (435 ng g^{-1} wet wt.) which have low contamination status by organotin in mussels (Fig. 13.9). The higher risk may happen in some other Asian countries which have elevated exposure to BTs. Concentrations of TBT or the sum of TBT and DBT (TBT + DBT) exceeded respective TARL values in some of the mussels from southern China, Hong Kong, South Korea, Malaysia, India, the Philippines, and Thailand (Fig. 13.9). In addition to mussels, consumption of other seafood items such as fish can also contribute to higher exposure.

Although the magnitude of contamination by BTs in coastal waters of Indonesia is low, and no immediate public health problems could be seen, increasing levels of BTs contamination in recent years still causes concern. Information concerning organotin contamination and its potential effects on the ecosystems in Indonesia are still scarce. Continuous monitoring studies are required to observe future trends and to delineate toxicological implications.

13.7. Conclusions and recommendations

Available data searched from literatures revealed widespread contamination by polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polybrominated diphenyl ethers (PBDEs), and hexabromocyclododecanes (HBCDs) as well as butyltin compounds (BTs) in Indonesia comprising aquatic and terrestrial environment and biota including human. From several monitoring studies, it is evident that concentrations and the contamination patterns of these compounds varied within specimens and locations. Some locations were considered as hot spots by specific contaminants and part of the population in Indonesia is highly exposed to environmental contaminants, particularly DDTs as the most prominent pollutant. Although, in general, the residual concentrations of PTS are still low when compared to global contamination levels and standards, the occurrence of imposex, an indication of possible toxicity of TBT, has been observed in the mollusks. Moreover, specific residents are still subjected to elevated levels of pesticides—a cause for concern on human health. Estimated infant daily intake of DDTs and HCHs through lactation in some donors also exceeded WHO guideline. Levels of some OCs such as DDTs and PCBs decreased recently; however, recent input and emission into the environment still continue. Fresh TBT input is a common phenomenon in coastal waters and the reduction trend in the environment still did not improved. Altogether, and in line with the various findings on increasing new candidate of POPs (PBDEs and HBCDs) in many environmental matrices (Hites, 2004) including Asia (Kajiwara et al., 2004), and also Asia seems to consume large quantities of BFRs (Watanabe and Sakai, 2003), the present situation highlight the need for continuous monitoring study of the levels of PTS in environment, people, and food, to delineate temporal trend, sources, and their potential effects as well as determining other routes of exposure of these compounds to the general population of Indonesia. The environmental conservation and monitoring under an international cooperation is highly requested in order to prevent subsequent pollution and toxic impacts on aquatic wildlife and humans in Indonesia. Cooperative research effort with scientists from developed countries is needed to strengthen the national capability and to enhance knowledge and understanding amongst decision makers, managers, industries, and public to meet the obligations of the International Conventions regarding the management and elimination of toxic chemical contaminants.

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Chapter 14

Persistent Organic Pollutants in Malaysia

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Abstract

The use of pesticides in Malaysia dated back since after the Second World War. These persistent pollutants were primarily used for agriculture and vector control. DDT, dieldrin and endrin found extensive use before they were banned recently. Most of the other persistent organic pollutants (POPs) have been banned in Malaysia. However, residues of these pesticides were found in various compartments of the environment such as water, sediment and biota. Non-pesticide POPs were not monitored as much but recent efforts have included monitoring and management of these POPs among other hazardous chemicals. This chapter presents the current status of POPs in Malaysia and various initiatives to manage these pollutants.

14.1. Introduction

Malaysia is situated in the tropical rainforest region and is traditionally an agriculture-based country. The use of pesticides for agriculture and vector control were quite extensive after the Second World War. Organochlorine pesticides (OCPs) such as DDT, dieldrin, and endrin had been used in agricultural plantations until they were banned in the late 1990s. High levels of persistent organic pollutants (POPs) such as lindane and endosulfan have been reported in water, sediment, and fish. Other POP pesticides were observed to be decreasing in concentration after they were banned from import and uses. Non-pesticide POPs are not well monitored in Malaysia. Inventory for PCBs is being developed and data on environmental levels of PCBs is scarce. Unintentionally produced POPs, dioxins, and furans, have practically not been studied in Malaysia. More effort should be put to monitor the status of the POP chemicals in Malaysia. For achieving a well-planned monitoring of these chemicals in Malaysia, gathering all the available information and evaluating the

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*Corresponding author: E-mail: sani@usm.my status of pollution in different facets of the environment and biota will form the first step in this direction.

14.2. Persistent organic pollutants (POPs) in Malaysia: An overview

Malaysia consists of Peninsular Malaysia, called West Malaysia, situated in mainland Southeast Asia and the two states of Sabah and Sarawak, called East Malaysia, situated in the northern part of Borneo Island. West Malaysia is made up of 11 states which, together with Singapore, gained independence from British rule in 1957 to form the Federation of Malaya. Malaysia itself was formed in 1963 with Sabah and Sarawak joining to form a 14-state nation. However, in 1965, Singapore left to become a separate country. Nine of the states are headed by sultans while the four states of Pulau Pinang, Melaka, Sabah, and Sarawak are headed by Heads of State (Yang Dipertua Negeri). Three Federal Territories have been created including Kuala Lumpur, Putrajaya, and Labuan. The main administrative center used to be Kuala Lumpur but has been recently moved to Putrajaya.

Malaysia is a constitutional monarchy and the country is headed by a king selected amongst the nine sultans and run by a prime minister elected in national elections. Malaysia has a population of 26.51 millions comprising Malay, Chinese, Indians, and several other ethnic groups (Jabatan Perangkaan Malaysia, 2006). The official language is Bahasa Melayu with English, Mandarin, Tamil, and other local dialects being spoken. The main religion is Islam but other religions are freely practiced.

Malaysia is traditionally an agriculture-based country and one of the world's leading producers of palm oil and rubber. However, it is gradually transforming into a multisector economy, particularly in the electronic and electrical appliance industries. Malaysia is fairly rich in natural resources such as petroleum, natural gas, timber, tin, copper, and iron ore (CIA, 2006). In fact, petroleum and natural gas products represented the second highest export group (USD 19.6 billion est.) behind electrical and electronic products in 2005 (Jabatan Perangkaan Malaysia, 2006). The gross domestic product (GDP) for 2005 was USD 130.5 billion with a GDP growth of 4.5% over the 2004 GDP. This amounted to a GDP per capita of USD 5035 for 2005 (Economist.com, 2006).

14.2.1. Physical and geographical settings

Malaysia lies above the equator between 2° and 8° N. West Malaysia and East Malaysia lie from 100° to 118° E, encompassing a large part of the

South China Sea. West Malaysia and East Malaysia are separated by about 640 km of the South China Sea. The total land area is 329,750 km^2 where West Malaysia has a total area of 131,573 km^2, Sarawak has a landmass of 124,449 km^2 and Sabah has a land area of 73,711 km^2. Approximately 80% of the combined land area is still covered with tropical rain forest while the remaining land is used for agriculture, namely, oil palm and rubber.

Figure 14.1 shows the map of Malaysia and the neighboring countries, which include Thailand in the north and Singapore to the south of Peninsular Malaysia while Brunei is sandwiched by Sabah and Sarawak in Borneo Island. Indonesia has the longest boundary line with Sarawak and Sabah while Sumatra Island is separated by the heavy shipping lane of the Straits of Malacca with Peninsular Malaysia. There are a few islands, the larger of which are Penang and Langkawi Islands in the Straits of Malacca while Tioman Island is situated in the South China Sea and Labuan Island off the coast of Sabah.

Topographically, West Malaysia is characterized by extensive coastal plains in the west and east with hilly and mountainous regions and steep slopes in the central mountain range of Titiwangsa and undulating terrain in other parts of the peninsular. Sabah is characterized by the western

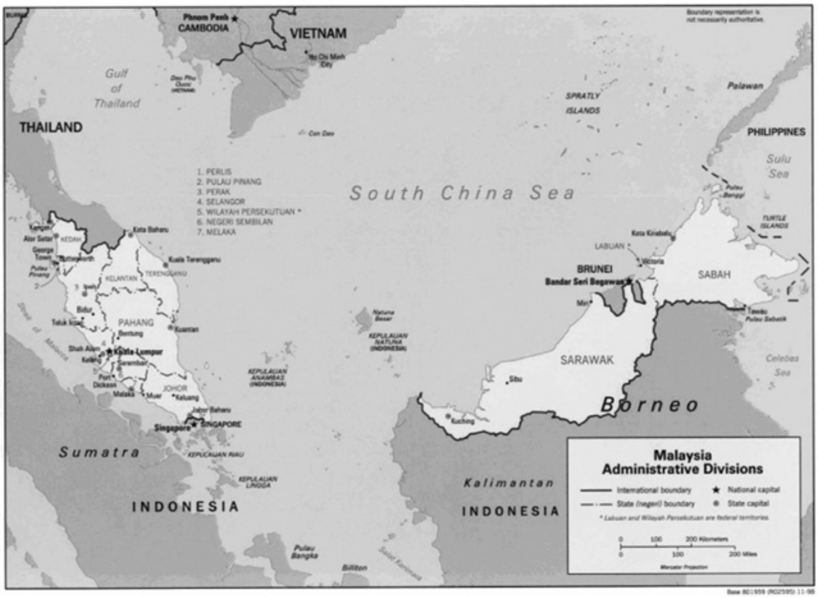

Figure 14.1. Map of Malaysia and neighboring countries.

lowlands, the Crocker Range, the central uplands, and the eastern lowlands whereas Sarawak is characterized by a seaward fringe of peat swamp. However, the tropical forest covers much of the interior highland beyond the border with Kalimantan in Indonesia. There are only ~0.3% of water bodies in Malaysia which are mostly meandering rivers.

14.2.2. Climate and ecological characteristics

The climate of West Malaysia is equatorial, characterized by fairly high but uniform temperatures (ranging from 23 to 31°C throughout the year), high humidity and copious rainfall (averaging ~250 cm annually). There are seasonal variations in rainfall, with the heaviest rains from October to December. The eastern coastal region receives the most abundant rainfall where it averages over 300 cm $year^{-1}$. Sabah and Sarawak in East Malaysia are slightly cooler due to ocean cooling and frequent tropical rainstorms particularly during the monsoon season in November to March when these areas receive heavy rainfall.

Malaysia is blessed with a rich tropical rain forest, which is one of the most diverse and complex ecosystems in the world. The forest contributes to ~95% of the land covers in Malaysia providing rich timber and other forest products. The coastal regions are generally covered with peat swamp (3.3%) and the ecologically sensitive mangroves (1.8%) (UNEP/EAP-AP, 1999). In 2003, Malaysia exported 13.97 million m^3 of timber and timber products (MTC, 2006).

14.2.3. Industrial and agricultural activities

The major exports of Malaysia in 2004 were electronic and electrical machinery (67.7%), petroleum and liquefied natural gas (7.3%), chemical and chemical products (7.3%), palm oil (5.3%), and textiles and clothing (2.7%) (Economist.com, 2006). Several multinational companies producing electronic and electrical goods have set up their production plants in designated industrial zones throughout the country. The chemical industry, which is governed by the Chemical Industry Council Malaysia, represents various industries dealing with products such as petrochemical, pharmaceutical, oleochemical, agricultural chemicals as well as domestic chemicals such as detergents and cosmetics. The oil palm industry is very important to the Malaysian economy from agricultural and industrial perspectives. The Malaysian Palm Oil Board, an institution established in 1998 under the Malaysian Palm Oil Act (Act 582), plays an important role in organizing and promoting the palm oil industry of Malaysia by carrying out research related to planting, production, harvesting, extraction, processing, storage, transportation, use, consumption, and marketing of oil palm and oil palm products.

Beside oil palm, rubber and cocoa are the other major agricultural crops in Malaysia with 1.3 and 0.1 million farmed hectares, respectively compared to 3.1 million hectares of oil palm plantations. Rice, the staple food of Malaysians, is grown in the low regions of north Peninsular Malaysia and Sabah but the production is insufficient to support the demand for rice. Other agricultural crops are pepper, produced mostly in Sarawak and various fruits and vegetables grown primarily for local consumption.

14.2.4. Marine environment

Malaysia has an extensive coastal line and the country is divided between the west and east by the South China Sea. The west coast of West Malaysia shares the Straits of Malacca with Sumatra Island. The Straits of Malacca, together with the Java Sea, South China Sea and the Gulf of Thailand, are part of the rich marine environment of the shallow Sunda Shelf. In recent years, the Straits of Malacca has become a very important shipping route connecting the oil rich West Asia to the Far East. Shipping accidents have occurred more frequently in these shallow and narrow channels (Chua et al., 2000). The South China Sea, on the other hand, is poorly understood in terms of its marine biota, ecology, and the human impacts upon it. However, it is anticipated that anthropogenic impacts, such as the over-exploitation of marine resources and pollutions, will threaten the sea (Morton and Blackmore, 2001).

The marine environments around Malaysia are rich in natural resources including fisheries, coral reefs, sea-grass beds, and mangroves, lining the coastlines. Petroleum and natural gas resources are quite abundant in the South China Sea where offshore mining and oil prospecting activities predominate significantly.

14.3. Sources of POPs in Malaysia

Historically, pesticides have been used in Malaysia to control pests in rubber, cocoa, and oil palm plantation since 1955 (Conway, 1973). DDT and dieldrin were introduced to control ring bark borer (*Endoclita hosei*) in Sabah's cocoa plantations in 1959 and continued to be used from 1960 to 1965. Other pesticides such as endrin, technical grade HCH, lindane, lead arsenate, and trichlorphon were also used in the cocoa plantations. Oil palm plantations in West Malaysia saw the use of DDT, dieldrin, and endrin to control cockchafers, bagworm, and rhinoceros beetles from 1956 up to 1964 (Conway, 1973). Even though rubber trees were relatively free from pest attacks, it was found that cockchafer grubs caused severe damage to young rubber trees. Before the Second World War, laborious hand digging was the only form of control but after the war, heptachlor was used as 0.1% emulsion to control the pests.

Rice fields in West Malaysia have also been sprayed with dieldrin, lindane, trichlorfon, and diazinon since 1955 to control rice borer pests. Their applications were terminated when it was discovered that several rice field fishes were found dying within 24 h after the application of 0.1% dieldrin spray in Tanjung Karang (Kok, 1973). The control of malaria mosquito vectors in the Borneo states of Sabah, Sarawak, and Brunei, using DDT and dieldrin at the rate of 2 g and 0.6 g m^{-2} of dwelling areas from 1955 to 1963, was very successful and became a model for World Health Organization (WHO) campaigns in other countries. However, the excessive use of these pesticides caused a decline in the population of house cats, which feed on the dead or infected cockroaches and house lizards (*geckos*). This in turn saw such an increase in the rat population and a near outbreak of house infestation that "operation cat drop" was undertaken by the WHO in cooperation with the Royal Air Force in Singapore (Conway, 1973).

14.3.1. Sources of pesticide POPs

Pesticides have been in use in Malaysia following the Second World War to control pests in agricultural plantations, namely rubber, oil palm, and cocoa. The regulation on the importation and handling of these pesticides comes under the Pesticide Act 1974. Under the Act, all pesticides imported into and used in Malaysia have to be registered with the Pesticides Board Malaysia. Importers have to supply information such as trade names, active ingredients, amounts, and formulations. The Pesticides Board reviews the registration of these pesticides from time to time when toxicity and ecotoxicological data become available. The 1997 registration listed a total of 1767 formulations of pesticides and herbicides. A number of POP chemicals was also in the registration list, including DDT, chlordane, endosulfan, lindane, atrazine, 2,4-D, chlorpyrifos as well as tri-*N*-butyltin naphthenate (Pesticides Board Malaysia, 1997). However, in the latest register, there are 2279 formulations of pesticides and herbicides while most of the controversial pesticides had been deregistered. Since there are no manufacturing facilities for these POP pesticides in Malaysia, most of them have been either banned or voluntarily withdrawn by the local importers. However, the use of endosulfan and lindane was still being allowed but limited to certain sectors. Endosulfan is not allowed to be used in cocoa and pepper plantations while lindane was only allowed in the oil palm and coconut plantations before it was totally deregistered in 2003 (Sufian Yek, 2005).

Chlordane and DDT were deregistered in 1997 and 1999, respectively. The registrations of aldrin, dieldrin, and heptachlor were not renewed and thus were banned in the early 1990s. Some of the POPs not on the Stockholm Convention list have also been banned including lindane and other HCH isomer mixtures, pentachlorophenol, and 2,4,5-T. There are still a number of persistent pesticides in use and this is a major concern. Pesticides such as endosulfan, atrazine, chlorpyrifos, and tributyltin (TBT) remain on the registration list and are available in the market. Endosulfan, even with known high toxicity effects to biota and humans, are still being used in Malaysia. It is being extensively used in rice fields in the northern region of West Malaysia to control rice borers and golden snails.

There is no available information on the amount of pesticides being imported into the country. Some POP chemicals such as DDT, dieldrin, and endrin had been in use following the Second World War until they were banned or de-registered. For instance, DDT was used to control malaria both in East and Peninsular Malaysia (since 1961 in the former and 1967 in the later) until it was replaced by delta-methrin and other pesticides after 1998. A record on the use of DDT as insecticide residual spray between 1991 and 1998 showed that ~253,989 kg of DDT had been applied as 25% emulsified concentrate or as 75% water-dispersible powder. The impact of interventions in malaria control using primarily DDT saw a drastic reduction of more than 70% recorded malaria cases (Hashim, 2003).

14.3.2. Industrial sources

The sources of unintentionally produced POP chemicals, polychlorinated dibenzodioxins (PCDD), polychlorinated dibenzofurans (PCDF), and hexachlorobenzene (HCB), has been estimated through the National Implementation Plan (NIP) for Malaysia. However, an official report has not been made public. The draft final report on the assessment of unintentionally produced chemicals conducted by Universiti Sains Malaysia indicated that the estimated total release of PCDD/PCDF from various industrial activities was 27.18 g TEQ year^{-1} (Universiti Sains Malaysia, 2004). The main contributing source was attributed to waste incineration accounting for ~50% of the total release of PCDD/PCDF even though currently, Malaysia does not have large domestic waste incineration facilities. There are a number of small waste incinerators in the larger islands with capacities between 3 and 10 tons day^{-1} and several small medical waste incinerators. There is a privately managed chemical/industrial waste treatment facility centrally located at Bukit Pelandok, ~100 km south of Kuala Lumpur which handles all 107 categories of scheduled wastes listed under the Environmental Quality (Scheduled Wastes) Regulations 1989. The chemical waste incineration plant operates a high temperature rotary kiln with an efficient flue gas cleaning system. The plant has the capacity of 33,000 tons year^{-1} and meets the PCDD/PCDF emission limit of 0.1 ng m^{-3}. From 1998 to 2004, ~15.5 tons of PCBs, 57 tons of pesticide stockpiles, and 22 tons of transformer oil had been treated in this facility (Idris, 2004).

There are a number of high temperature metal production and processing plants in Malaysia, which have contributed to the release of PCDD/PCDF. Chemical industries in Malaysia are dominated by the petroleum industries where there are six major oil refineries with a total capacity of ~500,000 bbl day^{-1}, a LNG processing plant in Sarawak and several oil terminals. Consumer products industries are not expected to release significant amounts of PCDD/PCDF except for pulp and paper production. Currently, there are 19 paper manufacturing companies in Malaysia with several production facilities throughout the country. The biggest paper production facility is the Sabah Forest Industries located at Sipitang, Sabah. Malaysia has a paper producing capacity of slightly more than one million tons per year which is still 50% less than the annual demand (Haron, 2002).

The release of PCDD/PCDF from transport activities was estimated to be very minimal and not reported for uncontrolled combustion processes (Universiti Sains Malaysia, 2004). In the Department of Environment Malaysia 1997 report, the major sources of air pollution in 1996 were motor vehicles, 82%, power stations, 9%, industrial fuel burning, 5%, industrial production processes, 3%, domestic and commercial furnaces, 0.2%, and open burning at solid waste disposal sites, 0.8% (Afroz et al., 2003). Leaded gasoline has been phased out since 1998 and most cars have been fitted with catalytic converters since then. Consequently, a minimal release of PCDD/PCDF is expected from motor vehicles that are mainly from diesel-powered vehicles. The released air pollutions monitored were CO, NO_2, SO_2, O_3, and suspended particulate matters.

A recent study by Omar et al. (2002) showed that the total polycyclic aromatic hydrocarbons (PAHs) concentrations in the atmospheric particles and roadside soil particles collected in Kuala Lumpur were 6.28 ng m^{-3} and 0.22 μg g^{-1}, respectively.

Domestic waste management is a burning issue in Malaysia. The Malaysian government is planning to build a large solid waste incineration plant in Broga, south of Kuala Lumpur which has a proposed capacity of 1500 tons day^{-1}. However, the initiative has met with opposition from local communities and several non-governmental organizations (NGO) (CAP, 2005). Currently, there are 246 waste disposal sites throughout Malaysia but most of them are not properly planned and managed. Open dumping is commonly practiced and more often than not, leachates have been found to seep into the nearby rivers where drinking water is sourced from Landfill fires are quite common sights which would definitely release PCDD/PCDF into the atmosphere. Other sources of PCDD/PCDF are widely practiced open burning of domestic wastes and frequent forest fires from neighboring countries. A major haze episode in Southeast Asia occurred in 1997 where it was estimated that 60 Tg of forests and vegetation were burned, producing thick smoke covering the whole of Malaysia and neighboring countries (Liew, 1998). Beside PCDD/PCDF, large amount of PAHs are also released during forest fire.

14.3.3. Polychlorinated biphenyl (PCBs) inventory

PCBs are not manufactured in Malaysia and the import of PCBs has been banned since 1995. However, there are still old transformers and capacitors in use that contain PCB-contaminated oil (Hashim, 2001). Since 1998, PCB stockpiles and PCB-contaminated transformer oils have been properly disposed of at the Kualiti Alam Integrated Waste Management Centre, Bukit Pelanduk. A total of 15.5 tons of PCBs and 22 tons of transformer oils was incinerated at the site from 1998 to 2004 (Idris, 2004). There is no available record on the total import of PCBs and PCB containing products. Under the National Implementation Plan for compliance to the Stockholm Convention, an exercise to produce a PCB inventory for Malaysia has been carried out but the report has not been made public.

14.3.4. Regional sources

Most of the countries in the region have banned the production, import, and use of most POP pesticides. All the countries in Southeast Asia are parties to the Stockholm Convention and have made every effort to reduce and eliminate the use of these chemicals in compliance with the Convention. However, the safe disposal of existing stockpiles and the availability of good alternative pesticides in this mainly agricultural region are some of the issues that need to be addressed very quickly (UNEP, 2002). Indonesia had the capacity to produce ~7000 tons of DDT per year but the production plant was closed in 1992. An average of 2500 tons of DDT had been used every year in various parts of Indonesia (Purwono and Agustina, 2002). Thailand had been increasingly importing OCPs from ~5000 tons in 1971 to 34,000 tons in 1999. Extensive uses of pesticides in Thailand were reflected in the results of the studies by the Department of Agriculture from 1993 to 1999 where more that 40% of samples were analyzed positive for pesticides with a concentration range of <0.01–1.21 ug L^{-1} for water and <0.01–7.43 mg kg^{-1} for sediments (Chareonsong, 2002). DDT had been extensively used in countries in the region following the Second World War until it was banned in the late 1990s. Viet Nam, for instance, was using ~200 tons a year in 1992–1994 to control the spread of malaria (UNEP, 2002).

The regionally based assessment of persistent toxic substances for the Southeast Asian region (UNEP, 2002) had suggested a possible hot spot for the presence of PCDD/PCDF in Viet Nam where defoliant agents contaminated with PCDD/PCDF had been aggressively sprayed during the Vietnam War between 1962 and 1971. The application of herbicides such as 2,4-D and 2,4,5-T had resulted in the release of ~170 kg equivalent of TCDD (Le, 2002). With the persistency and long-range capability of PCDD/PCDF, it is possible that Malaysia, among other countries in the region, will be affected. PCBs were not manufactured in the region and its importation has been banned in all of the countries since the early 1990s. Inventories on stockpiles and PCB-contaminated equipment are being produced by countries in the region under the NIP initiatives for the Stockholm Convention.

The major concern for the region is the open burning of domestic wastes and forest fires in the tropical forest belt of Southeast Asia that resulted in severe hazes and the release of hazardous airborne chemicals, particularly PAHs. It became such a regional crisis that a Regional Haze Action Plan was instituted in 2001 to address the issue of transboundary haze (ASEAN, 2006).

14.4. Levels of POP contamination in Malaysia

The extensive use of pesticides has resulted in high levels of contamination in every environmental compartment in Malaysia. Reports as early as 1981 found that high levels of widely used pesticides, such as aldrin, dieldrin, DDT, and HCHs, had contaminated river water, sediments, and fish (Abdullah, 1995). In the review, the author summarized the findings of several earlier studies on levels of pesticide pollutions in aquatic environments in Malaysia as shown in Table 14.1. Studies conducted in the early 1980s showed high levels of dieldrin (200–500 ng L^{-1}), aldrin (100–1800 ng L^{-1}), and lindane (100–600 ng L^{-1}) in water and much higher levels in sediments and rice field fish. DDT and endosulfan were also found in rice fields and marine fish at levels of 800 ng/kg and 5400 ng/kg, respectively (Abdullah, 1995). A comprehensive survey on the pesticide residues in Peninsular Malaysian waterways was conducted in 1989–1990 by Tan et al. (1991) who found several pesticides such as dieldrin, endrin, DDT, heptachlor and endosulfan in the range from not detected to as high as 68.7 ng L^{-1}. Being surrounded by large bodies of seawater, quite an extensive amount of data is available on concentration of POPs in fishes and marine organisms. However, very few studies have been reported on POP contamination in terrestrial biota and humans.

14.4.1. POPs contaminations in water

Iwata et al. (1994) reported an exceptionally high concentration of HCHs in the Selangor River water in central Peninsular Malaysia at 900 ng L^{-1} as

Table 14.1. Organochlorine pesticides in Malaysian aquatic environments prior to 1990 (Abdullah, 1995)

Location	Year compounds	Compounds	Levels (range/mean)
Krian River Basin, Perak	1981		
Water		Dieldrin	200–500 ng L^{-1}
		Aldrin	100–1800 ng L^{-1}
		Lindane	100–600 ng L^{-1}
Sediment		Dieldrin	800–4700 ng kg^{-1}
		Aldrin	100 ng kg^{-1}
		Lindane	400–800 ng kg^{-1}
Rice field fish		Dieldrin	6.6–24.9 ng g^{-1}
		Aldrin	0.3–1.1 ng g^{-1}
		Chlordane	2.8–17.1 ng g^{-1}
Tanjung Karang, Selangor	1982		
Water		Lindane	100 ng L^{-1}
Fresh water fish		Lindane	10–100 ng g^{-1}
Penang	1984–1987		
Rice field and marine fish		Dieldrin	0.2 ng g^{-1}
		DDT	0.8 ng g^{-1}
		Endosulfans	5.4 ng g^{-1}

compared to water samples from Thailand (0.18–75.00 ng L^{-1}) and Viet Nam (1.90–19.00 ng L^{-1}) in their study on persistent organochlorines in air, water, and sediments from Asia and Oceania. In a more recent study (Leong et al., 2003) on the same Selangor River, it was reported that all nine sampling locations recorded the presence of lindane ranging from 16.87 90.32 ng L^{-1}. More alarmingly, the nearby Klang River was found to contain the high level of 1953.2 ng L^{-1} of lindane as well as other pesticides. Industrial formulation activities and irresponsible dumping of contaminated waste and agricultural run-off may be the reasons for the high levels of lindane in the Selangor and Klang Rivers. The latest report in this monitoring program (Mustafa, 2005) has shown a drastic decrease in the lindane concentration in the Selangor River water (not detected to 64 ng L^{-1}). This may be attributed to the fact that lindane had been deregistered for use in Malaysia in 2003. Our study (Tan, 2001) on levels of OCPs in several rivers in northern Peninsular Malaysia reported much lower levels of HCHs in the range from not detected to 8.88 ng L^{-1} suggesting the localized contamination of lindane in the Selangor area. However, studies in three farming regions in Peninsular Malaysia and Sabah (Lee et al., 2003) have reported high levels of most pesticides in water as well as sediments. Water samples collected in the Muda River rice basin in 1998 found it to contain high levels of heptachlor epoxide (567.1–3606.0 ng L^{-1}) and dieldrin (316.3–568.0 ng L^{-1}) but no DDTs or HCHs. Water samples from Kundasang in Sabah have been found to contain relatively high levels of α-endosulfan (236.9–718.3 ng L^{-1}), lindane (ND-464.2 ng L^{-1}), and 4,4′-DDT (ND-442.3 ng L^{-1}). Cameron Highland regions which supply fresh vegetables to local markets in Malaysia were found to have water samples containing high concentrations of most pesticides such as aldrin (ND-1107.5 ng L^{-1}), 4,4′-DDT (442.0–450.7 ng L^{-1}), and lindane (ND-113.6 ng L^{-1}).

Table 14.2 summarizes available data on selected POP contamination in water in Malaysia. DDTs were found in most rivers in Malaysia but the concentration levels varied from region to region with centrally located rivers being detected to be highly contaminated. Surprisingly, DDTs concentration increased in these rivers as compared to rivers from other parts of the country even after DDT was banned from use in 1999. Endosulfans were not detected in most rivers in the 1989 survey but were found at relatively high concentrations in later studies (Table 14.2). Concentrations of other pesticides in river waters have also been reported in these studies. In the earlier study (Tan et al., 1991), aldrin, dieldrin, endrin, and heptachlor were also found in some of the rivers. The concentration levels were ND-0.5 ng L^{-1} for aldrin, ND-0.3 ng L^{-1} for dieldrin, ND-3.2 ng L^{-1} for endrin, and 0.3–3.4 ng L^{-1} for heptachlor. Our study

Table 14.2. Selected OCPs contamination (ng L^{-1}) in several river waters in Malaysia

Year	Location	DDTs	HCHs	Endosulfans	References
1989	Selangor River	9.6	ND	ND	Tan et al. (1991)
1989	Muda River	69.4	ND	ND	Tan et al. (1991)
1989	Perai River	4.8	ND	ND	Tan et al. (1991)
1989	Perak River	0.6–20.9	ND–1.4	ND–0.5	Tan et al. (1991)
1990	Selangor River	1.7	900	–	Iwata et al. (1994)
1998	Muda River	ND	ND	ND–128.2	Lee et al. (2003)
1998	Cameron	458.7–504.2	ND–113.6	47.8–260	Lee et al. (2003)
1998	Kundasang, Sabah	ND–442.3	ND–464.2	236.9–718.3	Lee et al. (2003)
1998	Muda River	0.9–3.1	0.3–4.2	1.0–24.4	Tan (2001)
1999	Perai River	2.6–5.4	1.7–12.1	0.2–4.9	Tan (2001)
2000	Perak River	ND–23.0	ND (all)	ND–13.0	Tan (2001)
2002	Selangor River	ND–417.6	ND–90.3	ND–285.7	Leong et al. (2003)
2002	Klang River	ND–184.2	ND–1953.2	ND–242.1	Leong et al. (2003)
2004	Selangor River	ND–165	ND–64	ND–1663	Mustafa (2005)

in the Perai and Juru Rivers in 1999 (Tan, 2001) found that aldrin concentrations were ND-1.1 ng L^{-1}, while dieldrin, and endrin concentrations were 0.9–3.0 and 0.2–2.2 ng L^{-1}, respectively. However, a survey at nine stations along the Perak River, one of the longest rivers in Peninsular Malaysia, revealed the absence of other pesticides beside DDT and endosulfan.

PCB concentrations in river waters have not been studied or reported except for one sample studied by Tanabe's group (Iwata et al., 1994) where it was found that total PCB concentration was 0.45 ng L^{-1} in the sample taken from the Selangor River. We have monitored other POP chemicals such as PAHs, phenols, and phthalate esters in river waters. In the 1998 study (Tan, 2001), we found that the Perai River contained 357–2644 ng L^{-1} of total PAHs, 3625–4380 ng L^{-1} of total phenols, and 3215–14855 ng L^{-1} of total phthalate esters. The Muda River was found to contain 986–1507 ng L^{-1} of PAHs, 210–1114 ng L^{-1} of phenols, and 964–6096 ng L^{-1} of phthalate esters. The Perak River, on the other hand, was relatively free from PAHs (17–435 ng L^{-1}) and phenols (26–214 ng L^{-1}) but highly contaminated with phthalate esters, especially near the estuary with concentration levels ranging from 175 to 17,929 ng L^{-1}.

There was only one report on the levels of POPs in surface seawaters (Iwata et al., 1993). The authors reported studies on seawaters from various parts of South Asia. The surface water from the Straits of Malacca was found to contain 480 pg L^{-1} of HCHs, 9.4 pg L^{-1} of chlordanes, 6.4 pg L^{-1} of DDTs, and 20 pg L^{-1} of PCBs. South China Sea was found to contain similar levels of the POP contaminations.

14.4.2. POP contaminations in sediments and soil

Contaminations of several OCPs in sediments collected in Malaysia had been studied in 1981 where dieldrin and lindane were found at levels of 0.8–4.7 μg kg^{-1} and 0.4–08 μg kg^{-1}, respectively in sediments taken from the Krian river basin in Perak (Abdullah, 1995). Iwata et al. (1994) found in the 1990 sampling of the Selangor River that there were 1.8 μg kg^{-1} DDTs, 0.18 μg kg^{-1} HCHs, 1.0 μg kg^{-1} chlordanes, and $<$5.0 μg kg^{-1} PCBs in a sediment sample. Similar concentration levels were observed in a 1992 study (Tan and Vijayaletchumy, 1994) on sediment from Selangor River with 4.03 μg kg^{-1} HCHs and 5.35 μg kg^{-1} of endosulfans. A report by Lee et al. (2003) revealed very high concentrations of several pesticides in sediments collected in Cameron Highlands and Kundasang in Sabah where extensive vegetable farming is carried out. Sediments collected in the Cameron Highlands areas contain all of the OCPs studied including 4,4′-DDT (21.1–22.6 μg kg^{-1}), endrin (19.9–98.7 μg kg^{-1}), and aldrin (6.7–39.6 μg kg^{-1}), amongst others. Sediments from Kundasang were reported to contain high levels of aldrin (42.1–92.0 μg kg^{-1}), endrin (32.0–53.1 μg kg^{-1}), and 4,4′-DDT (18.8–26.3 μg kg^{-1}). In the same report, however, sediment samples from the Muda River basin were found to contain substantially lower pesticide residues such as aldrin (ND-83.4 ug g^{-1}) and lindane (16.1–33.4 μg kg^{-1}).

Our studies on levels of OCPs in sediments collected from rivers in northern Peninsular Malaysia showed similar distributions (Hossain, 2001; Tan, 2001; Syahidah et al., 2003). Table 14.3 summarizes the concentration levels of some of the POP chemicals in sediments collected in Malaysia. Two studies have reported on coastal sediments from the west coast of Peninsular Malaysia. In the 1995 study, Wood et al. (1999) reported the presence of most OCPs in sediment samples collected in this area. The mean concentrations of the OCPs were similar to the findings of our study (Hossain, 2001) on similar samples 4 years later (Table 14.3). For example, the total heptachlor found was 3.74 μg kg^{-1} in the 1995 study and 1.84 μg kg^{-1} in the 1999 survey.

Beside OCPs, studies on other POP chemicals in sediments have also been conducted. In 1992, we conducted a study (Ibrahim et al., 1996) on levels of PAHs in Langkawi Island when a major oil spill occurred in the vicinity. Due to quick and efficient recovery operations, minimal impact of the oil spill was experienced with the total PAHs found being in the range of 34–273 μg kg^{-1} which was slightly above the concentration of controlled samples. Contamination of PAHs, particularly in coastal sediments, was attributed to oil tankers carrying crude oil from the Middle East in the Straits of Malacca and the off-shore oil platform in the South China Sea (Zakaria et al., 2001).

Table 14.3. Selected OCPs contamination (μg kg^{-1}) in sediments in Malaysia

Year	Location	DDTs	HCHs	Endosulfans	References
1981	Krian River	–	1.0–8.8	–	Abdullah (1995)
1988	Sabah	0.1–34.7	0.1–1.1	–	UNEP (2002)
1990	Selangor River	1.8	0.18	–	Iwata et al. (1994)
1992	Bernam River	–	3.52	0.96	Tan and Vijayaletchumy (1994)
1992	Selangor River	–	4.03	5.35	Tan and Vijayaletchumy (1994)
1995	Straits of Malacca, coastal sediment	ND–6.84	ND–2.36	ND–3.42	Wood et al. (1999)
1998	Muda River	ND	32.7–92.2	3.0–13.3	Lee et al. (2003)
1998	Cameron	38.3–78.3	19.0–113.8	1.54–25.5	Lee et al. (2003)
1998	Kundasang, Sabah	28.3–63.6	27.5–61.7	ND–18.7	Lee et al. (2003)
1998	Muda River	–	0.93	1.67	Tan (2001)
1999	Straits of Malacca, coastal sediment	0.2–3.6	0.6–9.7	0.1–9.5	Hossain (2001)

14.4.3. POP contamination in fishes and marine organisms

Fishes and other marine organisms have been well monitored in Malaysian environments. Numerous studies had been reported on the levels of POPs, particularly OCPs in fishes since the early 1980s (Table 14.1). We conducted two studies on the levels of OCPs in several species of marine organisms from the Straits of Malacca. In the first study in 1999 (Hossain, 2001), we analyzed seven marine species for levels of OCPs. The results are presented in Table 14.4. DDTs, endosulfans, endrins, and HCHs were found in relatively high concentrations in all species studied. For examples, blood cockles (*Anadara granosa*) were found to contain 0.04–1.24 ng g^{-1} ww of DDT and 0.74–10.23 ng g^{-1} ww of HCHs which are equivalent to 3.2–99.2 and 59.2–818.4 ng g^{-1} lw, respectively. High concentrations of HCHs were found in bottom feeder species such as green mussels (*Perna viridis*) at 12.4–437.2 ng g^{-1} lw, shrimps (*Metapenaeous monoceros*) at 397.6–4313.3 ng g^{-1} lw and the blood cockles. However, marine fishes were found to have slightly lower concentrations of OCPs. Catfish (*Arius sp.)* were found to contain all OCPs in every sample analyzed, for example, DDT (11.5–367.8 ng g^{-1} lw) and HCHs (103.4–678.2 ng g^{-1} lw).

In the second study (Muhammad, 2006), we analyzed six species of fresh water fishes and seven species of marine organisms. Beside OCPs, we also analyzed congener-specific PCBs in order to determine the toxicity equivalent (TEQ) attributed to PCB contaminations in these samples. All samples of fresh water fishes collected in the northern region of

Table 14.4. Levels of OCPs in several species of marine organisms in Malaysia (Hossain, 2001)

Marine species	% Lipid (mean)	Concentration range of OCP (ng g^{-1} wet wt.)					
		Aldrin	DDTs	Dieldrin	Endosulfans	Endrins	HCHs
Blood cockle (*Anadara granosa*)	1.25	0.02–2.5	0.04–1.2	0.01–0.7	0.10–3.3	ND–3.3	0.74–10.2
Catfish (*Arius* sp.)	0.87	0.2–2.5	0.1–3.2	0.02–0.5	0.3–0.8	0.1–5.4	0.9–5.9
Green mussel (*Perna viridis*)	2.58	0.02–15.7	ND–7.8	ND–0.9	ND–2.6	ND–9.1	0.32–11.3
Jew fish (*Pennahia* sp.)	4.21	0–9.5	0.1–6.0	0.02–0.9	0.3–3.8	0.1–6.2	2.7–7.1
Mullet (*Valamugil* sp.)	1.54	ND–2.2	0.01–4.9	0.02–0.8	0.5–1.8	ND–13.0	0.3–8.3
Shrimps (*M. monoceros*)	0.83	0.2–26.5	ND–4.1	ND–0.6	ND–0.6	ND–2.7	3.3–35.8
Seabass (*Lates calcarifer*)	1.03	0.5–8.0	0–0.5	ND–1.0	0.01–3.4	ND–9.1	1.7–5.1

Peninsular Malaysia were found to contain endosulfans with mean values ($n = 5$ for each of six species) of between 2.1 and 2.6 ng g^{-1} ww (Table 14.5). Contrary to studies on water and sediment samples from the central region of Peninsular Malaysia (Lee et al., 2003), low levels of HCHs were found in these fish samples with mean concentrations ranging from 0.04 ng g^{-1} ww for the snakehead fish to 0.21 ng g^{-1} ww for the sultan fish. DDTs levels in these fish samples were comparable to other reported values for fishes in this region. PCB concentrations in these fresh water samples (7.8–22.5 ng g^{-1} ww) were slightly higher that those reported for fishes (1.5–10 ng g^{-1} ww) from this region (Kannan et al., 1995). The congener-specific analysis revealed that consistently high concentrations of PCB 167 were observed in most samples while the more toxic PCB 126 was only detected in the snakehead fish at the very low concentration of 0.03 ng g^{-1} ww. Toxicity equivalents calculated from these data showed similar TEQ values of $\sim$200 pg g^{-1} TEQ lw for all species. The second part of the study (Muhammad, 2006) on marine organisms showed a similar distribution of OCPs and PCBs to that in the fresh water fishes (Table 14.6). Significantly high concentrations of DDTs and endosulfans were observed compared to HCHs. There seemed to be a decrease in levels of several pesticide residues for the same species when compared to the findings of an earlier study by Hossain (2001). A drastic

Table 14.5. Levels of POPs in several fresh water fishes in Malaysia (Muhammad, 2006)

Marine species	% Lipid (mean)	Concentration range of POPs (ng g^{-1} wet wt.)				
		DDTs	Endosulfans	HCHs	PCBs	PCBs (pg g^{-1} TEQ lw) (mean)
Catfish (*Clarias batrachus*)	1.08	ND–5.0	0.1–3.8	ND–0.2	0.08–33.9	268.4
Snakehead (*Channa striatus*)	1.03	0.8–3.6	0.8–4.8	ND–0.48	1.69–20.4	216.0
Gourami (*Trichogaster* sp.)	1.08	ND–2.2	0.4–3.9	ND–0.17	0.11–52.3	206.0
Javanese carp (*Puntius gonionotus*)	1.04	1.7–3.6	1.1–4.8	ND–0.22	0.04–22.2	211.8
Sultan fish (*Leptobarbus hoevenii*)	1.09	1.2–2.8	1.7–2.7	ND–0.35	5.2–43.7	204.7
Climbing perch (*Anabas testudineus*)	1.01	0.7–1.2	0.4–4.2	ND–0.4	0.38–14.2	174.5

Table 14.6. Levels of POPs in several marine species in Malaysia (Muhammad, 2006)

Marine species	% Lipid (mean)	Concentration range of POPs (ng g^{-1} wet wt.)				
		DDTs	Endosulfans	HCHs	PCBs	PCBs (pg g^{-1} TEQ lw) (mean)
Small mackerel (*Rastrelliger* sp.)	1.20	0.9–5.1	ND–2.5	ND–0.63	0.03–2.5	184.3
Bigeye croaker (*Pennahia macrophthalmus*)	1.16	1.4–3.3	1.1–5.4	ND–0.2	0.13–1.7	258.1
Mullet (*Mugil cephalus*)	1.35	0.4–1.7	0.6–2.1	ND–0.04	0.09–1.9	199.8
Queenfish (*Scombereroides commersonnianus*)	1.04	0.3–2.7	1.4–5.5	ND–0.4	0.07–5.2	194.1
Catfish (*Arius* sp.)	1.20	0.8–1.9	1.8–3.3	ND–0.09	0.18–3.3	362.4
Shrimps (*Metapenaeus* sp.)	1.04	1.4–1.7	0.3–1.6	0.02–0.4	0.12–2.1	257.9
Blood cockles (*Anadara granosa*)	1.06	0.6–2.0	0.1–1.7	0.02–0.4	0.05–3.7	197.2

example can be seen in shrimps; earlier, they had been found to contain between 3.3 and 35.8 ng g^{-1} ww of HCHs but a later study revealed a level of only 0.02–04 ng g^{-1} ww. Catfish samples were found to contain 0.1–3.2 ng g^{-1} ww of DDT in the earlier samples (Hossain, 2001) and 0.8–1.9 ng g^{-1} ww in the later study (Muhammad, 2006). PCB concentrations in these marine organisms were generally lower than in the fresh water fishes and comparable to the levels reported by Kannan et al. (1995). Toxicity equivalent values for these marine species were similar to the TEQ values for the fresh water fishes (Tables 14.5 and 14.6).

POPs in mussel studies have been used as indicators for persistent organic pollutions in the marine environments. Through the Global Mussel Watch Programme, large volumes of data were made available to assess the status of POPs in various regions of the world (UNEP, 2003). Rohani et al. (1992) reported that as high as 180.9 ng g^{-1} ww of HCHs were detected in mussels collected in the Penang coast, 123.7 ng g^{-1} ww of which was lindane. Monirith et al. (2003) collected mussel samples from 13 different locations throughout Malaysia in 1998–1999 and reported the levels of POP contaminations as part of the Global Mussel Watch Program (Table 14.7). The levels of POPs in mussels revealed the distribution of POPs contaminations in Malaysia. Levels of DDTs and HCHs were similar in all samples, either from Sabah in East Malaysia or from Peninsular Malaysia. However, chlordanes and PCBs were significantly higher in mussels from Peninsular Malaysia. Surprisingly, levels of HCHs in these

Table 14.7. Levels of POPs in mussels collected in Malaysia (Monirith et al., 2003)

Location	% Lipid (mean)	Concentration range of POPs (ng g^{-1} lw)			
		DDTs	Chlordanes	HCHs	PCBs
Kuala Penyu, Sabah	0.73	100	8.7	<1.4	7.5
Troyang, Sabah	0.65	32	4.1	3.1	8.3
Sangkar Ikan, Langkawi	0.92	95	41	9.4	6.0
Tanjung Rhu, Langkawi	1.1	16	2.5	4.9	5.1
Penang Bridge, Penang	1.0	71	180	<0.10	60
Bagan Lalang, Selangor	1.2	26	24	3.3	<4.2
Lukut, Negeri Sembilan	1.5	53	50	1.0	54
Pasir Panjang, Negeri Sembilan–1	1.8	71	41	4.8	24
Pasir Panjang, Negeri Sembilan–3	1.6	93	60	3.5	11
Tangjung Batu, Malacca	1.3	100	610	12	22
Pasir Putih, Johor–2	2.1	130	470	5.2	250
Pasir Puteh, Johor–3	2.1	270	170	<0.5	230
Butterworth, Penang	1.2	110	220	<0.8	42
Teluk Bahang, Penang[a]	2.6	17.6	–	155.4	–
Kerian Estuary, Kedah[a]	2.48	15.7	–	132.1	–
Muda Estuary, Kedah[a]	2.62	150.4	–	144.8	–

[a] *Source*: Hossain (2001).

mussels were significantly low even though numerous studies on HCHs in water and sediments reported high concentrations. Our study on mussels from three locations in northern region of Peninsular Malaysia showed high concentrations of HCHs and comparable levels of DDTs (last 3 entries in Table 14.7).

Contamination of butyltin compounds in Malaysian marine environments has been specifically reported (Sudaryanto et al., 2004a). In this study, 16 green mussel samples, 10 species of fish, and 13 sediment samples were collected from coastal waters of Peninsular Malaysia. The results on the butyltin contamination in green mussel from Malaysian waters were reported in earlier paper under the Asia-Pacific Mussel Watch Programme (Sudaryanto et al., 2002). Total butyltin compounds detected in the green mussels from Malaysian waters were relatively high particularly for samples collected in the aquaculture areas in the Straits of Malacca when compared to samples collected from other Asian countries except for from Hong Kong. The levels of TBT, which is normally the major constituent of butytin compounds, in the green mussel ranged from 3.5 ng g^{-1} ww. in samples collected from Sabah to 730 ng g^{-1} ww. in sample collected at Pantai Lido, Johore Bahru (Sudaryanto et al., 2002). Various types of fish collected in Malaysian waters recorded total butyltin contamination between 5.3 and 210 ng g^{-1} ww. The coastal sediment samples were found to contain 16–1400 ng g^{-1} dw of total butyltin compounds where the highest level was found in sediment collected in Pantai Lido, Johore Bahru. The levels of butyltin compounds in these samples were reported to be comparable to reported values from some developed countries but highest among Asian developing nations. The parent compound, TBT, was found to be higher than its degradation compounds, dibutyltin and monobutyltin suggesting very recent input of TBT to the Malaysian marine environment (Sudaryanto et al., 2004a). The high levels of butyltin compounds in Malaysia waters may be attributed to the high maritime activities particularly in the busy Straits of Malacca and the fact that TBT is still available in the Malaysian market (Pesticides Board Malaysia, 1997).

14.4.4. POP contaminations in humans

Studies on levels of POPs in the Malaysian population are either scarcely carried out or not reported. Two available reports described studies on human breast milk and human cord blood. In the first report, Sudaryanto et al. (2004b) described a study on breast milk samples collected from primiparas mothers from Penang and Kedah in 2003. The study found that levels of pesticides in ng g^{-1} lw. were as follows; DDTs (180–5700), HCHs (27–1000), chlordanes (8.2–54), and HCB (1.3–78). PCB levels were 23–450 ng g^{-1} lw. with high components of mono-ortho PCBs. PCDDs were found in the range 34–200 pg g^{-1} lw. and PCDFs were in the range of 3.3–20 pg g^{-1} lw. The calculated TEQ on the levels of PCDDs, PCDFs, and PCBs were between 3.0 and 24 pg g^{-1} TEQ lw. Based on the mean TEQ of 13 pg g^{-1} lw., the authors concluded that the levels of POP contaminations were much lower than those reported for the developed nations and slightly higher than those for developing countries (Sudaryanto et al., 2004b). It is interesting to note that a recently identified endocrine disrupter, *tris*(4-chlorophenyl) methane (TCPMe) was detected in all the human milk samples analyzed in this study. From the positive correlation between TCPMe and DDTs, the study suggested that technical DDT that have been used in Malaysia may be a source of TCPMe (Sudaryanto et al., 2005).

The other study on human cord blood collected in a Kuala Lumpur hospital (Benjamin Tan and Mustafa, 2003) reported that only chlopyrifos was found in 18% of the samples at levels of ND-1.15 ng mL^{-1} while other pesticides analyzed, such as lindane, diazinon, endrin, and endosulfans were not detected. In the same study, bisphenol-A and nonylphenols were detected in more than 80% of the samples at concentration levels of ND-4.05 and ND-15.17 ng mL^{-1}, respectively. Several alkylphenols were also found in these blood samples.

14.5. Management of POPs in Malaysia

14.5.1. Existing regulations

Regulations for the management of chemicals in Malaysia are sufficient and are often being updated to handle new issues. The Pesticide Act 1974 is the principle legislation to regulate the management of pesticides in Malaysia. The Pesticides Board is set up to implement the Act under the jurisdiction of the Ministry of Agriculture, Malaysia; the Act includes the registration of all pesticides, herbicides and other chemicals used in agriculture, licensing for the storage and sale of pesticides, libeling and the registration of pest control operators. Several amendments have been made recently to the Pesticides Act (1974) such as the control of importation of pesticides as registration samples and control of possession or use of unregistered pesticides. All nine pesticide POPs under the Stockholm Convention are banned from import and use in Malaysia. Under the Pesticides Board decisions, lindane was banned in 2003; and recently, it was decided that endosulfan would be phased out effective from August 15, 2005 under the pesticide risk reduction program due to its extreme toxicity to fishes and other aquatic life (Sufian Yek, 2005).

Other related regulations on the management of pesticides are the Environmental Quality Act 1974, the Food Act 1983 and the Occupational Safety and Health Act 1994 (Sufian Yek, 2005). The primary objective of the Environmental Quality Act 1974 is to control the discharge of chemical and industrial wastes including pesticides into the environment, so that there will be no adverse effects on human health and the environment. The disposal of pesticides has not been a significant problem in Malaysia as it is an offence to discharge any toxic waste into the environment. There is a chemical waste treatment facility, which is able to handle all the chemical wastes produced in the country. The Food Act 1983 (under Schedule 16 of its Food Regulation 1985) prescribes the maximum residue levels of certain pesticides in food. The Occupational

Safety and Health Act 1994 provides the legislative framework to promote, stimulate and encourage high standards of safety and health of workers handling chemicals, including pesticides and hazardous wastes.

The Environmental Quality (Dioxin and Furan) Regulation 2004, which came into force on May 1, 2004, was devised to control the emission of dioxins and furans into the atmosphere from selected facilities (DOE Malaysia, 2005). The regulation was initially applied to various types of new and old incinerators in Malaysia, such as the domestic waste incinerators, schedule waste incinerators, sewage sludge incinerators and pulp and paper industry sludge incinerators. Under the regulation, new facilities would need to comply with a dioxin and furan emission of less that 0.1 ng/Nm^3 TEQ while existing installations are required to comply with the emission limit within 3 years of the regulation coming into force.

14.5.2. The Malaysian network for integrated management of chemicals and hazardous substances for environment and development (my-niche)

MyNICHE aims to enhance an integrated management and research approach to chemicals and hazardous substances in Malaysia. Even though it is still at a discussion stage, overwhelming response to the first Round Table dialogue indicated serious commitment of various stakeholders from relevant ministries and government agencies to industries and NGO. The network for integrated management of chemicals was proposed to assist the Government of Malaysia through various ministries and agencies in developing cooperation networks at local, national, and global levels to strengthen efforts in managing chemicals and hazardous substances including POPs (Lestari UKM, 2005). Under the proposal, six focus areas were initially defined as working approaches to the integration of chemical management. They are policy and institutional, transport and storage, trade and economy, green technologies and waste management, integrated chemical information system and inventories, and also chemical risk management. These focus areas would address issues relevant to chemicals such as pollutions, human health impact, environmental contaminations, sustainable resources, and economic well-being.

14.6. Data gaps

The peril of persistent toxic chemicals was realized long after tons of these chemicals had been spread throughout the world. Once hailed as perfect chemicals for their intended uses, these long lasting OCPs, for examples, become burden to the environment and ecosystems where they have been applied. In Malaysia, thousand of tons of these POP chemicals have been released to the environment but records of their applications were not properly kept and hardly available. Sources of pesticide POPs in Malaysia are probably not important as all of them have been banned from import and use. Stockpile of banned pesticides have been disposed but we are not able to verify the report (POP Seminar, 2005). Information on PCB inventory awaits the NIP of Malaysia report. Data on releases of PCDD/PCDF by various industrial sources is still incomplete where more accurate assessment should be carried out either using the toolkit (UNEP, 2001) or direct measurement at source.

Levels of pesticides in water, sediments and fishes are adequately known and studies are continuingly being conducted. However, levels of POP chemicals in air are hardly available probably due to lack or expertise and laboratory capability to measure very low levels of these pollutants. Data on pesticide residues in various foodstuffs is also lacking. Our laboratory in collaboration with Food Quality Control Department, Ministry of Health, Malaysia, among others are working to collect more data on POP contamination in food. Data on PCB residues in the environment is scarcely available probably due to difficulties in measuring these complex congeners. There are very few studies on PCB contamination have been reported by local researchers. Similarly, there are hardly any data on levels of PCDD/PCDF in the environment due to difficulty in analyzing these compounds.

In Malaysia, pollution studies generally focus on toxic metals as they are relatively easier to analyze by conventional atomic absorption spectroscopy. Numerous data on heavy metals such as cadmium, nickel, mercury, lead, and others in various environmental compartments have been reported (Yap et al., 2004). Capability and capacity to analyze organic pollutants at very low concentrations were only realized recently. The ASEAN-Canada Cooperative Program on Marine Science and the Environmental Monitoring and Governance of EDC Pollutions in the East Asian Coastal Hydrosphere projects and the Japanese Society for the Promotion of Science program were helpful in training local researchers and providing funds to acquire analytical instruments (UNEP, 2002). More reliable data on OCP levels in water, sediment, and fish have been reported. However, emerging POPs of concern such as chlorinated paraffins, alkylphenols, and organometallic compounds in Malaysia have not been reported.

14.7. POPs research and initiatives in Malaysia

There are a handful of research groups in Malaysia working on POP chemicals. Most of them are university based researchers working on chemical monitoring and analyses and toxicity studies. Analytical instruments such as gas chromatographs and mass spectrometers are available in most of the universities and research centers but technical expertise and fund for monitoring work are limited. There is no national program to study POPs pollutions in Malaysia, however, a number of programs will be commissioned to assess the status of POPs in compliance with the Stockholm Convention.

We are working with the Food Quality Control Department of the Ministry of Health to study the contamination of OCPs and PCBs in local fish and chickens. This project is in line with our current effort to assess the health risk arising from consumption of food contaminated with POP chemicals. The health risk assessment of POPs through dietary intakes project involved analyses of OCPs and PCBs in various foodstuff, initially raw materials which will be extended to cooked food. Unfortunately, we do not currently have the capability to analyze PCDD/PCDF in our laboratory but there are two high resolution mass spectrometers in the country that are capable of analyzing PCDD/PCDF. National and international collaborations will definitely improve the country capacity to monitor POPs not only those listed in the Stockholm Convention but other toxic chemicals found in the environment.

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Chapter 15

Persistent Organic Pollutants in Singapore's Marine Environment

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Abstract

Singapore is one of the busiest ports in the world and has many shipyards, petroleum refineries and pharmaceutical manufacturing plants are located on its coastline. Data on the prevalence of persistent organic pollutants (POPs) in Singapore's coastal ecosystems are therefore important in order to support research on the potential threats to the local marine environment and human health. This chapter presents data on the prevalence of POPs in the seawater, sediments, biota and mangrove habitats of Singapore. Data are presented for a range of POPs including polycyclic aromatic hydrocarbons (PAHs), organochlorine compounds (OCPs), polychlorinated biphenyls and polybrominated diphenyl ethers (PBDEs). Local studies confirm the ubiquity of POPs in the marine environment of Singapore. The prevailing ocean currents in the region govern the fate and transport of POPs in coastal waters, where the presence of localized high levels of POPs is likely to be a function of local shipping and industrial discharges. Land reclamation activities may also be a factor in the prevalence of POPs in seawater, where compounds are released from sediments and transported to the water column by seabed dredging. The land area under agricultural use in Singapore is negligible, and there is no direct application of OCPs in the country. However, pesticides may be easily transported through the atmosphere following volatilization from soil, and the presence of OCPs in Singapore's marine waters is likely to be a function of their use in neighbouring countries, with subsequent atmospheric transport and deposition. A biomagnification phenomenon was observed amongst the species collected and analysed from mangrove sites, but levels of POPs were not found to exceed relevant food safety standards. However, PCB concentrations in mangrove fish muscles were found to be higher than mean levels of PCBs found in seafood commonly

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consumed in Singapore. Overall, available data on the prevalence, fate and transfer of POPs in Singapore's marine environment highlights the ubiquity of these pollutants, and supports the need for a greater awareness on their fate, transport and bioaccumulation in local ecosystems.

15.1. Introduction

Persistent organic pollutants (POPs), including organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) are of significant concern due to their potential toxicity and prevalence in a wide range of environmental media, even at remote geographical locations (Iwata et al., 1994; Kallenborn et al., 1998). Ecotoxicological effects of POPs in the environment have caused much concern in recent years, and this has led to the control or complete ban on the use of these chemicals in many countries. PAHs are mainly derived from incomplete fossil fuel combustion and oil-related discharges to the environment (UNEP, 1997). When released to the aquatic environment, PAHs can adversely impact upon a wide variety of flora and fauna. Chlorinated organic compounds have a wide range of industrial and agricultural applications, and include the pesticides DDT (p,p'-dichlorodiphenyl trichloroethane) and Lindane (γ-hexachlorocyclohexane), as well as the PCBs. The latter have been used historically in an extensive range of industrial applications, including as dielectric fluids in electrical transformers. Such chemicals can readily enter the aquatic environment via atmospheric deposition, groundwater leaching, soil run-off and sewage discharge (Harrad, 2000), and subsequently impact the marine ecosystem.

POPs are known to adversely affect the endocrine system in both wild fauna and humans, have a propensity to bioaccumulate in the lipid fraction of biological tissues and are subject to biomagnification in both terrestrial and aquatic food webs (Li et al., 2006). POPs are also highly recalcitrant to chemical and biological degradation, and therefore persist in the environment for long periods. Humans are chronically exposed to environmental POPs via the ingestion and inhalation pathways (Duarte-Davidson and Jones, 1994), and many such compounds have been detected in a range of human tissues including serum, breast milk and adipose tissue (Dewailly et al., 1993; Newsome et al., 1995). In 2001, many countries signed the Stockholm Convention under the United Nations Environment Programme (UNEP) to implement measures to reduce and eliminate the release of POPs into the environment, including bans on production, import, export, and use of certain POPs (UNEP 2001).

Singapore is one of the busiest ports in the world with an annual visiting shipping tonnage in excess of 857 million gross tons per year, representing more than 140,000 ship movements (Nautilus, 1999). In addition, many ship building yards, petroleum refineries and pharmaceutical manufacturing plants are located along the coastline and are associated with both operational and fugitive discharges of POPs. Data on the prevalence of POPs in Singapore's coastal waters is therefore important in order to support research on potential threats to the local marine ecosystem and human health. This chapter presents data on the prevalence of POPS in the seawater, sediments, biota and mangrove habitats in Singapore's coastal marine environment.

15.2. POPs in seawater

Marine water samples within 1 km of the coastline of Singapore were analysed to determine prevalent concentrations of a range of POPs by Basheer et al. (2003a). Samples were collected from 0.5 m and mid-depth (approximately 14 m depth) at 22 coastal locations (Fig. 15.1). POPs analysed are classed as USEPA priority pollutants, and included: 16 PAHs; 8 PCBs; and 12 OCPs.

15.2.1. Polycyclic aromatic hydrocarbons

The individual and total concentrations of PAHs at surface (S) and mid-depth (M) for northeastern (NE) and southwestern (SW) sampling locations are shown in Tables 15.1a and 15.1b, respectively. All 16 PAHs were detected in all water samples from both depths at every sample location. Total PAH concentrations in seawater ranged from 93.0 to 1419.6 ng L^{-1} and from 88.4 to 1472.8 ng L^{-1} in the northeastern and southwestern region, respectively. The overall mean total PAH concentrations for seawater depth levels were as follows: surface, 235.1 ± 46.2 ng L^{-1}; and mid-depth, 343.1 ± 61.5 ng L^{-1}. The highest total PAH concentrations measured in the northeastern and the southwestern regions were at stations NE-02 and SW-02, respectively. These two stations are in the vicinity of shipyards and industrialized coastal areas (i.e., Jurong and Sembawang). The lowest concentrations of total PAHs for these regions were at NE-12 and SW-04. Both of these locations are remote from industrial areas and the water column is well mixed by strong oceanic currents. Among the 16 PAHs measured, the highest individual PAH concentrations measured were for six ring indeno[1,2,3-*cd*]pyrene i.e., 712.9 ng L^{-1} and 218.8 ng L^{-1} at northeastern and

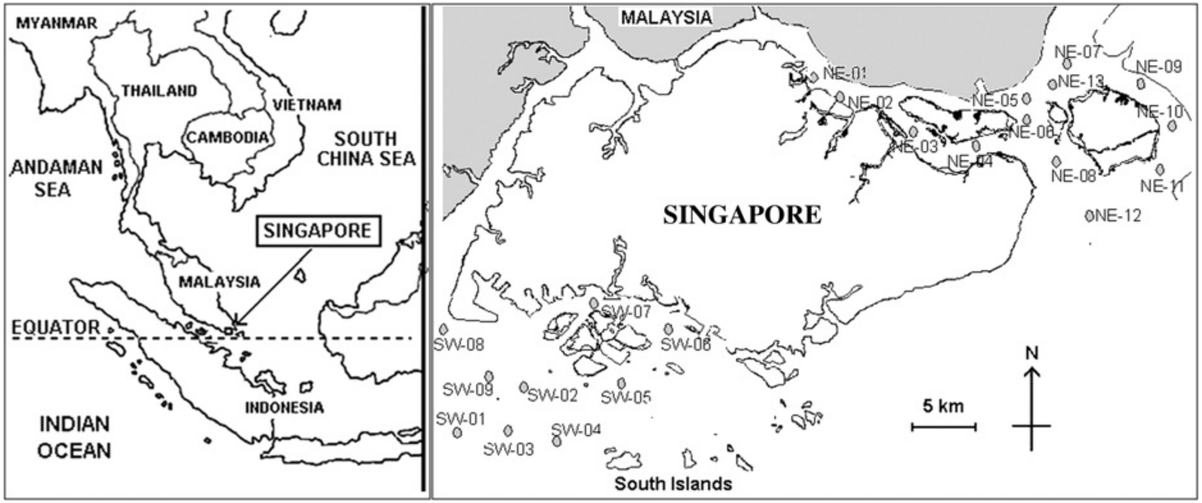

Figure 15.1. Sample locations in the northeastern and southwestern regions of Singapore's Coastal Waters.

Table 15.1a. Concentration of PAHs in seawater of the northeastern coastal region of Singapore (ng L^{-1})

	NE-01		NE-02		NE-03		NE-04		NE-05		NE-06	
	S	M	S	M	S	M	S	M	S	M	S	M
Naphthalene	0.68	2.41	2.62	4.32	2.20	1.92	2.49	3.87	2.07	2.19	2.85	0.22
Acenaphthylene	nd	0.66	0.64	0.52	0.69	0.18	0.73	0.64	0.17	0.61	0.51	0.30
Acenaphthene	0.12	1.11	0.93	1.17	0.58	0.43	0.96	1.14	0.64	0.23	1.01	0.03
Fluorene	0.85	0.39	0.49	1.14	1.12	1.19	1.14	0.61	0.68	0.85	1.63	0.68
Phenanthrene	2.73	4.06	5.87	4.49	10.82	1.00	6.50	3.63	4.50	1.96	2.87	1.72
Anthracene	16.68	30.03	48.64	37.41	73.66	8.73	45.56	22.33	23.42	6.48	24.32	11.81
Fluoranthene	1.18	4.53	2.04	2.44	3.37	1.11	2.30	0.97	5.18	0.84	0.86	1.00
Pyrene	5.96	19.41	3.27	6.20	16.96	5.61	14.85	4.91	5.26	4.21	4.33	5.03
Benz[*a*]anthracene	3.99	4.65	6.89	6.02	1.59	1.37	3.77	4.38	6.29	6.62	5.14	1.86
Chrysene	2.41	9.30	13.79	2.74	3.17	2.74	7.55	8.10	2.08	13.24	10.29	1.86
Benzo[*a*]fluoranthene	11.88	11.60	4.18	4.05	15.10	5.88	9.07	18.06	17.05	5.52	8.84	13.86
Benzo[*k*]fluoranthene	3.71	3.02	2.77	3.56	20.57	5.89	3.30	30.38	9.04	5.54	5.31	7.52
Benzo[*a*]pyrene	6.01	1.53	2.12	0.94	7.64	2.77	1.74	9.14	5.44	2.80	4.47	3.80
Indeno[1,2,3-*cd*]pyrene	54.51	86.48	22.89	189.68	607.92	97.75	136.26	526.53	66.13	214.03	343.02	53.42
Dibenz[*a,h*]anthacene	5.56	4.11	2.27	22.95	403.08	4.22	6.28	68.12	10.43	10.82	27.93	6.10
Benzo[*ghi*]perylene	5.41	2.63	2.27	22.93	251.10	9.70	13.52	68.06	6.56	7.21	34.03	4.94
Sum	121.69	185.93	121.69	310.52	1419.57	150.49	256.03	770.86	164.95	283.14	477.40	114.13

Table 15.1a. (*Continued*)

NE-07		NE-08		NE-09		NE-10		NE-11		NE-12		NE-13	
S	M	S	M	S	M	S	M	S	M	S	M	S	M
0.41	0.56	1.78	1.62	2.49	1.67	3.55	0.69	0.41	0.23	0.43	0.84	0.38	1.84
0.72	1.26	1.33	0.53	nd	0.57	0.44	0.17	0.40	0.51	0.35	0.12	0.15	1.01
0.23	0.22	0.18	0.56	0.57	0.66	1.30	0.32	0.34	0.16	0.45	0.14	0.26	0.58
1.36	1.16	2.69	0.33	0.28	1.44	1.87	0.34	1.28	0.62	0.92	0.29	1.03	0.58
3.46	2.72	11.55	1.65	1.37	2.87	7.66	3.23	4.95	1.68	1.48	3.86	3.01	3.23
14.05	15.46	77.96	18.99	8.09	21.30	49.02	26.76	23.93	15.40	31.70	34.52	23.10	17.52
1.56	2.81	5.01	5.25	2.92	0.51	1.07	1.97	0.70	3.09	0.67	2.92	2.09	1.51
5.03	10.17	25.26	4.56	14.73	8.19	5.38	9.94	3.51	15.55	3.39	14.73	6.78	10.06
3.77	5.96	1.59	3.17	2.52	3.72	2.52	0.88	2.68	4.87	5.63	8.48	4.65	5.74
7.55	7.77	3.17	16.53	4.82	7.44	5.14	7.66	1.31	9.74	4.27	16.96	9.30	3.17
17.58	3.85	6.74	2.99	17.96	5.29	1.19	6.36	18.52	7.40	9.45	9.42	11.02	15.45
9.45	13.79	6.76	7.24	15.01	5.31	29.28	1.73	18.57	7.42	3.10	5.21	11.05	6.76
7.50	5.28	3.41	0.90	7.58	2.68	5.28	2.36	9.37	3.74	1.56	4.38	5.58	3.77
91.21	133.36	194.40	328.13	107.92	437.50	418.97	180.23	712.94	119.91	24.71	23.26	308.87	41.79
5.45	13.24	19.30	32.58	9.85	43.44	78.84	9.20	70.79	4.73	2.45	2.31	30.67	4.15
4.51	4.00	19.28	4.72	9.84	43.40	78.76	9.19	70.72	5.44	2.45	2.31	30.64	4.15
173.83	221.63	380.43	429.75	205.94	586.00	690.28	261.03	940.41	200.49	93.02	129.77	448.58	121.30

Table 15.1b. Concentration of PAHs in seawater of the southwestern coastal region of Singapore (ng L^{-1})

	SW-01		SW-02		SW-03		SW-04		SW-05		SW-06		SW-07		SW-08		SW-09	
	S	M	S	M	S	M	S	M	S	M	S	M	S	M	S	M	S	M
Naphthalene	0.86	1.23	0.62	0.55	2.66	0.84	0.31	0.88	2.68	1.29	0.69	0.65	2.49	0.34	0.46	1.40	0.76	0.40
Acenaphthylene	0.80	0.85	0.17	0.77	1.20	nd	0.52	0.77	1.90	0.70	0.38	0.30	1.49	0.79	0.40	0.54	0.62	0.27
Acenaphthene	0.20	0.20	0.16	0.31	0.96	0.28	0.11	0.24	0.39	0.43	0.35	0.15	0.52	0.14	0.08	0.38	0.16	0.19
Fluorene	0.92	2.02	0.88	1.05	3.92	1.67	1.45	2.35	3.73	1.94	0.95	2.25	2.97	1.21	1.21	1.54	1.51	1.60
Phenanthrene	3.19	4.63	4.43	9.48	6.37	5.13	2.04	1.97	3.77	4.32	1.65	9.05	6.28	0.31	1.79	7.28	3.05	1.78
Anthracene	14.89	36.70	15.72	63.85	31.96	18.10	7.76	20.21	23.29	31.57	nd	59.42	37.28	11.36	16.30	59.93	24.38	17.77
Fluoranthene	2.09	2.99	3.74	1.37	4.62	2.79	3.39	3.04	4.76	1.81	1.62	1.56	4.02	0.81	2.97	5.32	1.44	0.97
Pyrene	10.52	3.86	11.11	9.47	23.27	13.80	12.63	15.32	23.97	9.12	8.19	16.14	20.23	4.09	4.91	26.78	7.25	4.91
Benz[*a*]anthracene	3.50	3.23	2.68	1.64	7.22	4.38	1.09	5.09	9.13	6.13	0.82	0.88	3.12	7.44	7.38	6.13	5.91	4.16
Chrysene	7.00	61.40	4.16	3.28	9.08	8.76	2.41	4.60	18.28	12.26	2.95	15.21	5.03	5.03	12.48	9.63	11.82	8.32
Benzo[*a*]fluoranthene	15.10	14.21	11.27	29.31	25.94	6.28	13.60	14.31	5.42	14.87	4.21	4.76	19.56	9.40	10.49	31.69	1.70	15.71
Benzo[*k*]fluoranthene	5.13	8.13	4.04	29.39	26.01	3.48	10.49	15.32	5.44	17.07	5.54	4.77	16.51	9.42	5.28	31.77	5.13	13.64
Benzo[*a*]pyrene	1.29	4.10	3.03	14.83	4.76	3.18	6.06	12.40	3.77	8.62	2.13	2.09	8.99	4.76	1.17	8.18	0.86	5.60
Indeno[1,2,3-*cd*]pyrene	86.85	196.22	93.75	73.75	218.75	76.67	22.17	200.94	38.15	198.04	140.26	103.92	175.51	90.48	90.12	85.76	146.80	210.76
Dibenz[*a,h*]anthacene	8.62	14.00	7.54	502.13	7.90	7.61	2.20	19.95	3.79	19.67	5.27	13.93	14.76	8.98	5.02	6.03	14.58	11.58
Benzo[*ghi*]perylene	8.62	19.47	7.53	731.56	7.89	4.29	2.20	19.93	3.78	7.32	11.03	11.68	17.41	3.78	8.94	16.55	14.56	9.84
Sum	169.58	373.24	170.84	1472.75	382.51	157.25	88.44	337.32	152.26	335.13	186.03	246.76	336.15	158.36	168.99	298.91	240.54	307.51

southwestern regions, respectively. The lowest concentrations of acenapthylene detected (three ring) were 1.3 ng L^{-1} and 1.9 ng L^{-1}, respectively. This distribution profile may reflect the different properties of low and high molecular weight PAHs, where low molecular weight compounds have higher vapour pressure and water solubility, and are therefore more readily volatilized and degraded by microbial activity. In contrast, higher molecular weight PAHs are more likely to be associated with the particulate phase within the water column and undergo sedimentation, thereby accounting for their higher concentration at mid-depth. Similar vertical distributions have been previously noted in a study of Baltic coastal waters by Broman et al. (1991). At mid-depth, PAHs were dominated by indeno[1,2,3-*cd*]pyrene, but other abundant compounds included dibenzo[*ah*]anthracene, benzo[*ghi*]perylene and anthracene.

Overall, higher molecular PAH compounds were more prevalent in Singapore coastal waters than lower molecular weight compounds. The prevailing ocean currents in the region most likely govern the fate of PAHs, and the presence of localized high levels of PAHs may be a function of petroleum discharges from shipping and the petrochemical industry where hydrocarbons rapidly become associated with both hydrophobic organic and suspended particulates (Capone and Bauer, 1992). In the coastal waters of Singapore, land reclamation activity may also be an additional factor in the increase of POPs in the water column. POPs are readily released from sediments and transported to the water column as a result of disassociation or and solubility of colloidal organic matter upon suspension.

The highest total PAH concentration detected in Singapore's coastal waters (i.e., 1472.8 ng L^{-1}) is greater than that reported for Xiamen Harbour, China (i.e., up to 945 ng L^{-1}; Zhou et al., 2000); the German-Baltic sea (i.e., 6.7 ng L^{-1}; Witt, 1995); the Coral Sea, Australia (i.e., 240 ng L^{-1}; Smith et al., 1987); Chesapeake Bay, USA (i.e., 14.05 ng L^{-1}; Ko and Baker, 1995); the Northwestern Black Sea, Ukraine (i.e., 0.7 ng L^{-1}; Maldonado et al., 1999); and Admiralty Bay, Antarctica (i.e., 80 ng L^{-1}; Bícego et al., 1996), but lower than concentrations reported for Rhode Island, USA (i.e., 115,000 ng L^{-1}) during an oil spill event (Reddy and Quinn, 1999). Overall, the data indicates extensive PAH contamination of Singapore's coastal waters.

15.2.2. Organochlorine pesticides (OCPs)

The individual and total concentrations of OCPs at surface and mid-depth for northeastern and southwestern sampling locations are shown in Tables 15.2a and 15.2b, respectively. In Singapore, extensive agricultural

Table 15.2a. Concentration of OCPs and PCBs in seawater of the northeastern coastal region of Singapore (ng L^{-1})

POPs	NE-01		NE-02		NE-03		NE-04		NE-05		NE-06	
	S	M	S	M	S	M	S	M	S	M	S	M
OCPs												
α-BHC	0.39	0.42	0.15	0.82	1.42	0.13	0.21	0.96	0.45	0.14	2.29	0.41
Lindane	0.02	0.06	0.02	0.02	0.21	0.03	0.03	0.14	0.07	0.02	0.34	0.06
β-BHC	11.41	4.92	4.14	3.12	2.31	2.39	5.01	8.22	8.74	6.37	3.24	2.59
Heptachlor	0.07	0.04	0.05	0.03	0.03	0.04	0.03	0.16	0.02	0.06	0.14	0.04
Aldrin	0.18	0.27	0.06	0.45	0.55	0.06	0.15	1.26	0.05	0.02	0.58	0.03
Dieldrin	3.84	1.12	2.27	1.92	3.48	3.48	0.34	1.71	2.03	2.74	0.96	1.68
Endrin	1.81	0.23	0.37	0.52	nd	0.48	0.42	0.34	1.71	1.87	1.13	0.71
Endosulfan II	0.07	0.14	nd	0.48	0.58	nd	nd	1.03	0.23	0.07	0.32	0.30
p,p′-DDD	0.06	0.06	0.09	0.32	0.52	0.03	0.08	0.76	0.05	0.08	0.22	0.02
p,p′-DDT	0.07	0.02	0.05	0.19	0.67	0.02	0.05	0.72	0.02	0.02	0.36	nd
Endrin aldehyde	0.13	nd	nd	nd	0.33	nd	0.21	nd	nd	nd	nd	nd
Methoxychlor	nd	nd	nd	nd	0.02	nd	nd	0.01	nd	nd	nd	nd
Sum	18.05	7.27	7.20	7.86	10.13	6.67	6.54	15.32	13.37	11.40	9.57	5.84
PCBs												
2-Chlorobiphenyl	0.01	0.03	0.01	0.02	nd	0.01	0.43	0.05	0.02	nd	0.43	nd
2,3-Dichlorobiphenyl	0.15	0.09	4.95	2.19	0.03	0.57	5.65	0.42	0.44	0.04	5.65	0.11
2,4,5-Trichlorobiphenyl	0.04	0.07	0.08	0.01	0.01	0.05	0.02	0.04	0.05	nd	0.13	0.04
2,2′,4,4′-Tetrachlorobiphenyl	0.12	0.03	0.10	0.08	0.09	nd	0.97	0.03	0.07	nd	0.97	0.06
2,2′,3′,4,6-Pentachlorbiphenyl	0.02	0.01	4.40	1.56	0.05	0.27	1.42	0.19	0.24	nd	4.17	0.10
2,2′,4,4′,5,6′-Hexachlorobiphenyl	0.02	0.01	1.33	0.19	0.08	0.06	0.54	0.04	0.04	nd	0.54	0.07
2,2′,3,3′,4,4′,6-Heptachlorobiphenyl	nd	0.08	0.05	0.11	nd	0.07	nd	0.03	0.04	nd	0.04	0.08
2,2′,3,3′,4,5′,6,6′-Octachlorobiphenyl	0.03	0.03	8.50	6.64	1.75	1.59	3.54	0.86	1.04	nd	3.54	0.12
Sum	0.38	0.35	19.42	10.79	2.01	2.62	12.55	1.65	1.94	0.04	15.46	0.57

Table 15.2a. (*Continued*)

NE-07		NE-08		NE-09		NE-10		NE-11		NE-12		NE-13	
S	M	S	M	S	M	S	M	S	M	S	M	S	M
OCPs													
nd	0.54	0.87	0.26	nd	0.77	0.97	0.22	0.29	0.14	0.55	0.25	0.50	0.84
nd	0.02	0.13	0.02	nd	0.12	0.15	0.04	0.04	0.07	0.03	0.04	0.07	0.13
3.72	3.99	5.93	6.70	1.93	6.36	6.42	6.11	15.16	10.24	6.97	1.68	17.87	5.72
0.03	0.04	0.04	0.06	0.03	0.03	0.05	0.10	0.03	0.06	0.05	0.02	0.02	0.09
0.03	0.11	0.58	0.06	0.06	0.65	1.48	0.10	0.38	0.05	0.03	0.02	0.03	1.08
1.92	2.63	2.45	1.21	3.41	3.40	6.91	2.06	2.28	2.05	0.76	1.61	1.68	1.42
0.24	0.33	1.21	0.34	nd	0.66	0.22	0.40	0.98	nd	0.61	0.26	1.33	0.58
nd	nd	0.53	nd	nd	1.29	1.77	nd	0.30	0.16	nd	nd	0.23	0.73
0.01	0.03	0.36	0.10	0.02	0.65	1.17	0.05	0.27	0.14	0.04	0.11	0.10	0.29
0.17	0.08	0.29	0.04	0.03	0.46	1.41	0.04	0.20	0.05	0.04	0.10	0.10	0.37
nd	nd	nd	nd	nd	nd	0.13	nd	0.15	nd	nd	nd	0.11	nd
nd	nd	nd	nd	nd	nd	0.01	nd	0.01	nd	nd	nd	0.02	nd
6.11	7.77	12.39	8.78	5.47	14.38	20.70	9.13	20.09	12.96	9.10	4.09	22.04	11.24
PCBs													
0.08	0.02	nd	0.01	nd	0.00	nd	0.03	0.04	0.02	0.02	0.06	0.06	0.04
0.01	0.06	0.07	0.10	0.04	0.13	0.03	0.08	1.77	0.06	0.65	0.09	12.16	4.17
0.02	0.41	0.09	0.07	0.03	0.01	0.01	0.04	0.16	0.04	1.00	0.08	0.59	0.04
0.30	nd	0.02	nd	0.07	0.02	0.01	nd	0.02	0.06	0.01	0.06	nd	nd
0.53	0.06	1.12	0.09	0.10	0.04	0.22	0.05	0.89	0.44	0.44	0.01	7.34	2.39
0.11	0.05	0.03	0.03	0.08	0.07	nd	0.04	0.14	0.03	0.04	nd	0.84	0.36
0.03	0.04	0.02	0.10	0.02	0.02	0.06	0.07	0.03	0.11	0.04	0.08	0.07	nd
2.66	2.19	0.19	0.18	2.12	0.09	0.30	0.13	5.11	0.21	1.23	0.07	40.71	12.10
3.75	2.82	1.54	0.57	2.46	0.38	0.65	0.43	8.15	0.97	3.44	0.45	61.76	19.11

Table 15.2b. Concentration of OCPs and PCBs in seawater of the southwestern coastal region of Singapore (ng L^{-1})

POPs	SW-01		SW-02		SW-03		SW-04		SW-05		SW-06		SW-07		SW-08		SW-09	
	S	M	S	M	S	M	S	M	S	M	S	M	S	M	S	M	S	M
OCPs																		
α-BHC	0.46	0.35	0.14	0.90	0.10	0.94	0.81	0.94	1.19	0.28	0.72	0.34	0.39	nd	0.12	1.10	0.77	0.63
Lindane	0.07	0.02	0.02	0.14	0.02	0.14	0.12	0.14	0.18	0.04	0.03	0.05	0.07	nd	0.02	0.17	0.12	0.01
β-BHC	2.32	6.49	1.85	6.29	11.45	3.38	8.14	3.38	10.12	3.36	3.14	1.11	4.95	2.89	2.09	15.08	6.36	6.69
Heptachlor	0.03	0.04	0.04	0.02	0.03	0.08	0.03	0.08	0.03	0.05	0.06	0.03	0.04	0.10	0.12	0.10	0.03	0.04
Aldrin	0.04	0.13	0.13	1.17	0.02	0.05	0.04	0.05	1.03	0.12	0.07	0.04	0.05	0.03	0.06	0.68	0.65	0.13
Dieldrin	1.72	0.82	0.22	5.21	0.75	1.14	0.33	1.14	2.78	1.48	0.58	2.44	1.33	1.23	0.91	2.52	3.40	0.88
Endrin	0.29	1.18	nd	0.32	0.31	0.24	nd	0.24	1.78	0.20	0.18	nd	0.50	0.36	0.30	0.21	0.66	0.81
Endosulfan II	nd	nd	0.52	1.24	nd	nd	nd	nd	0.95	nd	nd	nd	0.07	nd	nd	0.99	1.29	nd
p,p′-DDD	0.05	0.03	0.03	0.81	0.02	0.04	0.06	0.04	0.62	0.03	0.02	0.05	0.04	0.04	0.05	0.41	0.65	0.11
p,p′-DDT	0.06	0.05	nd	1.12	0.05	0.05	0.05	0.05	0.62	0.07	0.09	0.05	0.06	0.04	0.08	0.50	0.46	0.06
Endrin aldehyde	nd	nd	nd	0.16	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.16	nd	nd
Methoxychlor	0.01	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.00	nd	nd	0.01	nd	0.01
Sum	5.06	9.13	2.95	17.38	12.76	6.06	9.57	6.06	19.30	5.63	4.90	4.12	7.50	4.69	3.75	21.93	14.38	9.37
PCBs																		
2-Chlorobiphenyl	0.03	0.06	0.01	0.05	0.02	0.06	0.05	0.04	0.14	nd	0.03	0.03	0.08	0.04	0.03	0.02	0.04	0.02
2,3-Dichlorobiphenyl	0.18	0.14	0.46	0.03	0.09	0.05	0.02	0.06	0.06	0.06	0.06	0.04	5.98	0.07	0.33	0.04	0.40	4.01
2,4,5-Trichlorobiphenyl	0.01	1.10	0.07	0.01	0.01	0.03	0.02	0.07	0.02	0.03	0.01	0.84	0.02	1.12	0.02	0.02	0.04	0.21
2,2′,4,4′-Tetrachlorobiphenyl	nd	nd	2.78	0.09	nd	0.04	0.01	0.02	0.03	0.07	0.09	0.01	0.07	0.01	0.10	0.07	nd	nd
2,2′,3′,4,6-Pentachlorbiphenyl	nd	0.04	4.17	0.07	nd	0.10	0.02	0.08	0.02	0.04	0.08	0.06	4.62	0.06	0.22	0.02	0.24	0.28
2,2′,4,4′,5,6′-Hexachlorobiphenyl	nd	0.07	0.51	0.00	0.01	nd	nd	0.04	0.01	0.03	nd	0.05	0.83	0.02	0.02	0.04	0.05	0.42
2,2′,3,3′,4,4′,6-Heptachlorobiphenyl	nd	0.18	0.06	nd	0.11	nd	0.02	0.12	0.18	0.02	0.10	nd	0.11	0.02	0.07	0.04	0.02	0.05
2,2′,3,3′,4,5′,6,6′-Octachlorobiphenyl	nd	0.14	4.15	0.03	0.14	0.14	0.10	0.08	0.18	0.12	0.16	0.09	2.47	0.78	0.58	0.24	0.78	15.42
Sum	0.22	1.72	12.21	0.28	0.38	0.41	0.24	0.51	0.62	0.36	0.52	1.12	14.19	2.13	1.37	0.49	1.57	20.41

activities have been phased out for more than two decades. Although some minimal agricultural activities remain, they do not generally involve extensive use of the types of pesticides discussed in the present work. However, OCPs were detected in samples taken at both depths from all locations from both the northeastern and southwestern regions.

Total OCP concentrations ranged from 4.0 to 22.0 ng L^{-1} and 3.0 to 21.9 ng L^{-1} at the northeastern and southwestern regions, respectively. The highest total OCP concentrations occurred in the northeastern region at location NE-13 (i.e., 22.0 ng L^{-1}) and in the southwestern region at location SW-08 (i.e., 21.9 ng L^{-1}). Overall, higher concentrations were detected in the northeastern region, which is most likely due to the confined configuration of the coast, and the presence of the Pasir Gudong river estuary, which limits hydrodynamic dispersion of contaminants. This river runs across agricultural, commercial and industrial land in Malaysia and into the Straits of Johor, adjacent to Singapore. Lindane (BHC) and Dieldrin were the most abundant pesticides present and their levels ranged from 0.13 to 17.87 ng L^{-1} and 0.34 to 6.91 ng L^{-1} in northeastern and southwestern regions, respectively. In both regions, the highest concentrations recorded were: Lindane, 0.34 ng L^{-1}; Endrin, 1.97 ng L^{-1}; *p,p′*-DDT, 1.14 ng L^{-1}; and *p,p′*-DDD, 1.17 ng L^{-1}.

OCPs are, to a variable extent, insoluble in seawater (not more than 1 ppb), but are readily soluble in fat and adsorb strongly onto suspended particulates in the water column. The surface layer of the sea comprises a film of about 1 mm of thickness, which is known to contain surfactants, protein and lipids. Due to the lipophilic and persistent nature of OCP, accumulation in this surface layer is known to occur (Zhou and Rowland, 1997). OCP enrichment of the surface film may be of considerable importance to surface living organisms or to birds that skim food off the sea surface. Surface plankton and other organic particulates are readily associated with OCPs and undergo subsequent sedimentation. At the following locations higher amounts of OCPs were detected at mid-depth i.e., NE-01, NE-05, NE-09, and SW-01, SW-02, and SW-08. These locations are close to industries and shipping anchorages, where hydrodynamic dispersion is confined.

The land area under agriculture use in Singapore is negligible and there is no direct application of organochlorine pesticides in the country. However, pesticides may be easily transported through the ambient environment by different mechanisms including volatilization from soil and spray drift during application to crops (Dörfler and Scheunert, 1997). The presence of OCPs in Singapore's marine waters is probably a function of their use in neighbouring countries, including Malaysia and Indonesia.

Concentrations of OCPs measured in Singapore seawater are comparatively lower than those detected in water from the Selangor River in Malaysia i.e., Aldrin, up to 884.00 ng L^{-1}; Dieldrin, up to 850.00 ng L^{-1}; Endrin, up to 10,970.00 ng L^{-1}; α-Endosulfan, up to 8.90; β-Endosulfan, up to 12,270.00 ng L^{-1}; Heptachlor, up to 13,710.00 ng L^{-1}; Lindane, up to 4,0950.00 ng L^{-1}; *p,p′*-DDT, up to 44,770.00 ng L^{-1}; *p,p′′*-DDE up to 2310.00 ng L^{-1} (Mustafa et al., 2000); as well as the Surabaya river, Indonesia *p,p′*-DDT up to 49.63 ng L^{-1} (Dewi, 2000); Philippine coastal waters, α-BHC up to 21.00 ng L^{-1} and Aldrin at 7.00 ng L^{-1} of (Santiago, 2000).; the Dampha and Balat estuaries in Vietnam, DDT i.e., 30.00 ng L^{-1} (Viet et al., 2000); Bohai Sea, China, DDE, DDD and DDT up to 50.00 ng L^{-1} (Yeru and Hao, 2000). However, OCP levels in Singapore's coastal waters are higher than those found in the Coral Sea, Australia where total OCP concentrations have been measured at 1.21 ng L^{-1} (Tanabe et al., 1984), and 5.50 ng L^{-1} (Kurtz and Atlas, 1990).

15.2.3. Polychlorinated biphenyls (PCBs)

The individual and total concentrations of PCBs at surface and mid-depth for northeastern and southwestern sampling locations are shown in Tables 15.2a and 15.2b, respectively. PCBs represent a group of compounds that have been widely used in a range of industrial applications. All eight PCBs analysed in the study were detected at each region for the majority of sample stations.

Total PCB concentrations in seawater from both regions varied from 0.04 to 61.7 ng L^{-1} and 0.22 to 20.1 ng L^{-1} in northeastern and southwestern regions, respectively. The highest total concentrations of PCBs measured were at station (NE-13 i.e., 61.7 ng L^{-1}) and SW-09 (i.e., 20.1 ng L^{-1}). The prevalence of PCBs in these locations may be due to their proximity to contamination sources including the industrial sources in the southwest of Singapore, and the Bedok and Slater municipal wastewater treatment plants in the northeast. The highest measured concentration of an individual PCB congener i.e., 2,2′,3,3′,4,5′,6,6′-octachlorobiphenyl was 40.71 ng L^{-1} and 15.42 ng L^{-1} at the northeastern and southwestern regions, respectively.

Long-range atmospheric transport is likely to be a source of PCBs detected in remote waters and results in low-level concentrations in nearly all environmental matrices (Bidleman et al., 1989). However, higher levels can be associated with proximity to industry, as well as waste discharges from shipbuilding yards and municipal sewage plants located in coastal regions. PCBs are hydrophobic compounds with an octanol–water partition coefficient (K_{ow}) ranging from 4.5 to 8.2. The aqueous solubility is less than 5 mg L^{-1} for the more chlorinated congeners (i.e., >2 chloro group) (Patil, 1991). The distribution of PCBs in coastal waters contrasts with that of PAHs, where the surface was more contaminated than at mid-depth for the majority of sample locations. The concentration of PCBs in seawater samples shows that the northeastern coastal region of Singapore is more extensively polluted than the southwestern region. These variations are most likely due to historic and episodic inputs from industrial sources, hydrodynamic factors, as well as possible discharges form Malaysian and Indonesian coastal regions.

The maximum level of PCB contamination detected in Singapore coastal waters (i.e., 61.7 ng L^{-1}) is lower than that recorded from Xiamen, China and Victoria Harbour, Hong Kong (i.e., 151 ng L^{-1}; Hong et al., 1995); Jamaica-Kingston Harbour (i.e., 3500 ng L^{-1}; Mansing and Wilson, 1995); Doñana National Park, Spain (i.e., 237 ng L^{-1}; Fernàndez et al., 1992); and higher than levels measured in the Gulf of Mexico and Atlantic Ocean (North) (i.e., <0.003 ng L^{-1}; Sauer et al., 1989), the Northern Pacific Ocean (i.e., 0.59 ng L^{-1}; Tanabe et al., 1984) and the Dutch Wadden Sea (i.e., 0.62 ng L^{-1}; Duinker and Hillebrand, 1983).

For seawater, it can be concluded that concentrations of PAHs measured in Singapore's coastal waters were generally higher than levels reported elsewhere, and this is most likely due to the presence of Singapore's extensive petroleum industry. Seawater concentrations of OCPs and PCBS are generally lower than the reported levels for other Asian countries, but higher than some levels reported elsewhere in the world. Overall, results from this survey clearly show the prevalence of POPs in Singapore's coastal waters, and the need for further research to fully evaluate their fate, transport and biological impact in the marine environment.

15.3. POPs in the sea-surface microlayer

The sea-surface microlayer (SML) of the ocean represents the boundary layer between the atmosphere and the ocean surface body, and has a typical thickness of 40–100 μm. The SML has a distinctive chemical composition compared to the bulk seawater underneath, including enrichment of naturally occurring surfactants, proteins and lipids. Hydrophobic organic pollutants, like POPs, tend to hyper accumulate in the SML in a range of 0.2–100 as reviewed by Wurl and Obbard (2004). The SML plays an important role in the transfer of material controlled by complex physicochemical processes and may have substantial effects on the global distribution of POPs as hypothesized by Wania et al. (1998). The role of the SML in the air–sea gas exchange of POPs was recently shown using data from field experiments (Wurl et al., 2006).

The first scientific data on POP concentrations and enrichment factors in the SML for Southeast Asia were reported from Singapore's marine environment (Wurl and Obbard, 2005a, 2006). SML samples were collected using a rotating glass drum sampler designed for trace organic analysis and described in details in the same reference. The concentration ranges for ΣHCH, ΣDDT and ΣPCB in the SML were 0.6–64.6 ng L^{-1} (mean 9.9 ng L^{-1}), 0.01–0.7 ng L^{-1} (mean 0.2 ng L^{-1}) and 0.07–12.4 ng L^{-1} (mean 1.3 ng L^{-1}), respectively. In subsurface seawater (1 m depth), the concentration ranges were 0.4–27.2 ng L^{-1} (mean 4.0 ng L^{-1}), 0.01–0.6 ng L^{-1} (mean 0.1 ng L^{-1}) and 0.05–1.8 ng L^{-1} (mean 0.5 ng L^{-1}) respectively. The enrichment factors (EF) in the SML relative to subsurface water for ΣHCH, ΣDDT and ΣPCBs were 0.8–6.9, 0.2–7.6 and 0.7–39.6 respectively, but generally ranged between 1.2 and 4. EF values were higher for temperate climatic zones and were in a range of 0.1–23.1 for an estuary in Argentina (Sericano and Pucci, 1984) and 0.2–93 in coastal offshore waters of Croatia (Picer and Picer, 1992). Comparable EF values of 1.7–3.5 were reported for SML samples collected in the sub-tropical zone of Alexandria (Abd-Allah, 1999). The temporal distribution of contaminants in the SML and subsurface water is related to the rainfall pattern of Singapore during the repeated sampling events between November 2003 and March 2004 (Figs. 15.2–15.4). In general the concentrations during the second survey (January–February) were lower by a factor of up to 50 compared to the first survey (November–December). The concentrations increased during the third survey in March by a factor of up to 10 compared to the previous survey. Rainfall patterns for Singapore in 2003 and 2004 show that most rain fell between October and December 2003 during the northeast monsoon (approximately 250 mm per month) and March 2004 (400 mm), whereas February 2004 had the lowest rainfall incidence (approximately 25 mm) (NEA, 2004). During this study SML and subsurface water prior to and after a heavy rainfall event could be collected for the first time. A load factor (LF) as the enrichment of contaminants before and after rainfall was defined. The LF was insignificant for the subsurface water, but between 2 and 5.9 greater for the SML. It can be concluded that wet deposition is a significant source of POPs to the SML in tropical regions, but not directly for the subsurface water. Removal mechanism of POPs accumulated in the SML may be diffusion to the subsurface water, volatilization into the atmosphere and microbial degradation. Microbial degradation of PCBs in aquatic environments were reported by Sugiura (1992) and elevated concentrations of microorganism and enrichment of inorganic nutrients in the SML (Zaitsev, 1997) may support the microbial degradation of POPs in the SML. Air–sea gas exchange rates between the compartment

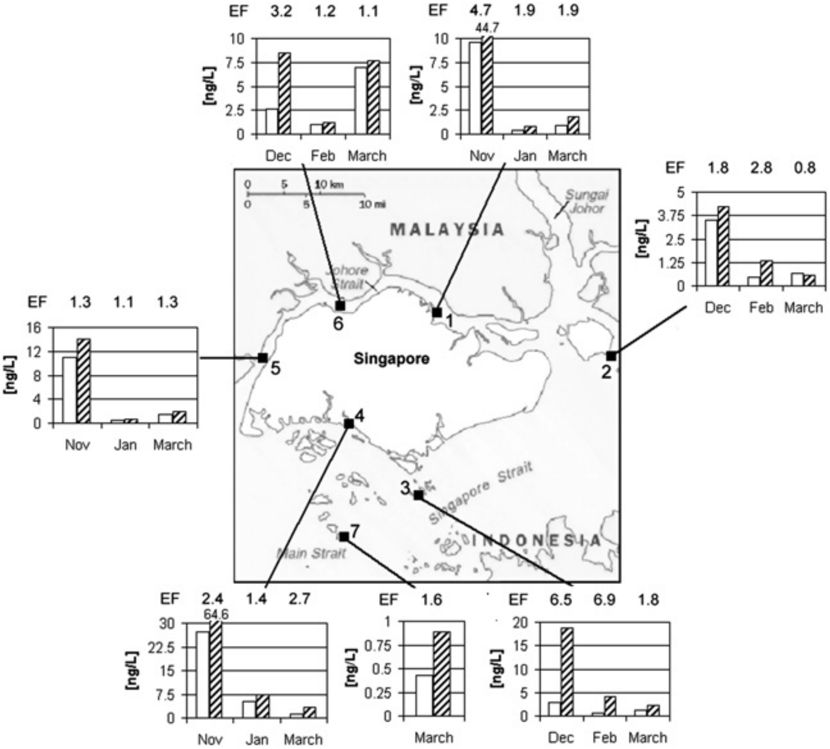

Figure 15.2. Concentrations and enrichment factors (EF) of ΣHCH in seawater (□) and SML (▨)

subsurface seawater and SML with the atmosphere were reported for selected PCBs, and HCHs using a classical two-layer model (Wurl et al., 2006). The model yields flux rates for ΣPCBs, ranging between 27 and 171 ng (m^2 day)$^{-1}$, whereas the values of ΣHCH fluxes are −111–69 ng (m^2 day)$^{-1}$ for the tropical region of Singapore. The negative flux data indicates adsorption of HCH isomers into the ocean. It was shown that physicochemical properties, like *n*-octanol/water partition coefficient and water solubility, may control the enrichment of POPs in the SML. Higher chlorinated PCBs tended to be enriched higher in the SML than lower chlorinated congeners (Wurl and Obbard, 2005a). Good correlations between the relationship between EF values and log K_{ow} support that the *n*-octanol/water partition coefficient is a key parameter for the enrichment of hydrophobic organic contaminants (Fig. 15.5).

In a further study the distribution of PCBs, HCHs and DDTs between the dissolved phase (DP) and suspended particulate matter (SPM) in the

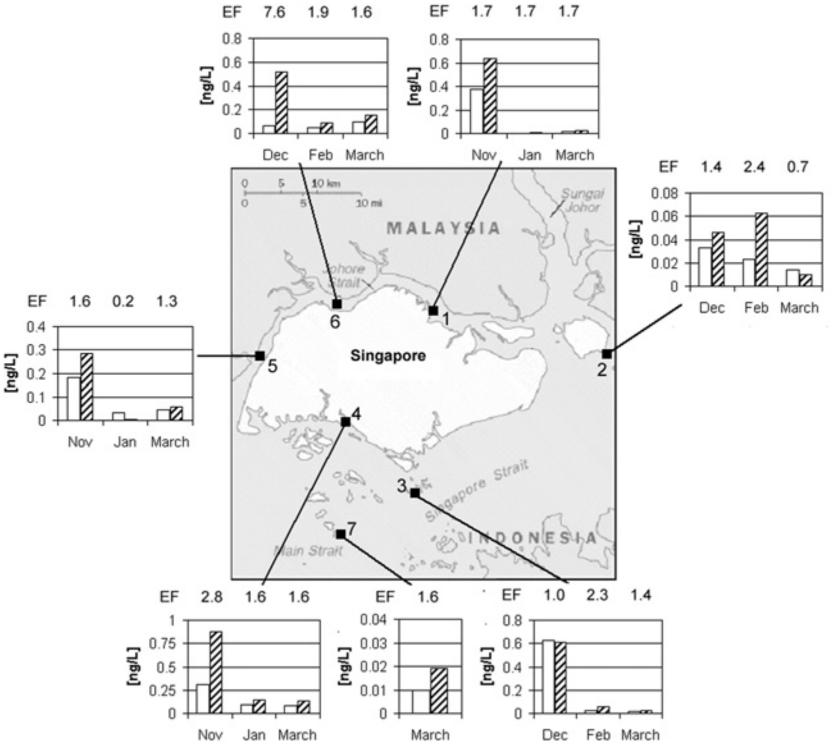

Figure 15.3. Concentrations and enrichment factors (EF) of ΣDDT in seawater (□) and SML (▨).

water column including the SML were investigated at two stations in Singapore's marine environment (Figs. 15.6, 15.7, and 15.8). It was reported that PCBs, HCHs and DDTs in the SML were in general dominant in the DP. The vertical distribution of ΣPCBs in the water column at both stations is similar (Fig. 15.6). Levels of ΣPCBs in the DP increase towards the surface. Enrichment of PCBs in the DP in the SML relative to subsurface water was found to be in the range of 1.3–7.2. Higher concentrations of ΣPCBs in the SPM were found in the bottom water with a trend of declining concentration to mid-depth. Near the surface and in the SML, the ΣPCB concentrations were enriched relative to water at mid-depth. The concentrations of ΣPCBs in the SPM were enriched in the SML by a factor (EF) of 1.2–7.2. This enrichment is most likely derived from small-size and/or flocculated particles floating on the water surface. Enrichment factors of ΣPCBs associated with the SPM in the bottom water at both stations were in the range of 2–3 compared to overlying

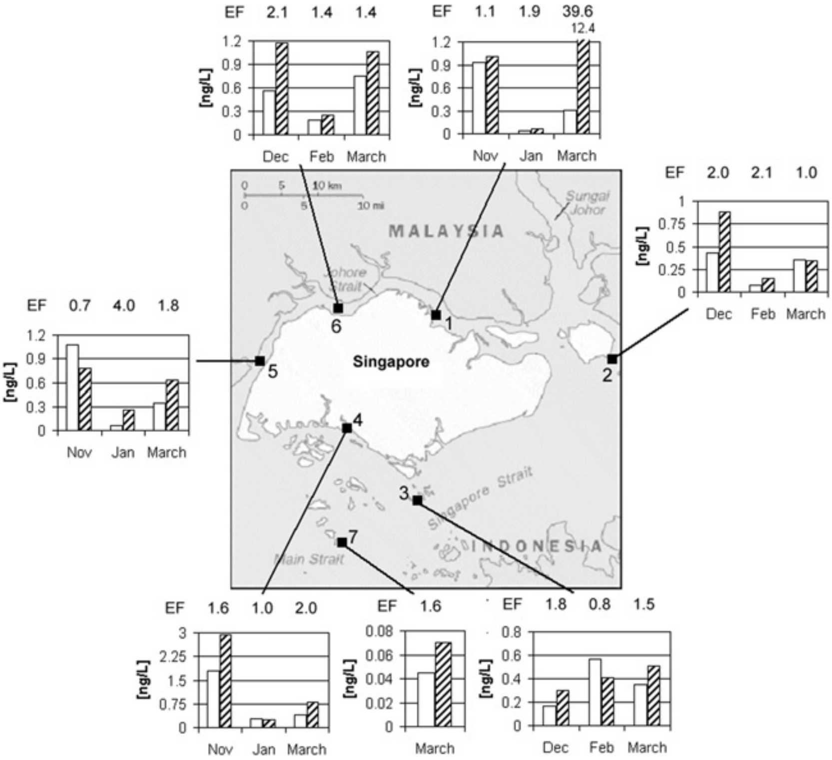

Figure 15.4. Concentrations and enrichment factors (EF) of ΣPCBs in seawater (□) and SML (▨).

water, but no enrichment of SPM was found in this layer at station 2. This phenomenon has also been reported recently for the Black Sea (Maldonado and Bayona, 2002). Different types and sizes of suspended particulates between water layers may lead to an enrichment of contaminant concentrations associated with the SPM, even though SPM itself is not enriched. The vertical distribution profile of OCs at both stations suggests that resuspension processes of contaminated sediments may be a key source of PCBs in the water column. However, wet and dry atmospheric deposition of OCs on the SML may act as secondary source, indicated by the enrichment in the SML.

The vertical profiles of ΣHCHs (Fig. 15.7) were characterized by a depletion in the DP of the bottom water compared to the overlying water at both stations. The trend of concentrations of dissolved HCHs decreased from the mid-depth to the subsurface layer. The vertical profiles for ΣHCHs associated with the SPM were similar at both stations with little

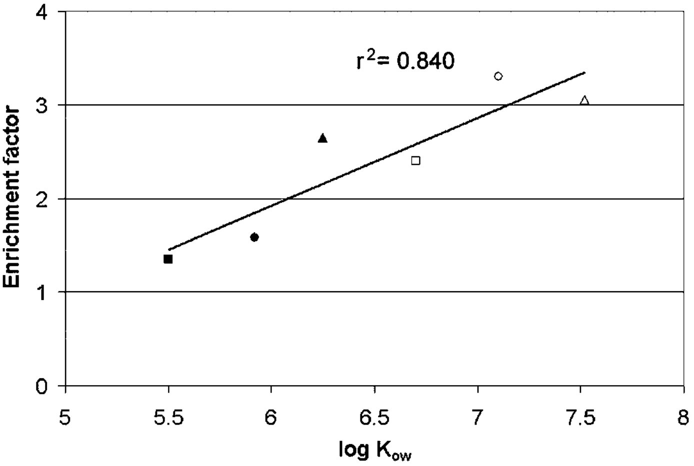

Figure 15.5. Correlation between average log K_{ow} value of tri- (■), tetra- (●), penta- (▲), hexa- (□), hepta- (○) and octa-chlorobiphenyls (Δ) and corresponding average enrichment factors (EF).

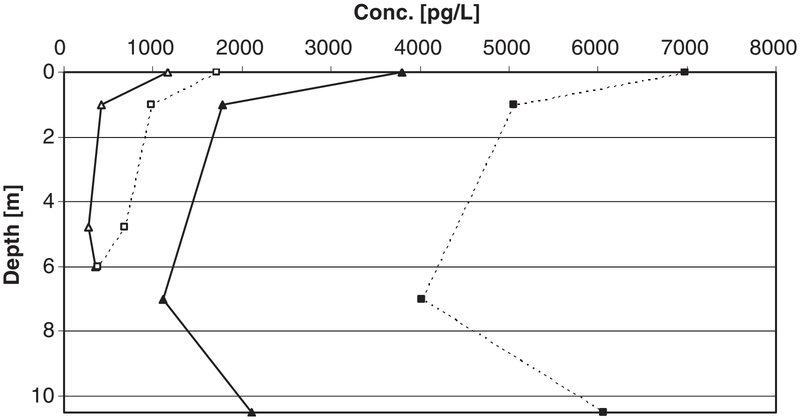

Figure 15.6. Vertical profiles of ΣPCBs in DP (□) and SPM (△) at station 1, and in DP (■) and SPM (▲) at station 2.

variation with depth. Exceptionally, an enrichment in the SML was found in a range of 1.1–7.2. In general the dissolved fraction occupies 60–99% of the total concentration of HCHs. Levels of ΣHCHs in the SPM were not enriched in the bottom water layer for both stations; although a high enrichment of SPM concentrations was apparent in this layer for station 1. This suggests that resuspension of sediments may not be a major source

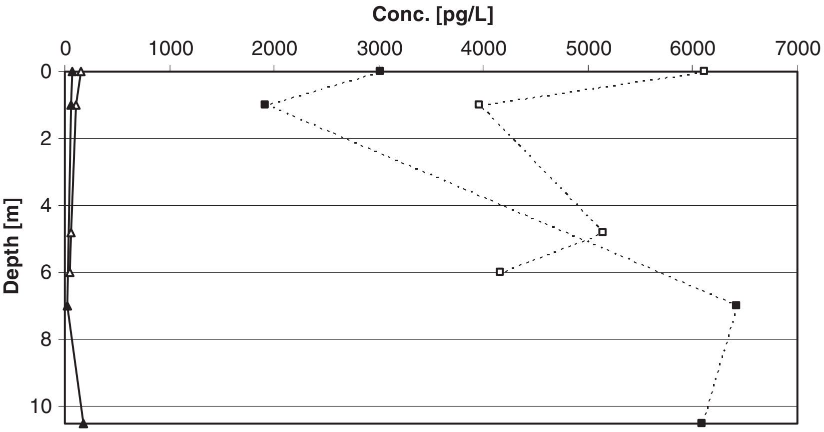

Figure 15.7. Vertical profiles of ΣHCHs in DP (□) and SPM (△) at station 1, and in DP (■) and SPM (▲) at station 2.

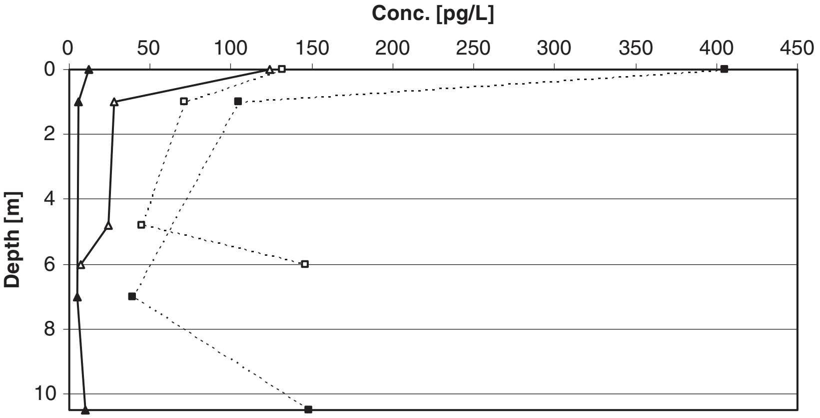

Figure 15.8. Vertical profiles of ΣDDTs in DP (□) and SPM (△) at station 1, and in DP (■) and SPM (▲) at station 2.

for HCHs into the water column. Enrichment in the surface layers of the water column and decreasing concentrations with the depths suggest that freshwater inputs, such as riverine discharge as well as wet and dry atmospheric deposition on the SML are the major inputs of HCHs into the marine water column.

Vertical distribution profiles for DDTs are similar at both stations (Fig. 15.8). An enrichment in the SML and bottom water of DDTs in the DP could be found in both water columns. The trend of concentrations decreased from the surface to the mid-depth layer. From the sub-surface to the bottom water layer, the concentrations in the SPM varied little, but an enrichment in the SML ($EF = 3.3–4.4$) was found. Deposition of atmospheric particulates will result in the enrichment of the SML and represent a source of particulate DDT into the water column. The concentration of DDTs in the Singapore's marine sediments was low compared to levels of PCBs and HCHs (Wurl and Obbard, 2005b), meaning that resuspension processes are unlikely to act as a significant source of DDTs into the water column, where runoff and precipitation inputs are likely to account for the observed enrichment in the SML and subsurface layer. ΣDDTs are known for their lower water solubility and higher affinity to sediments and particles compared to HCH isomers. The fraction of ΣDDTs associated with the SPM were dominant (up to 90%) in the Pearl River Delta (Luo et al., 2004) but not for the Yangtze River, China (Jiang et al., 2000), Danube Estuary and open water in the Black Sea (Maldonado and Bayona, 2002), Mediterranean Sea and estuary areas of the Ebro and Rhone River (Dachs et al., 1996), and coastal area of east Java, Indonesia (Hillebrand et al., 1989). In this study, ΣDDTs in the dissolved fractions represented between 44 and 90% of the total concentration present. This distribution is not consistent with the high K_{ow} values for DDTs. Relatively low carbon content were found in the SPM in this study, and this may affect the adsorption behaviour of OCs on particulates. The small particles and colloids ($<1.0\,\mu m$) of the SPM passed through the filter can be considered as a dissolved fraction. The relative high water temperature in the tropical area of Singapore will increase the solubility of OCs and shift the distribution pattern towards the dissolved fraction. It may be these factors that account for the observed distribution.

The partitioning of HCHs and DDTs between the SPM and DP was qualitatively assessed using the distribution coefficient K'_d and this is illustrated in Fig. 15.9 for station 1 and 2 respectively. The K'_d values for the two stations vary with depth implying that either the water bodies are not well mixed or more likely that the distribution of SPM is hetereogenous. The profile at station 2 (Fig. 15.9) is similar among OCPs. An increase of the K'_d or log K'_d value from the SML to the subsurface water and a decline towards the bottom water is distinctive for the profile at station 2. This may indicate that the characteristics of the water body or the SPM in the SML and subsurface water are different. The SML may be enriched with small or voluminous floating particulates, whereas subsurface water will typically be dominated by denser, sinking particles. The profile at station 1 shows that more HCHs and DDTs in the SPM appear proportionally in the SML and subsurface layer than in the mid-depth layer relative to the DP. The different profiles in the lower

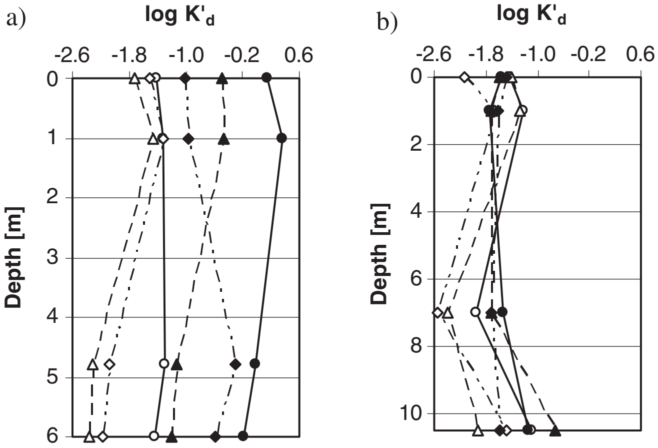

Figure 15.9. The distribution coefficient K'_d of α-HCH (○), γ-HCH (◇), β-HCH (△), *p,p*′-DDE (●), *p,p*′-DDD (◆) and *p,p*′-DDT (▲) with water column depth at station 1 (a) and 2 (b).

water bodies at stations 1 and 2 suggest that sediment resuspension processes at station 1 play a significant role in the release of OCPs into the water column, but only a minor role at station 2. However, the trends in the K'_d value from the SML to the subsurface layer suggest that the SML is another important compartment for the fate of OCPs, with more importance for the DP.

15.4. POPs in marine sediments

PAHs account for approximately 20% of total hydrocarbons present in crude oil, and are the most metabolically toxic of all the petroleum compounds (Neff, 1990). Oil spillage is a global problem where for example, in 1999 approximately 109,400 tons of oil was spilled worldwide into marine and terrestrial environments as the result of over 250 incidents. The Port of Singapore is one of the world's busiest ports, where the total cargo handled in January 2002 alone was in excess of 28.2 million tones (Nautilus, 2002). Singapore's coastal areas have also been extensively developed to support the petroleum industry, where the country is home to the world's third largest petroleum refining centre, with a processing capacity in excess of 1.3 M barrels of crude oil per day (SEDB, 1999). Singapore and the neighboring countries of Malaysia and Indonesia have experienced 10 major oil spill incidents between 1993 and 2002, including a major spillage of 28,500 tons of crude oil in the Singapore Straits in October 1997 (ITOPF, 2007). With continued industrial development and shipping activity within the coastal region of Southeast Asia as a whole, there is clearly an increasing risk of adverse regional marine contamination.

A study was undertaken to determine the prevalence of PAHs in the marine sediments of Singapore's coastal environment by Basheer et al. (2003b). A total of 22 stations were sampled for sediment analysis, as for seawater analysis (see Fig. 15.1). These stations were located in the northeastern (stations NE-1–NE-13) and southwestern (stations SW-1–SW-9) regions of Singapore's coastal environment. Sampling stations were all within 1 km of the coast and adjacent to busy shipping lanes and coastal petroleum refineries. Surface sediments were collected using a Van Veen grab (1000 cm^2 sampling area). Total PAH concentrations in sediments are shown in Fig. 15.10.

All 16 PAHs were detected in all surface marine sediments taken from the 22 sample stations in both the northeastern and southwestern regions of Singapore's coastal environment–see Tables 15.3 and 15.4, respectively. The highest total PAH concentration measured in the northeastern region was $82.4\,\mu g\,g^{-1}$ (at NE-4) and $93.85\,\mu g\,g^{-1}$ in the southwestern region (at SW-9). The lowest total PAH concentration was detected at station NE-3 (i.e., $15.2\,\mu g\,g^{-1}$) and at station SW-4 (i.e., $12.6\,\mu g\,g^{-1}$) for each region respectively. Overall, the concentrations of PAHs in sediments sampled from the northeastern region are comparatively higher than those of the southwestern region (see Tables 15.3 and 15.4), and this is consistent with seawater quality data. In the northeastern coastal region of Singapore, the marine hydrodynamics are relatively confined, as the tidal exchange of Johor Straits is restricted. This is in contrast to the southwest region, where stronger oceanic currents and lower sedimentation rates facilitate particulate dispersion.

Among the 16 individual PAHs quantified, the highest concentrations measured were for four-ring chrysene and six-ring indeno[1,2,3-*cd*]pyrene which reached maximum concentrations of $3.7\,\mu g\,g^{-1}$ and 15. $2\,\mu g\,g^{-1}$ in the northeastern region, and $1.6\,\mu g\,g^{-1}$ and $7.5\,\mu g\,g^{-1}$ in the southwestern region (see Tables 15.3 and 15.4). Other abundant PAHs included benzo[*a*]fluoranthene, anthracene, dibenz[*ah*]anthracene and benzo[*ghi*] perylene. The lowest PAH concentration measured in sediments was for three-ring acenapthylene i.e., up to $0.3\,\mu g\,g^{-1}$ and up to $0.2\,\mu g\,g^{-1}$ in northeastern and southwestern regions, respectively.

The distribution of individual PAHs reflects the different physiochemical properties of low and high molecular weight PAHs, where lower molecular weight compounds have a relatively higher vapour pressure and water solubility, and are therefore more readily volatilized and degraded. Higher molecular PAHs are more readily adsorbed onto the particulate phase and undergo sedimentation. This is reflected in the

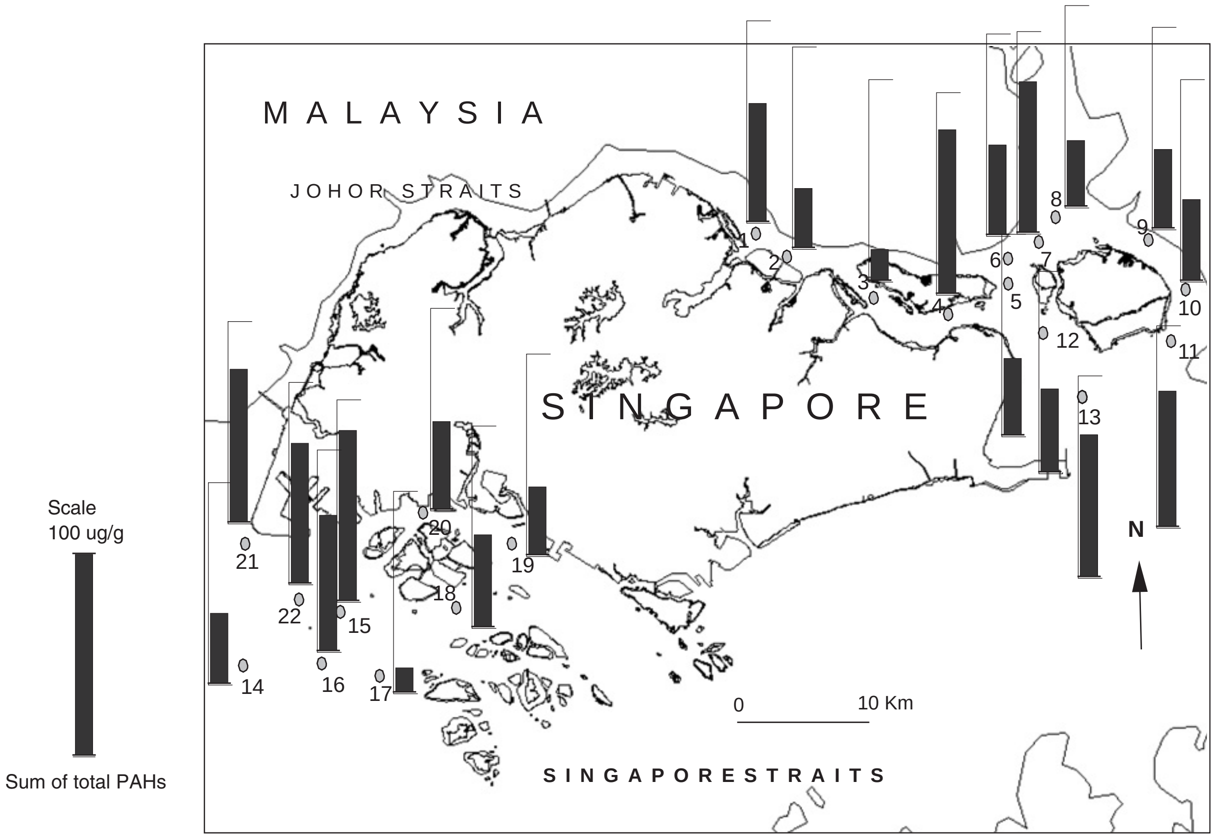

Figure 15.10. Total PAH concentrations in surface marine sediments of Singapore's coastal marine environment.

Table 15.3. Concentrations of PAHs in surface marine sediments of the northeastern coastal region of Singapore (μg g^{-1}, $n = 4$)

Stations	NE-01	NE-02	NE-03	NE-04	NE-05	NE-06	NE-07	NE-08	NE-09	NE-10	NE-11	NE-12	NE-13
Naphthalene	1.02	0.47	0.44	0.51	0.29	0.27	1.28	0.29	1.21	0.48	1.53	0.20	1.05
Acenaphthylene	0.17	0.23	0.05	0.08	0.08	0.09	0.23	0.08	0.24	0.06	0.19	0.06	0.22
Acenaphthalene	0.18	0.13	0.10	0.11	0.06	0.06	0.20	0.03	0.16	0.04	0.27	0.02	0.14
Fluorene	0.39	0.14	0.03	0.10	0.14	1.13	0.25	0.81	1.99	0.06	0.29	1.74	0.70
Phenanthrene	6.72	2.05	1.93	1.35	0.80	1.05	1.80	0.34	0.46	0.77	4.79	0.77	2.00
Anthracene	11.20	7.90	2.66	7.42	3.21	3.36	7.11	1.04	2.74	2.59	17.63	1.55	8.25
Fluoranthene	2.34	0.39	0.14	2.62	0.71	2.17	2.13	0.44	1.19	0.62	1.27	0.46	1.51
Pyrene	5.89	0.98	0.48	6.61	1.80	5.47	5.38	0.75	3.01	1.16	3.22	1.08	3.97
Benz[*a*]anthracene	7.42	0.60	0.03	18.95	5.15	7.18	14.39	0.58	8.06	3.53	7.36	2.89	11.81
Chrysene	7.42	1.27	0.11	25.27	7.07	9.58	19.21	0.77	10.76	4.71	9.82	11.24	15.74
Benzo[*a*]fluoranthene	1.94	3.53	1.46	2.75	3.80	4.47	6.08	3.79	1.62	1.70	1.73	3.05	3.11
Benzo[*k*]fluoranthene	1.94	2.84	2.46	2.48	3.81	2.24	6.09	3.65	1.31	1.72	1.85	3.29	2.82
Benzo[*a*]pyrene	0.98	1.44	1.24	1.25	1.92	1.13	0.99	1.84	0.51	0.86	0.87	0.77	1.57
Indeno[1,2,3-*cd*]pyrene	7.37	5.24	3.66	9.86	5.91	4.34	7.98	12.37	4.48	14.64	11.63	6.037	15.22
Dibenz[*a*,*h*]anthacene	1.70	1.31	0.40	1.54	1.76	1.97	1.09	3.37	1.06	3.95	2.73	1.40	1.81
Benzo[*ghi*]perylene	2.21	1.59	0.01	1.54	1.76	1.10	1.12	3.41	1.02	3.95	2.61	1.59	1.55
Total	58.88	30.12	15.19	82.42	38.25	45.61	75.33	33.58	39.83	40.82	67.78	30.09	71.45

Table 15.4. Concentrations of PAHs in surface marine sediments of the southwestern coastal region of Singapore (μg g^{-1}, $n = 4$)

Stations	SW-01	SW-02	SW-03	SW-04	SW-05	SW-06	SW-07	SW-08	SW-09
Naphthalene	0.45	0.26	0.95	0.14	0.74	0.21	0.30	0.90	0.46
Acenaphthylene	0.08	0.42	0.18	0.08	0.09	0.22	0.13	0.20	0.42
Acenaphthalene	0.09	0.06	0.12	0.05	0.08	0.02	0.03	0.16	0.09
Fluorene	1.35	0.21	1.08	0.09	0.86	0.08	0.28	1.43	2.87
Phenanthrene	1.72	1.01	1.36	0.57	0.75	0.46	1.81	3.84	2.46
Anthracene	6.41	4.15	4.76	2.09	2.98	1.05	6.04	5.26	9.45
Fluoranthene	0.58	4.50	9.33	0.16	2.10	0.42	2.52	1.44	6.53
Pyrene	2.71	22.66	5.43	0.80	10.18	2.14	12.68	6.84	17.71
Benz[*a*]anthracene	3.38	6.12	7.75	0.22	6.30	1.59	2.14	9.10	9.08
Chrysene	8.91	12.24	15.52	0.43	12.60	3.18	4.28	18.20	30.64
Benzo[*a*]fluoranthene	0.66	5.08	5.56	2.25	1.09	1.29	2.02	2.99	3.45
Benzo[*k*]fluoranthene	0.66	5.09	4.88	2.26	1.10	1.45	2.03	2.23	3.46
Benzo[*a*]pyrene	0.29	2.55	2.46	1.13	0.55	0.42	1.02	0.59	0.60
Indeno[1,2,3-*cd*]pyrene	3.92	7.29	7.12	1.63	4.55	5.65	5.05	7.52	3.78
Dibenz[*a*,*h*]anthacene	1.37	6.69	1.50	0.38	1.14	7.99	1.72	2.14	1.36
Benzo[*ghi*]perylene	2.79	6.59	0.37	0.38	1.03	7.98	1.72	13.88	1.48
Total	35.36	84.91	68.36	12.65	46.14	34.15	43.75	76.70	93.85

prevalence of higher molecular PAH found in sediment samples. The distribution of mean individual PAH concentrations is in the sequence of chyrsene > indeno[1,2,3-*cd*]pyrene > pyrene > benzo[*a*]anthracene > anthracene > fluoranthene > benzo[*ghi*]perylene > benz[*a*]fluoranthene > benzo[*k*]fluorantherne > dibenz[*a*]anthracene > phenanthrene > fluorine > benzo[*a*]pyrene > acenapthylene > acenaphthalene> naphthalene. Chrysene and fluoranthene are, therefore, prevalent in the coastal sediments of Singapore. Chrysene is the most abundant PAH and is believed to be a compound mainly derived from natural sources including pentacyclic triterpenes such as α- and β-amyrins which are, in turn, derived from epicuticular waxes of terrestrial plants via the process of microbial degradation (Wakeham et al., 1980). In contrast, fluoranthene is considered a good pollution indicator in environments impacted by urban and industrial activities (Chaudhry, 1994). The distribution pattern of fluoranthene in marine sediments from Singapore is similar and comparatively lower in concentration than previously detected in marine sediments from Australia (McCready et al., 2000).

As PAHs are widespread contaminants produced as a result of natural cycles (e.g., forest fires, plant decomposition and petrogenesis), as well as industrial activities, identification of anthropogenic PAHs contaminant sources is a challenge, particularly as atmospheric emissions are subject to long-range atmospheric transportation processes (Lockhart et al., 1992;

Peters et al., 1995). PAHs in marine sediments have been associated with various particulate sources where, for example, pyrene is typically found in particulates generated from hydrothermal sources, fluorene is associated with submarine volcanic extrusions and chrysene and benzo[*a*]pyrene are specific to the presence of oil (Chernova et al., 2001). Previous studies have vindicated the use of PAH isomer ratios for source identification (e.g., Kayal and Connell, 1989; Klamer and Fomsgaard, 1993). For example, as phenanthrene is a thermodynamically more stable three-ring aromatic isomer than anthracene, the phenanthrene:anthracene ratio has been used to differentiate PAH in the environment of petrogenic origin from those of pyrogenic origin (Klamer and Fomsgaard, 1993; Budzinski et al., 1997). Fluoranthene and pyrene are considered typical pyrogenic products generated from high temperature condensation of low molecular weight compounds (Soclo et al., 2000). During the combustion process, pyrene is more stable than fluoranthene, and hence pyrolytic products are usually characterized by a predominance of fluoranthene over pyrene at ratios greater than one (Baumard et al., 1999). Petrogenic PAH sources are generally characterized by a high ratio (>15), while those of pyrogenic origin have a lower ratio.

The kinetic/thermodynamic isomer ratios of phenanthrene:anthracene (three-ring) and pyrene:fluoranthene (four-ring) were derived from PAH marine sediment data for Singapore, and are shown in Fig. 15.11. An abundance of high molecular weight PAHs is typical of atmospheric

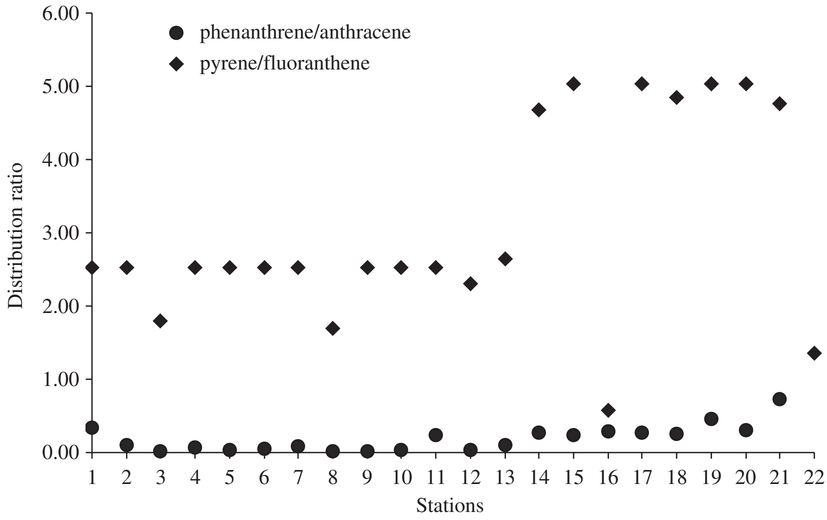

Figure 15.11. Distribution of PAH isomers ratios in surface marine sediments.

particles and urban aerosols (Ogata and Fujisawa, 1990), due to their low water solubility, low microbial degradation rate. The phenanthrene:anthracene ratio in sediments ranged from 0.02 to 0.73, and the pyrene:fluoranthene ratio ranged between 1.30 and 5.03. The relatively low isomer ratio suggests that PAHs of a pyrogenic origin are predominant in Singapore's coastal environment. The prevalence of four- and five-ring aromatic compounds in the sediments from both coastal regions in Singapore further suggests that PAH contamination in the coastal environment is a result of deposition of PAH-rich particulates produced by anthropogenic combustion processes (Muel and Saguem, 1985; Sicre et al., 1987). The survey also shows that the total concentrations of PAHs (based on dry weight) in Singapore's coastal marine sediments (i.e., 93.9 $\mu g\,g^{-1}$) are comparatively lower than that reported for sediments from Victoria Harbour, Hong Kong (i.e., up to 387 $\mu g\,g^{-1}$; Environmental Protection Department, 1997); Kitimat Harbour, Canada (i.e., up to 10, 000 $\mu g\,g^{-1}$; Simpson et al., 1996); Times Beach, New York, USA (i.e., up to 480 $\mu g\,g^{-1}$; Roper and Chery, 1994); Santander Bay, Spain (i.e., up to 344.6 $\mu g\,g^{-1}$; Viguri et al., 2002); Harbor of Refuge, Rhode Island Sound, USA (i.e., up to 730.0 $\mu g\,g^{-1}$; Ho et al., 1999); Sydney harbour, Australia (i.e., up to 380 $\mu g\,g^{-1}$; McCready et al., 2000); Kohtla-Järve, Estonia (i.e., up to 153.0 $\mu g\,g^{-1}$; Trapido, 1999), but higher than that reported for sediments in the Mediterranean Sea (i.e., up to 20.5 $\mu g\,g^{-1}$; Baumard et al., 1998); Pacific Coast, USA (i.e., up to 20 $\mu g\,g^{-1}$; Brown et al., 1998); Arkona Basin, Baltic Sea, Germany (i.e., up to 1.8 $\mu g\,g^{-1}$; Witt, 1995); and the Barents Sea, Svalbard, Norway (i.e., up to 2.0 $\mu g\,g^{-1}$; Stange and Klungsøyr, 1997); and Mai Po, Hong Kong (i.e., up to 1.0 $\mu g\,g^{-1}$; Zheng et al., 2000).

Overall, widespread PAH contamination in the coastal sediments of Singapore is apparent. PAH distribution profiles in both regions were dominated by pyrogenically derived PAH sources, signifying that inputs to the marine environment are dominated by the atmospheric deposition of contaminated particulates. With reference to studies conducted elsewhere, sediments in Singapore can be classified as moderately contaminated.

PCBs, polybrominated diphenyl ethers (PBDEs) and OCPs were reported in Singapore's coastal marine sediments by Wurl and Obbard (2005b) and concentration levels are summarized in Table 15.5 (PCBs and PBDEs) and Table 15.6 (OCPs). Sample stations are indicated in Fig. 15.12.Total PCB concentrations ranged widely from 1.4 to 329.6 $ng\,g^{-1}$. High concentrations were found in samples close to highly industrialized areas dominated by petrochemical plants. A notable decline in the concentration of ΣPCBs could be observed seawards from sample station SW3 over SW2 to SW1 (62.2–14.1 $ng\,g^{-1}$) (Fig. 15.12) and

Table 15.5. Sediment concentrations of major PCB congeners, ΣPCB and PBDE congeners in ng g^{-1} dw (mean ± sd, $n = 3$)

Station	SW1	SW2	SW3	SW4	SW5	NE1	NE2	NE3	NE4	NE5	NE6	NE7	NE8
PCB 28	<0.6	<0.6	<0.6	31.9±3.0	7.9±0.5	4.5±0.2	7.7±1.2	7.5±2.2	<0.6	<0.6	5.7±0.4	<0.6	<0.6
PCB 31	0.3±0.05	<0.03	8.0±0.7	8.9±0.5	<0.03	0.4±0.1	7.4±1.2	<0.03	7.2±0.8	<0.03	<0.03	1.0±0.1	0.2±0.01
PCB 33	<0.3	<0.3	14.3±2.1	11.4±1.2	<0.3	<0.3	12.7±0.5	1.7±0.2	<0.3	<0.3	<0.3	<0.3	<0.3
PCB 44	0.8±0.02	<0.2	<0.2	13.3±1.9	1.3±0.1	1.7±0.1	5.6±0.9	2.2±0.1	1.0±0.1	0.8±0.1	<0.2	3.4±0.2	<0.2
PCB 49	<0.3	<0.3	3.9±0.3	10.7±1.1	0.4±0.2	2.0±0.2	7.5±0.5	1.4±0.2	1.6±0.1	0.7±0.04	<0.3	<0.3	<0.3
PCB 53	0.63±0.1	<0.1	2.7±0.1	11.2±0.1	1.5±0.02	1.2±0.1	5.8±0.1	1.0±0.1	<0.12	<0.1	<0.1	2.7±0.3	<0.1
PCB 70	0.7±0.1	<0.2	3.2±0.6	13.3±1.6	1.2±0.4	1.5±0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
PCB 74	1.0±0.01	<0.3	<0.3	13.9±1.3	1.4±0.1	1.5±0.2	7.0±0.2	2.2±0.03	<0.3	<0.3	<0.3	3.0±0.5	<0.3
PCB 87	2.2±0.1	0.9±0.2	<0.3	13.3±0.4	<0.3	2.1±0.4	2.4±0.5	2.5±0.2	<0.3	1.2±0.2	<0.3	2.9±0.3	<0.3
PCB 118	1.5±0.1	<0.2	<0.2	13.6±1.6	<0.2	<0.2	4.0±0.9	<0.2	<0.2	<0.2	<0.2	3.4±0.7	1.2±0.1
PCB 128	<0.2	<0.2	1.3±0.3	13.1±0.1	1.2±0.2	<0.2	4.5±0.02	1.4±0.1	<0.2	<0.2	<0.2	1.8±0.1	<0.2
PCB 138	1.2±0.01	1.2±0.1	0.7±0.3	13.9±0.9	1.1±0.2	1.5±0.2	4.5±0.5	1.2±0.1	1.3±0.1	0.7±0.1	<0.4	1.8±0.1	<0.4
PCB 153	<0.2	13.3±3.3	19.4±2.1	0.6±0.2	0.9±0.2	21.9±1.6	13.6±2.7	1.7±0.04	2.2±0.2	<0.2	13.0±1.2	<0.2	<0.2
PCB 206+208	<0.4	10.0±0.7	<0.4	<0.4	41.0±2.4	16.7±0.9	21.3±0.9	36.1±2.0	15.0±1.8	35.8±3.7	15.5±1.0	27.7±1.8	<0.4
5PCB	14.1±0.7	29.1±3.6	62.2±2.7	329.6±7.7	72.5±1.8	60.6±7.8	138.5±5.8	79.8±2.8	34.6±2.4	44.7±4.4	38.3±0.5	55.4±0.8	1.4±0.1
BDE-47	3.4±0.9	4.0±0.6	11.1±0.9	4.5±0.5	4.7±0.9	3.7±0.7	13.8±1.1	5.1±0.7	4.0±0.6	3.8±0.3	5.5±0.5	4.3±0.3	12.7±1.2

Table 15.6. Sediment concentrations of OCPs in ng g^{-1} dw (mean ± sd, $n = 3$)

Station	SW1	SW2	SW3	SW4	SW5	NE1	NE2	NE3	NE4	NE5	NE6	NE7	NE8
α-HCH	4.4±0.8	4.9±0.5	7.2±0.5	0.9±0.2	2.0±0.2	2.6±0.1	8.4±0.7	5.8±1.6	6.4±0.8	4.6±0.6	9.3±1.6	2.9±0.6	2.4±0.4
β-HCH	3.2±1.6	5.3±1.4	4.6±0.6	0.7±0.2	2.6±0.7	4.3±0.1	11.1±0.9	5.2±0.2	6.0±0.4	4.1±0.7	4.2±0.4	4.3±0.4	2.7±0.4
γ-HCH	3.1±0.6	1.1±0.2	<0.7	0.8±0.2	3.5±1.1	2.7±0.5	13.4±0.9	8.8±2.8	5.7±0.3	7.7±0.5	<0.7	5.1±0.1	2.6±0.4
δ-HCH	3.1±0.3	1.4±0.4	7.2±0.8	0.9±0.2	3.3±1.1	5.3±0.9	13.3±1.3	2.9±1.4	5.2±0.6	4.0±0.6	8.0±0.9	3.8±0.2	2.3±0.7
ΣHCH	13.8±1.9	12.7±1.3	19.0±0.7	3.3±0.3	11.4±1.6	14.9±0.7	46.2±1.8	22.7±0.6	23.3±1.2	20.4±0.1	21.5±1.2	16.1±0.7	10.0±0.7
DDT	3.5±0.4	3.6±0.3	2.5±0.4	3.2±0.6	4.2±0.6	2.3±0.2	<0.5	2.1±0.7	<0.5	<0.5	0.6±0.2	1.9±0.2	2.2±0.3
DDD	2.8±0.2	1.5±0.2	3.5±0.4	4.0±0.6	3.7±1.1	1.8±0.4	1.3±0.2	2.4±0.4	1.5±0.2	1.5±0.2	2.1±0.2	3.2±0.3	3.8±0.6
DDE	2.5±0.4	0.6±0.3	2.7±0.8	4.7±0.9	2.6±0.5	1.1±0.1	0.9±0.3	1.6±0.3	0.7±0.1	1.2±0.1	1.6±0.3	4.1±0.5	3.7±0.3
ΣDDT	8.8±0.7	5.7±0.7	8.7±1.2	11.9±0.5	10.5±1.8	5.2±0.2	2.2±0.5	6.1±0.2	2.2±0.2	2.7±0.2	4.3±0.5	9.2±0.4	9.7±0.6
cis-Chlordane	0.8±0.2	1.0±0.2	<0.3	9.0±0.5	0.6±0.1	1.1±0.2	1.1±0.1	1.1±0.4	1.3±0.2	1.3±0.2	1.4±0.3	8.5±0.6	2.5±0.5
trans-Chlordane	1.5±0.1	2.9±0.4	1.4±0.1	9.7±0.5	1.2±0.4	1.7±0.2	1.5±0.2	1.3±0.1	1.4±0.2	1.9±0.1	1.3±0.3	10.0±0.6	4.0±0.4
Heptachlor	2.7±0.3	1.2±0.3	<0.9	0.9±0.2	2.0±0.2	4.2±0.7	<0.9	9.0±1.3	<0.9	2.3±0.6	<0.9	2.9±0.6	4.6±0.4
Heptachlor epoxide	6.8±0.6	2.9±0.2	<0.7	0.8±0.2	6.7±0.2	6.1±0.6	<0.7	5.9±0.9	<0.7	3.2±0.5	5.5±1.6	4.3±0.4	5.1±1.3
Aldrin	<0.3	<0.3	<0.3	<0.3	1.2±0.3	<0.3	<0.3	<0.3	0.6±0.1	1.4±0.4	1.1±0.4	1.0±0.4	0.5±0.2
Dieldrin	4.4±0.2	1.7±0.4	3.7±0.2	<1.2	1.9±0.4	3.4±0.5	3.8±0.2	4.0±0.4	2.2±0.2	3.8±0.1	2.3±0.7	3.9±0.2	1.6±0.3
Endrin	3.4±0.4	2.0±0.2	<1.3	<1.3	3.4±0.6	2.2±0.4	<1.3	<1.3	4.0±0.6	2.9±0.3	<1.3	<1.3	<1.3
Endrin aldehyde	2.9±0.5	3.0±0.4	<2.0	<2.0	2.5±0.2	3.4±0.6	2.1±0.3	<2.0	4.2±0.3	4.1±0.6	<2.0	<2.0	<2.0
Endosulfan I	<0.9	<0.9	<0.9	<0.9	2.2±0.2	1.0±0.2	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9
Endosulfan II	<1.0	<1.0	<1.0	<1.0	1.5±0.6	1.6±0.2	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Endosulfan sulfate	0.8±0.2	<0.7	<0.7	1.3±0.2	1.0±0.1	<0.7	<0.7	1.3±0.1	<0.7	<0.7	<0.7	<0.7	<0.7
Mirex	0.6±0.1	0.7±0.1	<0.1	0.6±0.1	<0.1	0.6±0.1	1.0±0.2	0.9±0.1	0.7±0.2	0.6±0.1	0.8±0.3	0.6±0.1	<0.1
Methoxychlor	1.2±0.2	<0.4	0.6±0.1	0.5±0.1	<0.4	0.6±0.1	0.5±0.3	1.2±0.3	<0.4	0.8±0.2	0.7±0.2	<0.4	<0.4

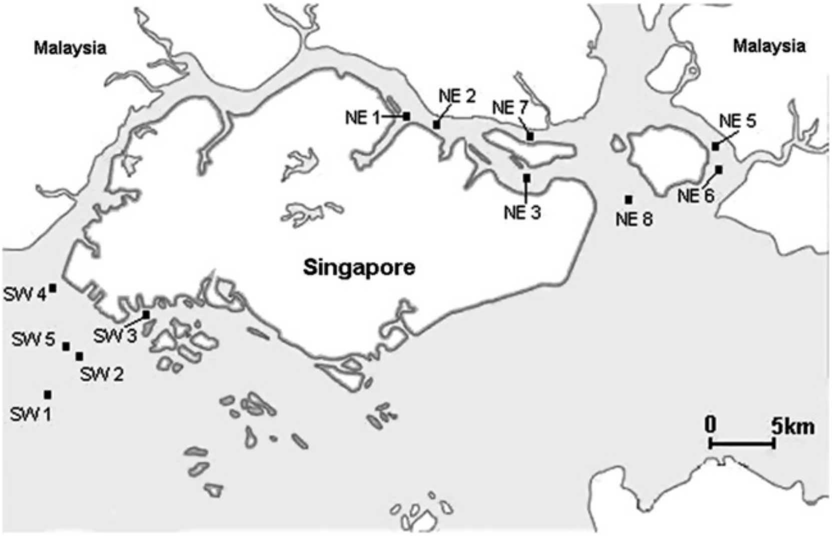

Figure 15.12. Sediment sample locations in the northwestern and southwestern regions of Singapore.

confirms a dispersion of PCBs moving seawards. A concentration of 138.5 ng g^{-1} was found in the Straits of Johor, northern part of Singapore (NE2). Shipyards and industry areas may be the sources for PCBs in this area. Lower concentrations of ΣPCBs between 1.4 and 55.4 ng g^{-1} were found in the northeastern part of Singapore, which is affected by agricultural and fish farming activities. The sediment sample corresponding to lowest concentration of 1.4 ng g^{-1} was mainly of mineral composition and showed the lowest TOC value. Significantly high concentration of higher chlorinated PCBs (62–69% chlorination grade) was found, which are less volatile and therefore more persistent.

Concentrations of ΣHCHs (sum of α-, β-, γ- and δ-HCH) ranged from 3.3 ng g^{-1} at station SW4 to 46.2 ng g^{-1} at station NE2. A slightly higher trend of concentrations of ΣHCH at sample stations in the NE region was observed, most likely due to the higher level of agricultural and fish farming activity to the north of Singapore. The levels are comparable to those found in Hong Kong (0.1–16.7 ng g^{-1}) reported by Richardson and Zheng (1999), but much higher than those reported for Daya Bay, China (0.3–4.2 ng g^{-1}) by Zhou et al., (2001) (Table 15.7). The mean percentage composition of α-,β-, γ-, δ-HCH to ΣHCHs for sediments analysed in our study are 27%, 25%, 23% and 25% respectively. The transformation of α- and γ-HCH to β-HCH, and the low degradation rate and lower vapor pressure of β-HCH (Wu et al., 1997; Willett et al., 1998) may be expected

Table 15.7. Comparison of OCPs, PCBs and PBDEs concentrations in sediments from coastal areas in Asia (ng g^{-1} dw)

Location	Year	ΣPCBs	ΣDDTs[g]	ΣHCH	Σchlordane[j]	ΣPBDEs[k]	Reference
Osaka Bay, Japan	1990	63–240[a]	2.5–11.9	4.5–6.2[h]	0.2–1		Iwata et al., 1994
Hong Kong	1997/98	n.d.–97.9[a]	0.3–14.8	0.1–16.7[i]	n.d.–11.3		Richardson and Zheng, 1999
Masan Bay, Korea	1997	1.2–41.4[b]	0.2–80.2	n.d.–1.3[i]	n.d.–1.7		Hong et al., 2003
North Coast of Vietnam	1997	1.1–66.4[c]	6.2–10.4	1.2–33.7[h]			Nhan et al., 1999
Minjiang River Estuary, China	1999	15.8–57.9[d]	1.6–13.1	3–16.2[i]			Zhang et al., 2003
Daya Bay, China	1999	0.9–11.2[c]	0.1–20.3	0.3–4.2[i]			Zhou et al., 2001
Osaka Bay, Japan	2000					0.2–651.9	Choi et al., 2003
Yangtze Estuary, China	2001	n.d.–19.0[e]	n.d.–0.6				Liu et al., 2003
Singapore	2003	1.4–329.6[f]	2.2–11.9	3.4–46.1[i]	1.4–18.7	3.4–13.8	This study

Note: n.d. = not detectable.

[a] PCB mixture basis (Aroclors).

[b] $2 \times \Sigma PCB_{18}$; twice the sum of PCB congeners 8,18, 28, 44, 52, 66, 101, 105, 118, 128, 138, 170, 180, 187, 195, 206 and 209.

[c] $5 \times \Sigma PCB_6$; sum of six PCB congeners 28, 52, 101, 138, 153 and 180 multiplied by a factor of 5 for 209 PCB mixture basis (Cullen et al., 1996).

[d] Sum of PCB congeners 1, 5, 28, 29, 47, 49, 77, 97, 101, 105, 118, 138, 153, 154, 169, 171, 180, 200, 204.

[e] Sum of PCB congeners 1, 11, 29, 47, 121, 136, 187.

[f] Sum of PCB congeners 18, 28, 31, 33, 44, 49, 53, 70, 74, 82, 87, 95, 99, 101, 105, 118, 128, 132, 138, 153, 156, 158, 169, 170, 171, 177, 180, 183, 187, 191, 194, 195, 199, 205, 206, 208, 209.

[g] Sum of *p,p′*-DDE, *p,p′*-DDD, and *p,p′*-DDT.

[h] Sum of α-HCH, β-HCH and γ-HCH.

[i] Sum of α-HCH, β-HCH, δ-HCH and γ-HCH.

[j] Sum of *cis*- and *trans*-chlordane.

[k] Sum of PBDE congeners 47, 99 and 100.

to lead to an accumulation of β-HCH in sediments and a much lower concentration of α- and γ-HCHs. However, this was not observed in this study and leads to the assumption that HCHs are still being introduced to the marine environment in the region of Singapore. Indonesia banned Lindane (γ-HCH) in 1991 and Thailand in 2002 (UNEP, 2002). However, Lindane may still be used in palm oil and coconut plantage in Malaysia (UNEP, 2002).

Concentrations of ΣDDT ranged from 2.2 to 11.9 ng g^{-1} in Singapore's coastal sediments compared to ranges in Hong Kong (Richardson and Zheng, 1999), Daya Bay (China, Zhou et al., 2001) and Osaka Bay (Japan, Iwata et al., 1994) of 0.3–14.8 ng g^{-1}, 0.1–20.3 and 2.5–11.9 ng g^{-1}, respectively (Table 15.7). The concentrations of DDT and its metabolites DDD and DDE are higher at sample locations around Jurong Island (SW series) by a factor of around 2 compared to sediments from the Straits of Johor (NE series), particularly concentrations of DDT. The highest concentrations for ΣDDT were found at sample locations SW4 and SW5 of 11.9 and 10.5 ng g^{-1}, respectively and the lowest at NE2 and at NE4 at 2.2 ng g^{-1}. However the ratio of DDT to the sum of DDE and DDD is much smaller than 1 (range of 0.2–0.8) at all locations, implying that there has been no recent introduction of DDT to the marine environment of Singapore. Bayen et al. (2004) made the same conclusion based on concentration levels of DDTs in the tissues of green mussels (*Perna viridis*). As DDT has been banned for a longer period than HCHs in many countries in Southeast Asia, DDT is less prevalent and present at a lower concentration. DDT was banned in Singapore in 1985, but later than this in other countries in the region and continues to be used in some countries such as the Philippines (UNEP, 2002).

Among the chlordane-related compounds (*cis*-Chlordane, *trans*-Chlordane, Heptachlor and Heptachlor epoxide), the concentration of ΣChlordane (*cis*-+*trans*-Chlordane) in sediments is high at sample locations SW4 and NE7 with 18.7 and 18.5 ng g^{-1} respectively, and higher by a factor of two compared with data from Hong Kong (Table 15.7). At the other sample locations, the concentration of ΣChlordane ranged between 1.4 and 6.5 ng g^{-1}, whereas the concentration of *cis*-Chlordane is either equal to or higher by a factor of two than the concentration of *trans*-Chlordane. Chlordane was banned in Singapore only in 1999, later than in some other Southeast Asian countries (UNEP, 2002). Heptachlor was detected at up to 9.0 ng g^{-1} and Heptachlor epoxide, a degradation product of Heptachlor, at a peak concentration of 6.8 ng g^{-1}. The concentrations of Heptachlor epoxide are higher by factors of 1.1–3.4 than Heptachlor, except for sediments from sample locations SW4 and NE3, where the concentration ratio of Heptachlor epoxide to Heptachlor is less than 1. The data can be interpreted on the basis that there has been no recent introduction of Heptachlor into Singapore's marine environment. Heptachlor was banned in Singapore in 1985 and in Malaysia in 1990 (UNEP, 2002).

Aldrin was detected in 50% of all sediments collected, with a higher frequency in samples from the Straits of Johor (NE series) at a low concentration range (0.6–1.0 ng g^{-1}). Concentrations of Dieldrin were higher, ranging from below the limit of detection i.e., 1.2–4.4 ng g^{-1}. Endrin was detected in a range from below the limit of detection i.e., 1.3–4.0 ng g^{-1}. Endrin aldehyde, a metabolite of Endrin, was found in a range of below the limit of detection i.e., 2–4.2 ng g^{-1}. Endrin ketone, a second metabolite formed only by exposure to sunlight, could not be detected. Endrin was banned in Singapore in 1995, and later in other Southeast Asian countries (UNEP, 2002).

Endosulfan I, Endosulfan II and Endosulfan sulfate were only detected in a few sample locations at low concentrations of between 0.8 and 2.2 ng g^{-1}. Mirex and Methoxychlor were found frequently among sample locations at low concentrations ranging from 0.6 to 1 ng g^{-1} and 0.5 to 1.2 ng g^{-1}, respectively.

Among the PBDE congeners measured i.e., BDE-47, BDE-99 and BDE-100 (detection limit of 0.98 ng g^{-1}, 0.92 ng g^{-1} and 0.87 ng g^{-1} respectively), only BDE-47 could be detected in sediments, at a concentration range of 3.4–13.8 ng g^{-1} (Table 15.5). The concentration of PBDEs was lower and less variable among sample locations relative to PCBs, indicating a more disperse input of this compound into the marine environment around Singapore. The highest concentrations were found at sample locations SW3, NE2 and NE8. The main source of PBDEs at these sample locations are likely to be harbours and industrial activities, shipyards and intensive shipping traffic. Among the other sample locations, the concentrations of BDE-47 in sediments varied between 3.4 and 5.5 ng g^{-1}.

A comparison of the concentration of PCBs and OCPs in Singapore's coastal marine sediments with the sediment quality guideline specified by the USEPA (1997) and the Canadian Council of Ministers of the Environment (CCME, 2002) (Table 15.8), and comparison with levels of contaminants reported from other locations in Asia, Singapore's marine sediments can be classified as moderately contaminated with probable ecotoxicological impacts to marine organisms.

15.5. POPs in marine biota

An assessment of the fate and transport of POPs in the global environment requires baseline measurements of such compounds. Global

Table 15.8. Minimum, maximum and average concentrations of major organochlorine contaminants in ng g^{-1}, and corresponding sediment quality criteria

	C_{min}	C_{max}	$C_{average}$	ER-L[a]	% above ER-L[b]	ER-M[c]	% above ER-M[b]	TEL[d]	% above TEL[b]	PEL[e]	% above PEL[b]
∑PCBs	1.4	329.6	73.9	22.7	84.6	180	7.7	21.55	84.6	188.79	7.7
p,p′-DDT	<0.46	4.2	2.1	1	69.2	7	0	1.19	69.2	4.77	0
p,p′-DDD	1.3	4.0	2.5	2	61.5	20	0	1.22	100	7.81	0
p,p′-DDE	0.6	4.7	2.2	2.2	46.2	27	0	2.07	46.2	374.17	0
∑DDT	2.2	11.9	6.7	1.58	100	46.1	0	3.89	76.9	51.7	0
γ-HCH	<0.66	13.4	4.3					0.32	> 84.6	0.99	76.9
∑Chlordane[f]	<1.67	18.7	5.4	0.5	100	6	23.1	2.26	84.6	4.79	23.1

[a] Effects range-law value.

[b] percentage of samples above level.

[c] Effects range-median value.

[d] Threshold effects level.

[e] Probable effects level.

[f] Sum of cis- and trans-Chlordane.

distillation is the most probable theory to explain the widespread and ubiquitous nature of POPs in the environment. According to this theory, POPs are volatilized into the atmosphere at tropical and temperate latitudes and undergo long range transport prior to deposition in the polar regions of the globe (Vallack et al., 1998). Bioaccumulation of POPs in the polar foodchains represents a significant risk for tertiary consumers, where adverse effects on the reproductive health and well-being of a range or polar organisms has been recently reported (Bard, 1999). Despite the importance of the tropical region as a source of POPs in the global cycling of these compounds, there is a paucity of data on the prevalence of PCBs and organochlorine pesticides in the Asian environment. More recently, PBDEs, which are widely used in fire retarded materials have become of increasing concern due to their potential ecotoxicological impact.

Almost all studies on the behaviour of PBDEs in the environment are derived from Europe, North America, Japan and the Arctic Pole (de Wit, 2002). There is no reported data on the prevalence of PBDEs in the tropical environment of Southeast Asia. Although highly industrialized, Singapore still has a wide diversity of marine habitats including sandy beaches, mangroves, rocky shores and coral reefs. However, many of these habitats are threatened by land reclamation and intense port activity, as well as marine pollution (Thia-Eng et al., 2000). Although DDT residues have been detected in human blood serum in Singapore and partly attributed to seafood consumption (Luo et al., 1997), there is a lack of data on the prevalence of POPs in Singapore's marine environment. Polychlorinated biphenyl use has been banned for more than two decades in Singapore. To date, PBDEs have not been reported in the tropical marine environment of Southeast Asia, although a study has been completed on fish tissue in Japan. In 2001, Akutsu et al. (2001) found elevated levels of pentabrominated diphenyl ethers (penta-BDE), especially BDE-47, in marine fishes in the Inland Sea of Japan. [There are some recent studies in Hong Kong and mainland China.]

The Green Mussel, *P. viridis*, is a filter feeding organism and therefore readily accumulates POPs from its environment via the ingestion of waterborne organic particulates. Consequently, *P. viridis* has been previously used as a bioindicator species for various POPs including pesticides and polychlorinated biphenyls (Tanabe et al., 2000). The Blue Mussel, *Mytilus edulis*, has also been used for monitoring various POPs, and recently for PBDEs in Atlantic waters (Christensen et al., 2002). A study was undertaken on the levels of PCBs and PBDEs detected in *P. viridis* collected from Singapore's coastal marine environment by Bayen et al. (2003) and represents the first baseline study of such compounds in Singapore's marine

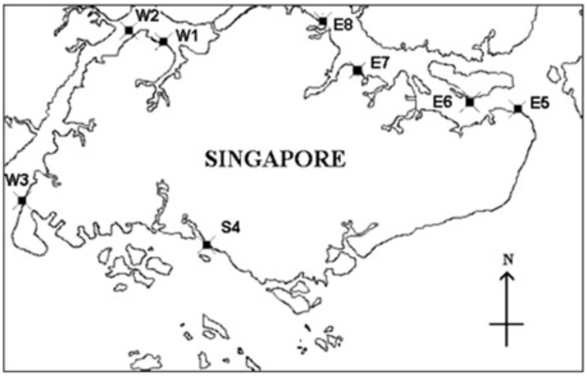

Figure 15.13. Sampling locations of *P. viridis* in Singapore's coastal environment.

biota, and is also the first report of the use of *P. viridis* for the monitoring of PBDEs in the tropical marine environment of Southeast Asia.

Specimens of *P. viridis* were collected from eight locations around Singapore's coastline between April and May 2002 (Fig. 15.13). The stations were chosen based on their proximity to industrial activities, and their position around the land-link causeway in the Straits of Johore. The causeway represents a physical barrier to marine hydrodynamics around Singapore's northern coast. Samples were collected from floating structures and shore defence walls. As the size of the individual is an important parameter affecting the level of pollutant bioaccumulation in *P. viridis* (Richardson et al., 2001), individuals were collected in the largest and most similar size range in all locations so as to target mature specimens for analysis.

15.5.1. PCB levels in P. viridis

Congener specific concentrations of PCBs in *P. viridis* samples on a dry-weight (dw) basis are given in Table 15.9. All PCB congeners in the analytical suite were detected in the mussel tissues. Total PCBs concentrations ranged from 6.1 to 82 ng g^{-1} dw. The highest concentrations were recorded in samples from E8 (i.e., 82 ng g^{-1} dw) and S4 (i.e., 44 ng g^{-1} dw) (Fig. 15.13), which are from locations adjacent to ship maintenance yards and busy shipping lanes located on the north (i.e., Sembawang) and east (i.e., Jurong) coasts of Singapore. Tissue levels of PCBs in stations W1, W2, W3, E5, E6 and E7 were lower (6.1–23 ng g^{-1} dw) with the lowest level recorded in *P. viridis* tissues from station W3. The causeway in the Straits of Johore separates hydrodynamic flow of marine water

Table 15.9. Concentrations for major PCB congeners in *P. viridis* tissue (ng g^{-1} dry basis)

	W1	W2	W3	S4	S4	E5	E6	E7	E7	E8
PCB 49	0.35	0.53	BLD	0.87	1.1	0.64	0.88	1.1	0.33	4.6
PCB 52	0.59	0.86	BLD	1.2	1.5	0.85	1.2	1.2	0.41	4.6
PCB 90/101	1.4	1.5	BLD	3.6	3.7	1.4	1.5	1.6	0.84	8.4
PCB 110	0.85	0.99	0.35	3.3	3.5	1.1	1.1	1.3	0.52	5.8
PCB 118	0.56	0.57	0.22	2.0	2.1	0.96	0.91	0.93	0.43	4.4
PCB 138	2.3	1.9	1.1	6.1	6.3	1.8	1.7	2.0	0.87	9.2
PCB 149	2.1	1.9	0.93	4.7	4.7	1.2	1.2	1.5	0.88	7.4
PCB 153	2.5	1.9	1.1	5.7	6.1	1.8	1.8	2.1	0.97	9.5
Total PCBs	17	23	6.1	44	47	15	15	18	7.1	82

Note: BLD – below limit of detection.

between the west and the east of the Straits of Johore, and this likely accounts for the observed differences in *P. viridis* tissue concentrations.

PCB data for *P. viridis* tissues are available for samples analysed elsewhere. On a wet weight basis (ww), PCB levels in Singapore (1.4–15 ng g^{-1} ww) are higher than values reported recently in neighbouring countries such as Malaysia (0.7–2.1ng g^{-1} ww), and Indonesia (0.2–2.7 ng g^{-1} ww) (Monirith et al., 2000). Hong Kong and Singapore have similarities in terms of size, human population and density and levels of industrial and shipping activities. However, the PCB burden in *P. viridis* reported from both clean and polluted marine zones of Hong Kong (Richardson et al., 2001) is higher than values reported here for Singapore, and range from 120 to 420 ng g^{-1} dw.

Pentachlorinated biphenyls and hexachlorinated biphenyls are the major PCB groups typically found in *P. viridis*. PCBs are sold commercially as technical mixtures, called Aroclors, each with a specific pattern of chlorination. Patterns have been determined for Aroclor mixtures 1221, 1232, 1242, 1248, 1254, 1260 and 1262 (Frame et al., 1996). Principal component analysis (PCA) was performed to compare the relative PCB congener profile of mussel tissues analysed in 2002 and the commercial Aroclor mixtures (Fig. 15.14). The closest match in the PCB data for *P. viridis* samples collected in Singapore from our study is the common Aroclor 1254. The slight discrepancy is due to the presence of PCB-149 in mussel tissue and a greater prominence of PCB-110 and -118 in Aroclor 1254. PCA analysis revealed that samples from the west Straits of Johore (W1, W2 and W3) contain more penta-CBs and less hexa-CBs than samples from the east Straits (E6, E7 and E8). The sample collected in the south of Singapore (S4) has an intermediary pattern of PCB contamination. A similar match has been observed in marine crabs and fishes

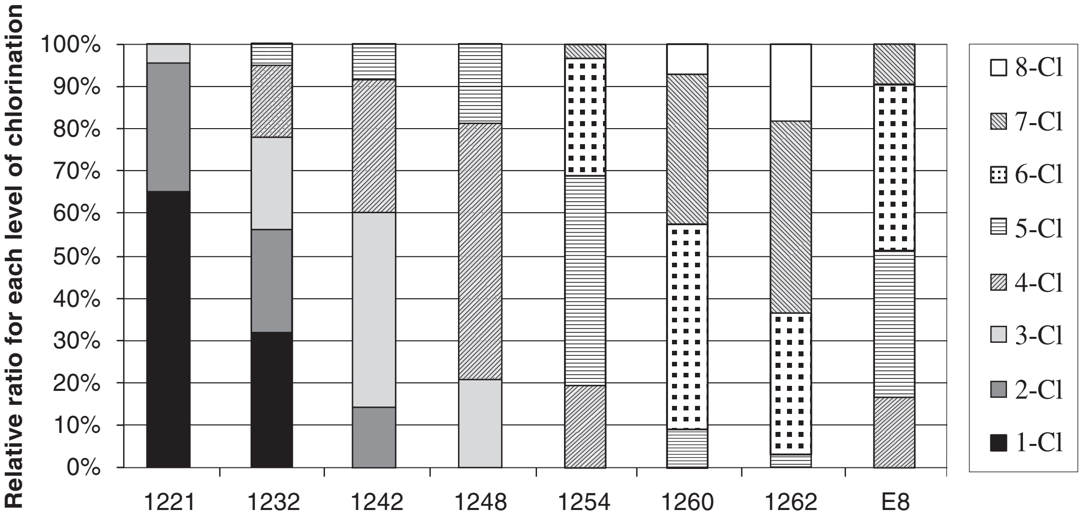

Figure 15.14. PCB profile for each level of chlorination in Aroclors compared to profile in *P. viridis* tissues from station E8. Nonachlorinated and decachlorinated PCBs were voluntary omitted as their amount is low compared to other levels of chlorination.

Table 15.10. Concentrations for major PBDE congeners in *P. viridis* tissue (ng.g^{-1} dry basis)

Congener	W1	W2	W3	S4	S4	E5	E6	E7	E7	E8
BDE 47	0.71	0.86	11	5.0	3.8	1.2	0.72	1.5	0.62	1.7
BDE 49	0.12	0.15	0.99	0.82	0.66	0.22	0.11	0.28	0.12	0.35
BDE 66	0.07	0.08	0.59	0.35	0.23	0.10	0.06	0.12	0.09	0.14
BDE 99	0.57	0.69	18	3.8	3.1	1.1	0.62	2.1	0.69	1.5
BDE 100	0.13	0.16	5.3	1.1	0.76	0.28	0.17	0.56	0.21	0.38
BDE 153	BLD	BLD	0.64	0.28	0.22	BLD	BLD	0.23	BLD	BLD
BDE 154	0.05	0.07	0.45	0.20	0.20	0.05	0.08	0.13	BLD	0.12
Total PBDEs	2.1	2.3	38	13	9.9	3.3	2.1	5.3	2.0	4.7
PCB/PBDE ratio	8.3	4.4	0.2	3.5	4.7	10	7.3	3.4	3.6	17

Note: BLD – below limit of detection.

in Hawaii (Miao et al., 2000). PCB 153, 138 and 149 are the major main congeners found in the tissues of *P. viridis* in Singapore, which are not classified as high-carcinogenic risk dioxin-like PCBs (Kumar et al., 2001).

15.5.2. PBDEs levels in P. viridis

Levels of PBDE congeners 17, 28, 32, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 120, 138, 153, 154, 166, 181 and 190 in *P. viridis* tissues are reported in Table 15.10. The sum total of individual congeners ranged from 2.0 to 38 ng g^{-1} dw and have a different geographical profile from PCBs. The highest concentration of PBDEs was found in tissue samples from station W3. This station is close to the industrial area of Tuas. station S4, which is adjacent to an industrialized area and shipping lane in the south of Singapore, also had an elevated PBDE concentration (13 ng g^{-1} dw). Tissue samples from the six other locations had lower concentrations and were similar in their PBDE patterns.

No comparative PBDE data are available for *P. viridis* outside Singapore, although PBDE levels have been previously reported in blue mussel (*M. edulis*) tissues from marine waters off Denmark and Greenland (Christensen and Platz, 2001; Christensen et al., 2002). Concentrations of the PBDEs 47, 99, 100 and 153 in *M. edulis* tissues ranged from 0.080 to 0.81 ng g^{-1} ww in Denmark and 0.11 ng g^{-1} ww in Greenland. On a wet weight basis *P. viridis* tissues from Singapore ranged from 0.29 to 8.6 ng g^{-1} ww. Therefore, in comparative terms, PBDE levels in mussel tissues from Singapore are up to an order of magnitude greater than the available data from elsewhere. PBDE levels found in this study are in the range of concentrations recorded in a range of fish and marine mammals (de Wit, 2002).

BDE-99 and BDE-47 are the two main components of the commercial pentabrominated diphenyl ethers mixture such as Bromkal 70–5DE, with composition of 35% and 37% respectively (Sjödin et al., 1998) and DE-71, with compositions of 47% and 25% respectively (Dodder et al., 2002). These two PBDE congeners were dominant in the *P. viridis* samples, with a lower contribution of BDE-100. In most sample locations (except W3 and E7), BDE-47 was present at higher tissues concentrations than BDE-99. Gustafsson et al. (1999) reported that the uptake of BDE-47 and BDE-99 in *M. edulis* is virtually identical, but the depuration rate of BDE-99 is faster. As a consequence, an organism, exposed to penta-PBDE contamination, can be expected to have a higher tissue concentration of BDE-99 than BDE-47. When the organisms are no longer exposed, BDE-99 is likely to be excreted and BDE-47 therefore becomes the dominant congener. In samples collected in Tuas (station W3) and Sembawang (station E7) in Singapore, BDE-99 was more prevalent, which indicates a relatively recent contamination event. Fig. 15.15 shows the relative ratio of each BDE in *P. viridis* from station W3. BDE-99 and BDE-47 were present at composition percentages of 46% and 30%, respectively, which is close to the composition of the commercial mixture DE-71, if we neglect the contribution of other BDEs which were not monitored in this study. Similar conclusions can be deduced for tissue

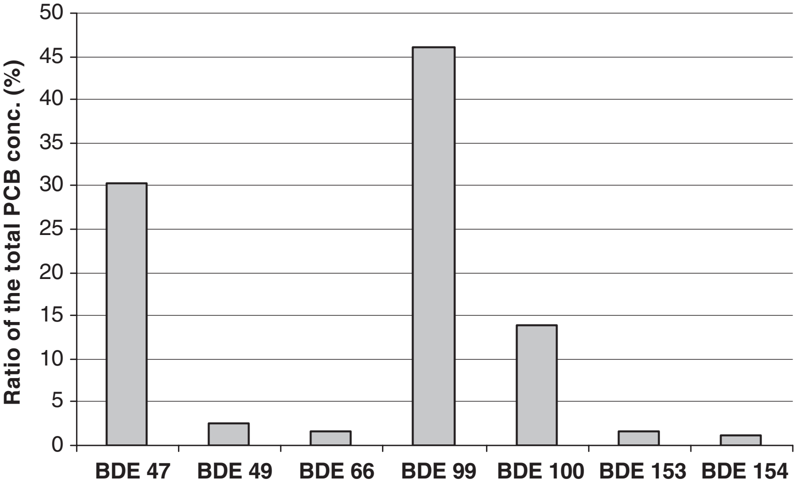

Figure 15.15. PBDEs congener profile in *P. viridis* tissues from station W3 as ratio of the total PBDE concentration.

samples from station E7 (i.e., 39% BDE-99 and 29% BDE-47). Amongst numerous studies summarized in a review by de Wit (2002), no reference reported this ratio for BDE-99 and BDE-47 in marine tissues. Important factor to consider: Debromination of BDE-209 occurs in marine organism forming lower brominated congeners, particular tetra- and penta-brominated congeners. BDE-209 is hardly reported in marine organism due to this effect. Commercial product DeBDE contains 97% of DeBDE and Asia demanded 42% of world market for DeBDE in 1999 (de Wit, 2002).

Ratios of total PCB:PBDE concentrations for *P. viridis* tissues have been calculated and are reported in Table 15.10. This ratio varies between 0.2 and 17. The mean ratio for samples from Singapore is close to 7, a value previously reported for Arctic biota samples (Christensen et al., 2002). However, stations W3 and E8, had respective ratios of 0.2 and 17, and therefore are likely affected by one or more specific local sources of contamination. The lack of correlation between these two pollutants in our study indicates that the sources of PCB and PBDE contamination are independent of each other. The difference may be due to the types of local industrial activities that are present, with emphasis on the electronics industry and shipping activities.

PCBs and PBDEs were detected in all *P. viridis* tissue samples collected from all sample locations in Singapore's coastal waters. Although the use of PCBs was banned several decades ago in Singapore, biological tissues still contain PCB congeners that have a similar profile to that of the commercial PCB Aroclor 1254. The busy shipping routes appear to be the most contaminated locations in Singapore's coastal waters, although levels are rather lower than recorded in Hong Kong (Richardson et al., 2001). *P. viridis* was also a useful bioindicator of polybrominated PBDEs in Singapore's marine environment. These POPs were also found in all tissue samples collected and measured levels were generally in the same concentration range as PCBs, although higher concentrations were measured in tissues collected from Tuas (station W3), adjacent to an industrial area. Tissue samples from all locations had elevated levels of pentabrominated diphenyl ethers which are characteristic of technical mixtures commonly used as flame retardants in a range of commercial and consumer goods. PBDEs can be readily emitted into the environment, where, for example, flame retardants may be discharged upon usage, and may also be leached from plastic and electronic wastes, construction material, textiles and sewage plants, or as direct emissions from industrial plants (de Wit, 2002). Levels of PBDEs in *P. viridis* tissue from Tuas (station W3) were an order of magnitude higher than the upper concentrations reported in *M. edulis* tissues from coastal waters adjacent to

Denmark (Christensen and Platz, 2001). Furthermore, individual congener analysis for BDE-47 and BDE-99 in tissue samples collected from stations W3 and E7 indicate that biotic exposure to PBDEs is current. Singapore, and more generally Southeast Asia, may represent a significant source of PBDEs on the global scale. As mussels are low in the food chain, higher concentrations of PCBs and PBDEs may be expected in organisms, such as marine mammals, at higher trophic levels.

15.6. POPs in mangrove habitats

Mangroves are an important, yet endangered tropical ecosystem in Southeast Asia. Mangroves once covered an estimated 13% of Singapore's total land area in 1820, but now represent less than 0.5% today (Ng and Sivasothi, 1999). They are unique ecosystems with a high level of biodiversity, and new species continue to be recorded in local mangrove habitats (Ng and Sivasothi, 1999). Mangroves also have an important socio-economic role in local aquaculture in Southeast Asia, and serve as nursing grounds for coastal fish stocks (Mumby et al., 2003). They also provide a wide range of food organisms that are commonly consumed by humans in Southeast Asia (e.g., mussels, rodong shell, crab, mullet and even monitor lizard) and aquaculture products (principally prawns and fish). The biomagnification of POPs in ecological food chains has been well documented for freshwater ecosystems (e.g., Stapleton et al., 2001), as well as marine food webs in polar (e.g., Dietz et al., 2000) and temperate regions (e.g., Law et al., 2003; Voorspoels et al., 2003). However, data on the prevalence of POPs in tropical mangrove ecosystems is restricted to just a few studies in Mexico (Páez-Osuna et al., 2002) and Hong Kong (Liang et al., 1999; Zheng et al., 2000), with sparse information on POP levels in biota.

For the purposes of study, organisms were collected within a one-week period in April 2004 at two mangrove sites in Singapore: Sungei Buloh and Sungei Khatib Bongsu (Fig. 15.16). These sites are located on each side of the land-link causeway between Singapore and Malaysia in the Straits of Johore. The causeway represents a physical barrier to marine hydrodynamics around Singapore's northern coast, where there is no exchange of seawater across the causeway. S. Buloh mangrove has been used in the past as a site for prawn aquaculture before being declared a protected nature reserve in 1989. S. Khatib Bongsu is not a protected site.

Criteria for species selection included abundant availability and trophic position within the mangrove food web. Fish were captured using a traditional cast net. Other organisms were collected directly from their

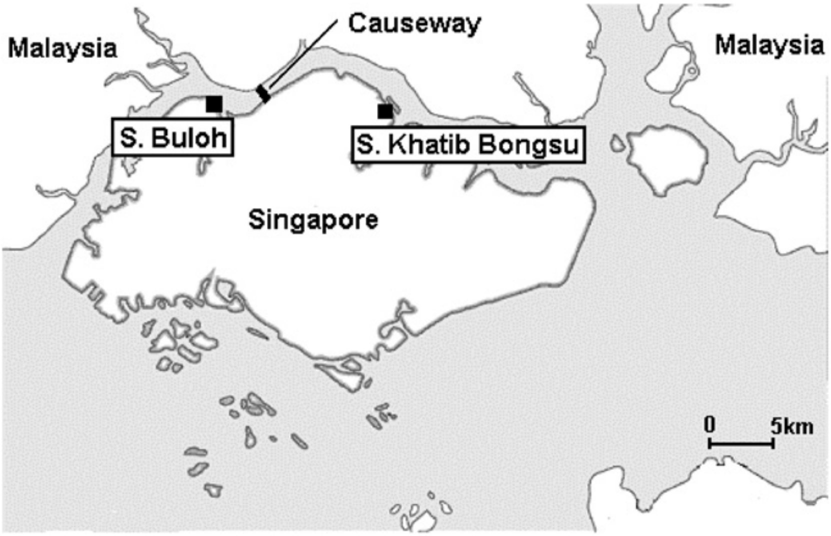

Figure 15.16. Location of Sungei Buloh and S. Khatib Bongsu mangroves in Singapore.

natural habitat. The number of individuals caught was different for each location and varied between 25 to 50 individuals for polychaetes, 6 to 40 individuals for molluscs, 5 to 170 individuals for crustaceans and 1 to 20 individuals for fish. All species sampled were available in large numbers, and a total of 15 species were common to both sites. Size and age are important parameters affecting the level of POPs accumulation (Stapleton et al., 2001), and organisms were selected for analysis in the most similar and available size range possible.

Levels of POPs in seawater and sediments in both mangrove sites are summarized in Table 15.11. All POPs, except PBDEs, were detected in subsurface seawater, SML and sediments. PCBs were the dominant POPs in subsurface seawater and SML with levels ranging from 0.1 to 6.7 ng L^{-1} and 2.4 to 26 ng L^{-1}, respectively. The PCB congener profile in subsurface seawater and SML samples was dominated by PCB 151, which represented more than 80% of the total PCB load at both mangrove sites. HCHs were the dominant OCP in subsurface seawater and SML samples with levels ranging from 0.1 to 2.3 ng L^{-1} and 0.9 to 9.0 ng L^{-1}, respectively. Levels DDTs were generally two orders of magnitude higher than HCHs. *p,p′*-DDT and β-HCH dominated the DDT and HCH profiles of seawater at both sites.

The PCB congener profile in mangrove sediments was dominated by trichlorinated biphenyls in S. Buloh (66% of the total PCB load), whereas

Table 15.11. Levels of POPs in sediments, subsurface seawater and sea surface microlayer collected from mangroves in Singapore

	POPs level in sediments (ng.g^{-1} dw)		POPs level in subsurface seawater (pg.L^{-1})		POPs level in sea surface microlayer (pg.L^{-1})		Enrichment factor microlayer/subsurface	
	SB	SKB	SB	SKB	SB	SKB	SB	SKB
PCBs	0.59–1.14 (0.88)	0.80–1.86 (1.33)	6700–7100 (6900)	140–1500 (910)	2400–26000 (14000)	1500–7300 (4100)	0.3–3.9 (2.1)	2.3–10.9 (6.7)
PBDEs	n.d.	n.d.	<80	<80	<80	<80	n.a.	n.a.
DDTs	<0.1–0.93 (0.29)	0.56–0.85 (0.70)	18–23 (21)	3–72 (32)	21–170 (95)	27–99 (61)	1.2–33 (17)	1.4–8.3 (4.0)
HCHs	1.8–6.0 (3.9)	1.2–1.6 (1.4)	2000–2300 (2100)	110–1100 (770)	4000–9000 (6500)	880–1400 (1100)	1.7–22 (11)	0.8–8.8 (3.6)
Endosulfan	<0.2	<0.2	280–630 (450)	25–40 (30)	330–1800 (1000)	59–240 (140)	2.8	2.4–9.7 (4.9)
Chlordanes	0.01–0.04 (0.02)	0.02–0.06 (0.04)	4–8 (6)	<1–3 (2)	<1–5	<1	1.3	n.a.

Note: n.d.– not detected; n.a.– not applicable.

hexachlorinated (54%) and pentachlorinated biphenyls (27%) were dominant in sediments in S. Khatib Bongsu. HCHs were the dominant organochlorine pesticide in mangrove sediments with levels ranging from 1.2 to 6.0 ng g^{-1} dw.

The concentrations of PCBs, PBDEs, Chlordanes, DDTs, HCHs, and Endosulfans in all mangrove biota samples are reported on a wet weight basis (ww) in Table 15.12. Concentrations in mangrove organisms ranged from BLD to 45 ng g^{-1} ww for Chlordanes, BLD to150 ng g^{-1} ww for DDTs, 0.6–190 ng g^{-1} ww for PCBs, BLD to 9.9 ng g^{-1} ww for PBDEs, BLD to 2.8 ng g^{-1} ww for HCHs and BLD to 25 ng g^{-1} ww for Endosulfans. The lowest concentrations of POPs were found generally in the algal species (*Chaetomorpha gracilis* and *Catellana* sp.), the tube worms (*Dioptra neopolitana*), the nerite snail (*Nerita lineata*), prawn species (*Aphoristia microrhynchus* and *Penaus* sp.) and the tree-climbing crabs (*Episesarma* sp.). The highest concentrations of POPs were found in the soft tissues of the thunder crab (*Myomenippe hardwicki*) and the fishes. Levels of POPs in fish liver and fish eggs were generally one to two orders of magnitude higher than in the muscle tissue. On a lipid weight (lw) basis, POPs in fish livers ranged from 41 to 270 ng g^{-1} lw for Chlordanes, 27 to 860 ng g^{-1} lw for DDTs, 65 to 1600 ng g^{-1} lw for PCBs, 1.8 to 87 ng g^{-1} lw for PBDEs, 1.8 to 17 ng g^{-1} lw for HCHs and 2 to 350 ng g^{-1} lw for Endosulfans.

Concentrations of Chlordanes, DDTs, PCBs and PBDEs, on a dry weight basis (dw), are summarized for the 15 species common to both sites in Fig. 15.17. Higher concentrations of PCBs and PBDEs were generally found in biota from S. Khatib Bongsu and Chlordanes in biota from S. Buloh. However, the differences between the two sites are generally less than three standard deviations and are not significant.

PBDE profiles for mangrove biota samples collected in S. Buloh and S. Khatib Bongsu are presented in Figs. 15.18a b respectively. BDE-47 was the most abundant PBDE congener in the samples accounting for $71 \pm 18\%$ of the total PBDE load. The general contribution to total load is BDE-47 > BDE-99 > BDE-100 > BDE-154 > BDE-153, where BDE-47, -99 and -100 represent $96 \pm 11\%$ of the total load. The percentage of BDE-99 as the total PBDE load in polychaetes, rodongs, oysters, marine prawns and tree-climbing crabs at S. Khatib Bongsu was significantly higher than all other species at this mangrove site, and all species in S. Buloh (Mann-Whitney, $p < 0.05$). Organisms higher in the food chain, especially in S. Khatib Bongsu, appear to have lower levels of BDE-99. BDE-99 was absent in lokan clams (*Polymesoda expansa*) at both sites. With the exception of mullet, BDE-47 was present in lower proportions in fish livers than in muscles.

Table 15.12. POPs concentrations (ng g^{-1} ww) in the mangrove biota samples collected in April 2004

Common name	Site[a]	CHLs	DDTs	PCBs	PBDEs	HCHs	Endosulfans
Green algae	W	0.37 ± 0.12	0.18 ± 0.08	1.1 ± 0.9	BLD	BLD	0.51 ± 0.73
	E	BLD	2.3 ± 1.9	0.71 ± 0.94	BLD	BLD	BLD
Red algae	W	0.13 ± 0.01	0.09 ± 0.04	0.63 ± 0.89	BLD	0.12 ± 0.01	BLD
Nereid worm	W	0.80 ± 0.03	1.1 ± 0.1	1.2 ± 0.2	0.09 ± 0.00	0.14 ± 0.00	0.22 ± 0.03
	E	1.2 ± 0.1	0.75 ± 0.06	3.5 ± 0.1	0.11 ± 0.01	BLD	0.19 ± 0.00
Tube worm	W	1.2 ± 0.0	0.61 ± 0.06	1.3 ± 0.3	0.04 ± 0.02	BLD	0.15 ± 0.00
	E	0.14 ± 0.01	0.34 ± 0.02	0.91 ± 0.26	0.05 ± 0.01	0.05 ± 0.07	0.05 ± 0.06
Nerite snail	W	0.36 ± 0.02	0.75 ± 0.18	1.0 ± 0.6	0.06 ± 0.04	BLD	BLD
	E	0.55 ± 0.20	0.23 ± 0.05	0.53 ± 0.26	BLD	BLD	BLD
Drill shell	W	11 ± 2	5.1 ± 0.8	10.1 ± 2.2	0.74 ± 0.03	0.21 ± 0.00	2.5 ± 0.3
	E	0.60 ± 0.11	0.73 ± 0.00	2.2 ± 0.0	0.16 ± 0.16	BLD	0.08 ± 0.12
Rodong shell	W	0.28 ± 0.00	1.6 ± 0.6	4.8 ± 0.1	0.01 ± 0.02	BLD	BLD
	E	1.2 ± 0.0	4.7 ± 0.1	10.7 ± 2.8	0.17 ± 0.01	0.09 ± 0.12	0.22 ± 0.30
Green mussel	W	1.5 ± 0.1	1.1 ± 0.0	2.7 ± 1.1	0.05 ± 0.01	0.09 ± 0.13	2.4 ± 0.3
Lokan (clam)	W	3.8 ± 0.6	3.1 ± 0.7	4.5 ± 1.9	0.07 ± 0.00	0.22 ± 0.07	4.3 ± 2.7
	E	1.5 ± 0.1	1.0 ± 0.1	3.6 ± 0.8	0.12 ± 0.02	0.06 ± 0.08	0.12 ± 0.16
Leaf oyster	W	5.6 ± 0.9	1.8 ± 0.2	3.6 ± 0.8	0.12 ± 0.15	0.33 ± 0.16	2.2 ± 0.4
Mangrove oyster	E	4.5 ± 0.3	2.5 ± 0.6	8.5 ± 0.5	0.16 ± 0.01	0.21 ± 0.30	1.0 ± 0.1
Barnacles	W	3.1 ± 0.1	0.70 ± 0.05	4.4 ± 2.0	0.09 ± 0.03	BLD	0.67 ± 0.05
	E	3.2 ± 0.2	0.92 ± 0.07	4.8 ± 0.3	0.22 ± 0.04	0.10 ± 0.15	0.35 ± 0.49
Snapping prawn	W	0.10 ± 0.02	BLD	3.5 ± 0.7	BLD	BLD	BLD
	E	0.06 ± 0.00	BLD	2.8 ± 1.0	BLD	0.09 ± 0.12	BLD
Marine prawn	E	0.29 ± 0.10	0.57 ± 0.20	1.9 ± 0.7	0.31 ± 0.07	BLD	BLD
Tree climbing crab	W	0.18 ± 0.00	0.25 ± 0.02	0.59 ± 0.59	0.09 ± 0.00	0.05 ± 0.06	BLD
Muscle	E	2.7 ± 0.0	1.0 ± 0.1	3.8 ± 1.0	0.11 ± 0.01	0.9 ± 0.13	0.19 ± 0.06
Tree climbing crab	W	0.33	1.3	5.3	0.27	0.50	BLD
Egg	E	2.8	7.3	31	1.1	0.68	0.60

Table 15.12. (Continued)

Common name	Site[a]	CHLs	DDTs	PCBs	PBDEs	HCHs	Endosulfans
Thunder crab	W	4.1 ± 0.1	1.8 ± 0.1	4.1 ± 0.7	0.22 ± 0.01	0.24 ± 0.02	0.83 ± 0.11
	E	15 ± 4	5.8 ± 2.9	23 ± 11	2.0 ± 1.2	0.14 ± 0.06	2.1 ± 0.6
Half-beak	W	1.9 ± 0.2	2.3 ± 0.9	4.0 ± 0.9	0.30 ± 0.04	BLD	1.3 ± 0.5
	E	1.5 ± 0.5	2.0 ± 0.6	6.7 ± 2.0	0.35 ± 0.20	0.05 ± 0.06	1.6 ± 1.7
Mudskipper (muscle)	W	BLD	0.17 ± 0.03	0.22 ± 0.25	BLD	BLD	BLD
Eggs		1.5	18	34	0.70	0.2	0.12
Goby (muscle)	E	1.2 ± 0.3	2.4 ± 2.1	24 ± 27	0.35 ± 0.01	BLD	BLD
Liver	E	6.8	70	93	1.8	2.8	0.35
Eggs	E	14	17	70	4.5	0.59	4.1
Glass perchlet	W	1.6 ± 0.3	1.5 ± 0.1	2.6 ± 1.3	0.07 ± 0.07	BLD	0.64 ± 0.40
Cardinalfish (muscle)	E	0.58 ± 0.10	1.6 ± 1.4	2.3 ± 1.3	0.18 ± 0.01	BLD	BLD
Liver	E	45	40	190	9.9	1.9	11
Mullet (muscle)	W	18 ± 2	6.2 ± 0.4	6.7 ± 0.2	0.59 ± 0.07	0.26 ± 0.37	12 ± 8
Liver	W	7.0	3.0	7.1	0.2	0.19	11
Muscle	E	4.7 ± 0.2	4.0 ± 0.3	9.2 ± 1.1	0.42 ± 0.24	0.33 ± 0.04	1.0 ± 0.1
Archer fish (muscle)	W	2.5 ± 1.5	4.8 ± 3.0	5.1 ± 3.1	0.46 ± 0.35	0.13 ± 0.13	3.8 ± 2.7
Liver	W	8.8	15	20	1.2	0.85	25
Muscle	E	1.1	6.8	3.4	0.32	BLD	0.31
Chromide (muscle)	W	0.46 ± 0.16	1.7 ± 1.2	2.3 ± 2.3	0.23 ± 0.12	BLD	BLD
Liver	W	14	47	90	4.8	0.73	4.2
Muscle	E	1.5 ± 0.5	6.7 ± 4.3	7.6 ± 3.8	0.33 ± 0.22	0.18 ± 0.27	0.4 ± 0.3
Liver	E	37	150	150	4.0	2.1	8.0

Note: BLD – below limit of detection.

[a] W: Sungei Buloh, E: Sungei Khatib Bongsu.

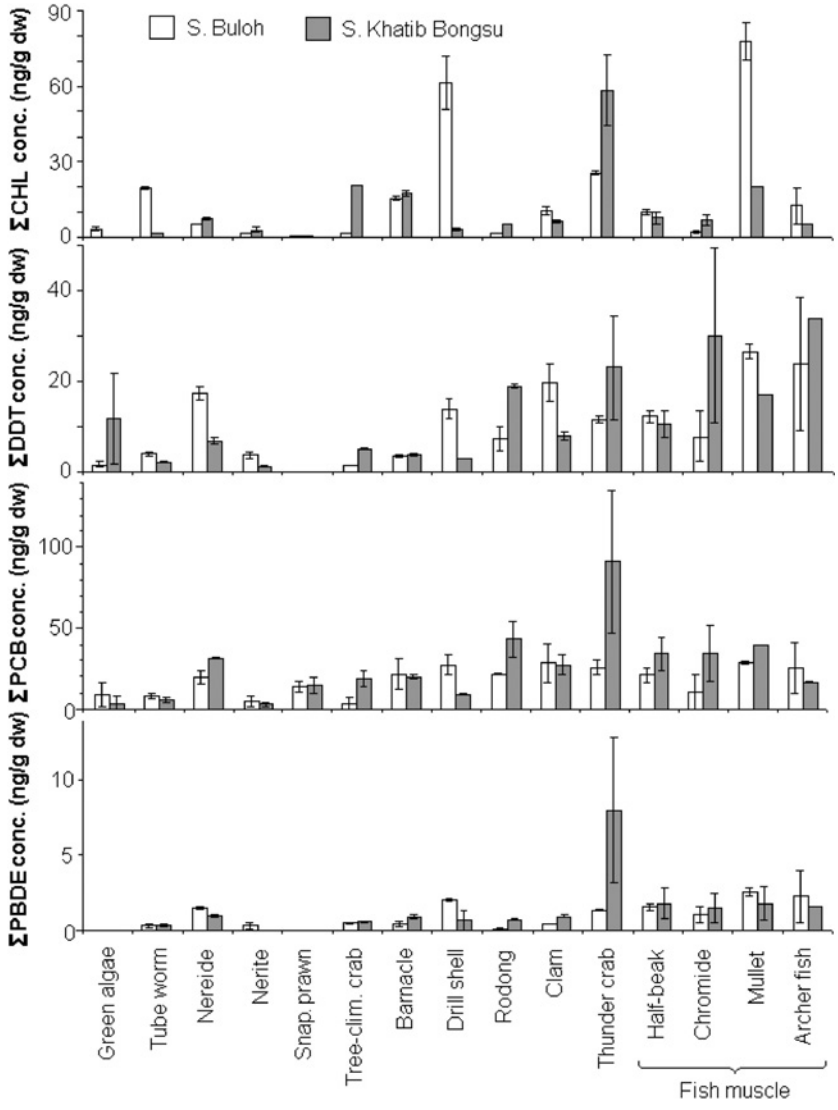

Figure 15.17. Concentrations of POPs in mangrove biota in Singapore (ng g^{-1} dw).

Hexachlorinated and pentachlorinated biphenyls dominated the PCB congener profile with an average of 39 ± 12% and 28 ± 10% respectively. PCB profiles were similar at both mangrove sites (See Figs. 15.19a b), where no clear difference in the PCB profile was discernable between the

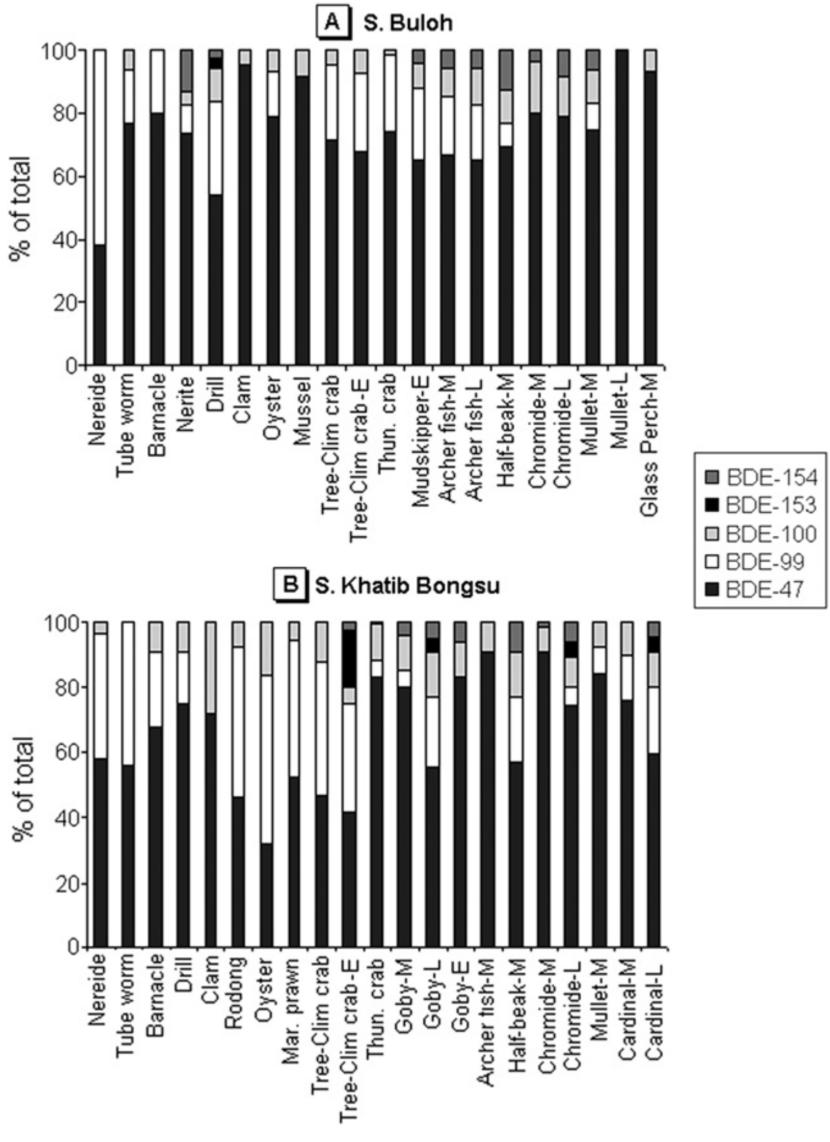

Figure 15.18. PBDE profiles in mangrove biota samples collected in Singapore. M: muscle; L: liver; E: eggs.

various mangrove species. The closest match in the PCB data for mangrove biota samples collected in this study is Aroclor 1254. α- and γ-Chlordane generally dominated the Chlordane congener profile of mangrove biota with an average of 38 ± 16% and 39 ± 16%, respectively

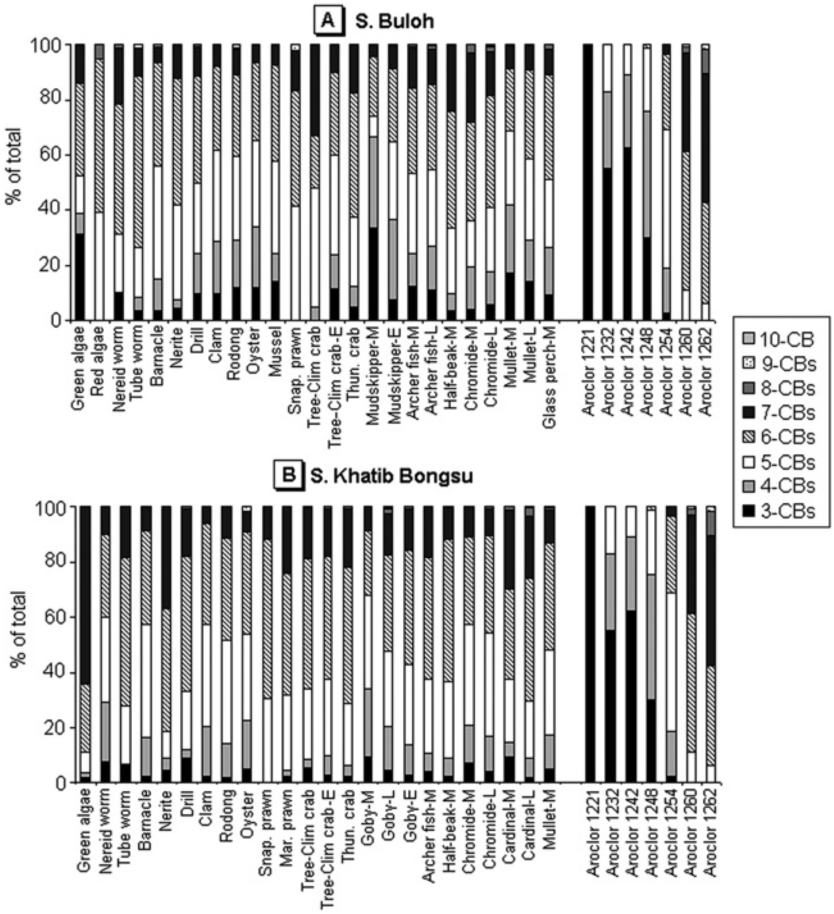

Figure 15.19. PCB profiles in mangrove biota samples collected in Singapore and in commercial Aroclor products. M: muscle; L: liver; E: eggs.

(See Figs. 15.20a b). However, a significantly lower percentage of α- and γ-Chlordane was found in the two crab species (Mann-Whitney, $p<0.05$), and Heptachlor epoxide dominated the profile in crab species. Gobies, mudskipper and shrimp tissues also contained a significantly higher percentage of Heptachlor epoxide (Mann-Whitney, $p<0.05$). *p,p′*-DDE was the dominant DDT congener in all samples, except in the green algae in S. Khatib Bongsu, representing an average of 84±15% of the total DDT load. β-HCH was the dominant HCH congener, representing an average of 72±37% of the total HCH load Fig. 15.21.

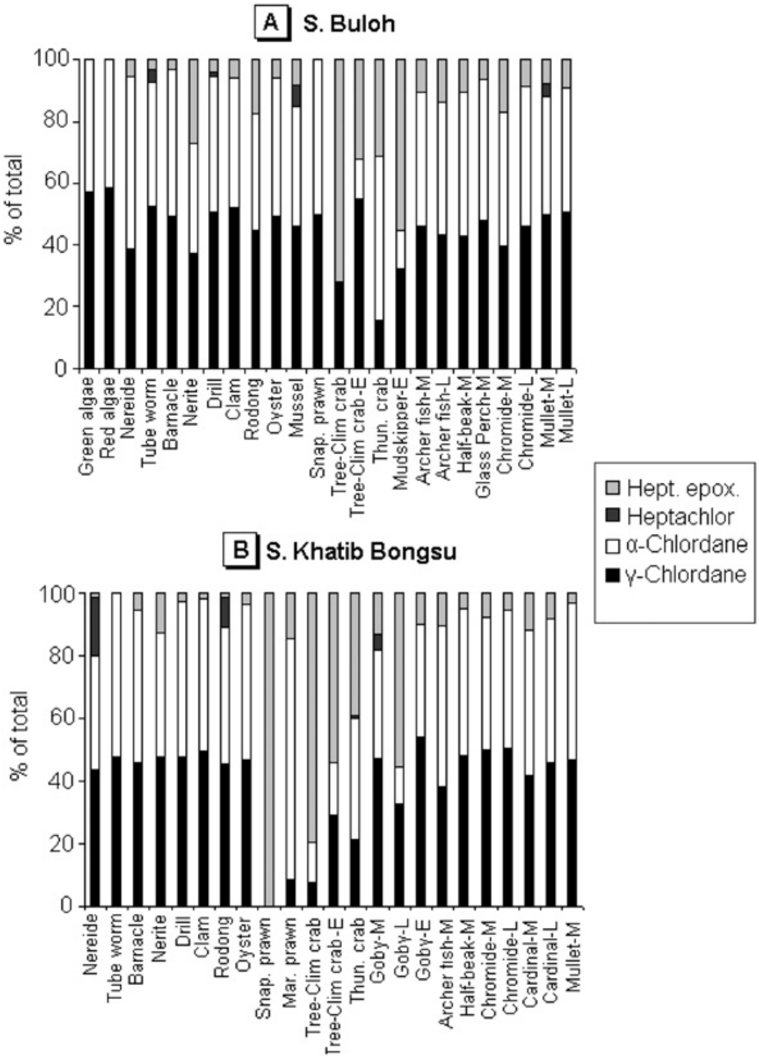

Figure 15.20. Chlordane profiles in mangrove biota samples collected in Singapore. M: muscle; L: liver; E: eggs.

Overall, the levels of POPs in mangrove sediments can be regarded as low (generally below or in the ng g^{-1} dw range), i.e., lower than what has been recorded in the marine sediments in Singapore (Wurl and Obbard, 2005b). Other studies have also reported that mangrove sediments have PCB levels lower or comparable to those in marine sediments, for

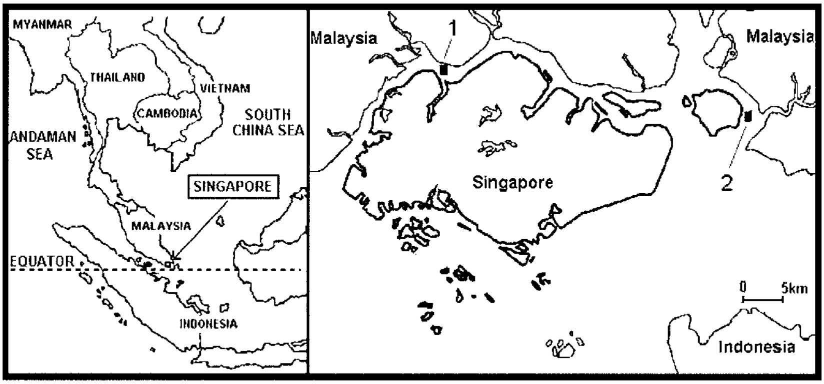

Figure 15.21. Sample stations.

example in Hong Kong (Tam and Yao, 2002; Zheng et al., 2000). Except for similarities between biota and sediments at S. Khatib Bongsu, the PCB congener profile was generally different for seawater, sediments and biota samples. *p,p′*-DDT was dominant in seawater and sediments, while the metabolite, *p,p′*-DDE, was generally dominant in biota samples. This difference may reflect an ability of the biomass to metabolize the parent DDT pesticide, still present in Singapore's marine environment. HCH concentrations in seawater samples were relatively high compared to other POPs, but were relatively low in biota. Biomagnification is not expected for contaminants with a K_{ow} lower than 5 and will only be significant for a $K_{ow} > 6.3$ (van der Oost et al., 2003). HCHs have a K_{ow} of 3.8 therefore have less propensity for bioaccumulation than PCBs and DDTs.

The dominant group of POPs in Singapore's mangrove biota was the PCBs, followed by the organochlorine pesticides DDT and Chlordane. PBDEs and HCHs were present at concentrations generally one or two orders of magnitude less than PCBs. This observation is consistent with the findings presented in a previous study using *P. viridis* as a bioindicator of marine contamination in Singapore (Bayen et al., 2003). Concentrations of POPs in food webs is related to the feeding habits and trophic level of organisms (Dietz et al., 2000; Kidd et al., 2001). The highest POPs concentrations were found in higher trophic status predator species (e.g., thunder crabs, drill shell, archer fish, chromide) and detritivores (e.g., rodong shell), while organisms at lower trophic levels (e.g., tube worm, nerite, prawns) had, in general, the lowest levels of POPs. In particular, the predator thunder crab (*M. hardwicki*) had higher tissue levels of POPs than found in leaf-eater crabs (*Episesarma* spp.), although organisms were collected from the same habitat. A similar observation is valid when comparing the predator polychaete, *Neanthes glandicincta*, and the filter-feeder tube worm (*Diopatra neapolitana*). Differences in POP concentrations between the invertebrates and fish were generally one to two orders of magnitude, which is consistent with other studies (Dietz et al., 2000; Boon et al., 2002). Major biomagnification stage is usually associated between the trophic level of fish and mammals.

Comparison of PBDE levels with other studies is more straightforward by limiting the comparison to the single congener always present in the highest concentration, i.e., BDE-47 (Boon et al., 2002; Voorspoels et al., 2003). The levels of BDE-47 detected in this study (BLD-5.9 ng g^{-1} ww for all mangrove samples; 1.8–69 ng g^{-1} lw in fish livers) cover the middle range of data reported from Europe, Japan and Canada (de Wit, 2002; Law et al., 2003; Voorspoels et al., 2003). Levels of BDE-47 in mangrove fish muscles were higher or in the range of levels recorded for tuna muscle tissue in the China Sea (Ueno et al., 2004). The prevalence of BDE-47 in the PBDE profile, and the relative percentages of other PBDE congeners, are consistent with previous studies (Boon et al., 2002; Voorspoels et al., 2003). BDE-47 was present in lower proportions in the liver of mangrove fish compared to muscle tissue, which is consistent with a previous report on marine fish in Belgium (Voorspoels et al., 2003), but no clear explanation is available. Higher proportions of BDE-99 were present in the PBDE profile of organisms at lower trophic levels in S. Khatib Bongsu (i.e., polychaetes, oyster, rodong shell, marine prawn, tree-climbing crab). In a previous study using *P. viridis* as a bioindicator (Bayen et al., 2003), BDE-99 levels in green mussel tissues were reported as greater than those for BDE-47 in samples collected in Punggol, i.e., near S. Khatib Bongsu, but not mussels collected in S. Buloh. The source of PBDE contamination observed in Punggol is also likely to impact the mangrove at S. Khatib Bongsu. As a result, organisms at low trophic levels in S. Khatib Bongsu (polychaetes, oysters, rodong shell, marine prawn and tree-climbing crab), with a high uptake and/or poor metabolism capability of PBDEs, will also present higher levels of BDE-99. Organisms at higher trophic levels (e.g., thunder crab, fish) may have lower loads of BDE-99 as a result of different uptake/metabolic processes. Gustafsson et al. (1999) showed that the uptake of BDE-47 and BDE-99 were virtually identical for the mussel *M. edulis*. However, Stapleton et al. (2004) demonstrated, in a controlled experiment, that a rapid assimilation of BDE-47 occurred in juvenile carps, whereas no assimilation of BDE-99 was observed. Such differences are likely to explain contrasting PBDE patterns observed in the mangrove organisms of S. Khatib Bongsu.

PCBs concentrations found in shrimps and fish in the mangroves of Singapore are similar to those reported in Hong Kong (Liang et al., 1999). PCB concentrations in mangrove fish correspond to the upper range of what has been recorded in various species of fish elsewhere in the Asia-Pacific region (UNEP, 2002). The PCB profile was generally dominated by penta and hexachlorinated biphenyls, matching the profile of the commercial product Aroclor 1254, one of the main components of Askarel, the common PCB-containing product previously used in transformers and capacitors (Erickson, 1992).

Concentrations of Chlordanes (sum of α- and γ-) are higher than reported values for other marine food webs in the Baltic Sea (Falandysz et al., 2001). Chlordane concentrations in mangrove fish correspond to the upper range of what has been recorded in various species of fish elsewhere in the Asia-Pacific region (UNEP, 2002). The Chlordane profile was dominated by α- and γ-Chlordane in all samples except for crabs and gobies. Falandysz et al. (2001) also noted differences in Chlordane levels between crabs and other marine organisms which were attributed to the potency of crabs to metabolize Chlordane into Oxychlordane.

DDT concentrations in mangrove fish correspond to the middle range of what has been recorded in various species of fish elsewhere in the Asia-Pacific region (UNEP, 2002). *p,p′*-DDE was the dominant DDT congener in mangrove biota, suggesting that no input of DDT has occurred to these ecosystems recently.

Many biological and environmental parameters affect the uptake of contaminants in marine biota. Therefore, a simple interpretation of pollutant data for a large number of organisms is not readily feasible when comparing the two mangrove sites studied. For example, organisms at S. Khatib Bongsu were generally smaller in size than those at S. Buloh. As POP concentrations are known to increase with organism size in some species, such as fish (Liang et al., 1999; Makarevicz et al., 2003), the comparison of the two sites may include a size-related bias. However, mangrove organisms collected in S. Khatib Bongsu generally have higher levels of PCBs and PBDE. This observation is consistent with the findings of previous studies (Bayen et al., 2003) where *P. viridis* was used as a bioindicator, where higher concentrations of PCBs and PBDEs were recorded in the organisms collected in the east Strait of Johore relative to those in the west.

Levels of POPs in marine mammals and birds liver are generally one to three orders of magnitudes higher than in fish liver which, in turn, are four orders of magnitude lower than human adipose tissues (Liang et al., 1999; Dietz et al., 2000). Mammals, such as smooth-coated otters (*Lutrogale perspicillata*), and over 100 species of birds have been recorded in the mangroves in Singapore (Ng and Sivasothi, 1999). If we use this species richness as a guide for mangrove food webs in Singapore, POPs levels in the μg g^{-1} ww range can be predicted in bird and mammal livers. The analysis of POPs in the eggs of fish-eating birds in Hong Kong, such as heron and egrets, revealed toxicological risks to breeding success (Connell et al., 2003). As levels in the present studies are comparable to those in Hong Kong, it is recommended that the risk for organisms at higher trophic levels in the mangroves of Singapore be evaluated.

As noted in Table 15.12 VI-1, at least 10 species of organisms analysed in the present study are commonly consumed by humans in Southeast Asia. Concentrations of POPs did not exceed the food safety standards of Singapore (Government of Singapore, 1990). However, PCB concentrations in mangrove fish muscles are also higher than the mean levels of PCBs in seafood commonly consumed in Singapore, which was found to increase the cancer incidence risk over a human lifetime (Bayen et al., 2004). Therefore, consumption of organisms from mangroves of Singapore should be considered carefully.

The study confirms the ubiquity of POPs, including PBDEs, in the marine environment of Singapore. A biomagnification phenomenon was observed amongst the species collected and analysed from both mangrove sites studied. Overall, available data on the prevalence, fate and transfer of POPS highlights the ubiquity of these pollutants in Singapore's coastal marine environment, and supports the need for a greater awareness of POP bioaccumulation and toxicity, particularly for organisms cultured locally and destined for human consumption.

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Chapter 16

Persistent Organic Pollutants and Adverse Health Effects in Humans in Singapore

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Abstract

Persistent organic pollutants (POPs) are man-made chemicals that have an intrinsic resistance to natural degradation processes, and are therefore environmentally persistent. The introduction of POPs into the environment from anthropogenic activities has resulted in their widespread dispersal and accumulation in soils and water bodies, as well as human and ecological food chains where they are known to induce toxic effects. Due to their ubiquity in the environment and lipophilic properties, there is mounting concern over the potential risks of human exposure to POPs. This has led to the establishment of a worldwide research program to determine prevailing levels of POPs in the population and investigate the health risks associated with background exposure. This paper reviews the state of knowledge regarding residual levels of POPs in human adipose tissue worldwide, and provides preliminary data on the levels of key POPs in female adipose tissues collected in Singapore. Organochlorine pesticides (OCPs) were found to be comparable to levels reported for Poland in 2001, with a mean of 0.98 $\mu g\,g^{-1}$ (or 0.84 $\mu g\,g^{-1}$ on a lipid weight basis). For total polychlorinated biphenyl (PCB) congeners, the mean concentration of 34 $ng\,g^{-1}$ (lipid weight basis) is lower than values reported from Japan in 1980 and Belgium in 2000. Polybrominated diphenyl ethers (PBDEs) are present at similar levels to Belgium in 2000, at 3.7 (or 4.7 $ng\,g^{-1}$ lipid weight basis).

16.1. Introduction

Environmental xenobiotic compounds that are both persistent and bioaccumulative have the potential to induce adverse effects on human health. Persistent organic pollutants (POPs) are a group of compounds

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that are prone to long-range atmospheric transport and deposition, and readily undergo biomagnifications in food chains. The global ubiquity of POPs became apparent following their detection in even remote regions of the Earth, including polar regions at levels posing risks to both wildlife (Barrie et al., 1992) and humans (Mulvad et al., 1996).

Of the numerous POPs that are prevalent in our environment, a ''black list'' (www.pops.int) of POPs has been designated under the diplomatic signing of the Stockholm Convention in 2001. The compounds include: pesticides, namely: aldrin, DDT, dieldrin, endrin, heptachlor, chlordane, mirex, and toxaphene; industrial compounds, namely: hexachlorobenzene and polychlorinated biphenyls (PCBs); and other chemical byproducts, namely: polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)—a general name ''dioxins'' is used for PCDDs and PCDFs. These POPs are known to be particularly toxic with a strong propensity for foodchain biomagnification, and have been associated with both carcinogenic and endocrine disrupting effects in a range of biota. Although the effects on human health from environmental exposure to these POPs remain unclear, there is a growing concern over elevated concentrations of a broad spectrum of POPs in a range of human tissues, including blood, adipose tissue, and breast milk. Due to their lipophilic properties, POPs readily accumulate in human adipose tissue following ingestion of contaminated foodstuffs, and serves as a useful matrix for comparing accumulated levels in different countries.

The ecotoxicological effects of POPs in the aquatic environment have been of great concern in recent years. Based on the global distillation theory, POPs are volatilized into the atmosphere at tropical and temperate latitudes and are subjected to long-range transport resulting in widespread environmental contamination (Iwata et al., 1993). The importance of tropical regions as a source of POPs in the global circulation of these toxic chemicals led us to conduct investigations into the prevalence of these contaminants in the highly urbanized environment of Singapore. It was observed that concentrations of polycyclic aromatic hydrocarbons were considerably higher in Singapore's coastal marine environment, whereas OCPs and PCBs were generally lower than the reported levels for other Asian nations (Bayen et al., 2003, 2004a, b, c; Chanbasha et al., 2003a, b; Gong et al., 2003; Karups et al., 2004a, b; Wurl and Obbard 2004; Li et al., 2005). POPs have also been detected in beach sediments (Chanbasha et al., 2003a), the sea surface microlayer (Chanbasha et al., 2003b), and in marine organisms including the green mussel, *Perna viridis* (Bayen et al., 2003, 2004a, b, c), barnacles (Karups et al., 2004a), and odontocete species (Karups et al., 2004b). POPs with endocrine disrupting activity on androgen and estrogen receptors have been identified in marine water samples from Singapore's coastal water (Gong et al., 2003). Enclosed coastal areas with weak tidal flushing were found to possess higher levels of endocrine disrupting chemicals in seawater extracts (Gong et al., 2003).

Since Singapore's marine environment is used for leisure, fishing, aquaculture, and desalination, bioaccumulation of POPs and their profound long-term effects on human health and reproductive function is a cause for concern. POPs may be introduced into the environment from a variety of emission sources and anthropogenic activities. Point, area, and line sources include releases from industrial installations, domestic premises, traffic, waste disposal operations such as incinerators and landfills, and activities such as crop stubble burning and the spreading of sewage sludge on land. Area sources can also include the release of POPs from diffuse sources such as contaminated land masses or water bodies that have accumulated POPs from both historical and ongoing deposition. The release of POPs into the environment may be subject to regulatory control (industrial installations, waste disposal operations), while others are unregulated (emissions from domestic premises, unmanaged releases from landfills) or adventitious (forest fires, spillages, and accidental releases).

The potential of a substance to bioaccumulate in an organism can be expressed by the bioaccumulation factor (BAF), the bioconcentration factor (BCF) or the octanol–water partition coefficient (K_{ow}). The BAF and the BCF measure the concentration of a particular substance in a living organism relative to its concentration in the surrounding medium. The criteria to determine the propensity of an organic chemical to undergo bioaccumulation were specified in the Toxic Substance Management Policy (TSMP) under the Canadian Environmental Protection Act of 1999 (www.ec.gc.ca). A BCF or BAF that exceeds 5000, or a logarithm of the octanol-water partition coefficient (Log K_{ow}) of the chemical substance that exceeds 5, indicates a propensity to accumulate in lipids. As a result of elevated hydrophobicity ($K_{ow} > 5$), POPs are readily concentrated and retained in the lipid tissues of biota. Humans, at the top of the food chain, typically accumulate the highest concentrations of these hydrophobic and persistent compounds.

For many years, residues of POPs have been readily detected in the human adipose tissue of individuals in a number of countries, including those living in Europe, Asia, Africa, and North America. In this chapter, we review available data from the scientific literature for levels of POPs in human adipose tissue from various countries around the world. We also report the first such data from Singapore and evaluate levels in the global context (Li et al., 2005) and the specific exposure risk to humans in Singapore via the consumption of seafood containing POPs.

16.2. Pesticides

Toxicity and persistence of pesticides are useful properties for killing their target organisms, but these qualities also cause problems for humans and the environment. The occurrence of organochlorine pesticides (OCPs) in the environment and subsequently in the food chain of humans and wildlife has been noted since the early sixties (Frederick, 1991). Toxicological investigations have shown that several pesticides are carcinogenic in animals, thus raising concern over human exposure (Krieger et al., 1994). To date, this concern has led to several OCPs being restricted or banned for agricultural and/or disease vector control under the joint sponsorship of the United Nations Environment Programme, the International Labour Organisation, and the World Health Organization. (www.inchem.org). However, secondary emissions of pesticides that have accumulated in various environmental compartments, including soils, sediments, and water bodies are expected to persist long into the future. Subsequent transport via the atmospheric pathway ensures that pesticides are widely dispersed from their source, regionally and even globally, thereby representing a ubiquitous global risk to human health and wildlife.

Dichlorodiphenyltrichloroethane (DDT) and its derivatives have now been found in most environmental media, and constitute the dominant OCPs found in human tissues, most notably adipose tissue. DDT is organochlorine compound that was first synthesized in Germany in 1874. DDT's insecticidal properties were realized in 1939, and subsequent commercial use began in 1945. In the human body, DDT is first dechlorinated to tetrachlorodiphenylethane (DDD) that is water soluble and less toxic to human health. Another group of DDT derivatives includes dichlorodiphenyldichloroethanes (DDEs), which readily accumulate in human adipose tissue, and represent a significant health threat due to its long half-life. DDE may be accumulated via the metabolism of DDT in the organism itself, or upon ingestion of DDE tainted foodstuffs (Frederick, 1991). Amongst the isomers in the DDE group, anti-androgenic 4,4′-DDE is the most abundant, with concentration levels in human adipose tissues ranging from 3.5 to 3229 $\mathrm{ng\,g^{-1}}$ on a lipid basis in Greenland (Smeds and Saukko, 2001). In contrast, other pesticides, including aldrin, dieldrin, lindane, heptachlor, and heptachlor epoxide, are generally present at low concentrations or below analytical detection limits at the $\mathrm{ng\,g^{-1}}$ level (lipid weight basis) (Dewailly et al., 1999).

Geographically, no major differences in the levels of DDT have been reported for human adipose tissues. Based on available data (Table 16.1), the mean concentration of ΣDDTs in the Asian region is $\sim 2.8\ \mu\mathrm{g\,g^{-1}}$, and

Table 16.1. Levels of pesticides in human adipose tissue from various countries

Country and sampling time	*p,p′*-DDE	*p,p′*-DDD	*p,p′*-DDT	ΣDDTs	α-HCH	β-HCH	γ-HCH	ΣHCHs	References
Japan, 1986–1987	√	√	√	2.4	√	√	√	1.8	Kashimoto et al. (1989)
Greenland	3.1	–	0.9	4.0	–	–	–	–	Dewailly et al. (1999)
Denmark	1.8	–	0.3	2.1	–	–	–	–	Dewailly et al. (1999)
Finland	2.150	–	–	3.476	–	–	–	–	Hattula et al. (1976)
Finland	0.360	–	–	0.383	–	–	–	–	Mussalo-Rauhamaa et al. (1984)
Finland	0.535	–	–	0.557	–	–	–	–	Mussalo-Rauhamaa (1991)
Finland	0.567	0.006	0.011	0.584	–	–	0.178	0.204	Smeds and Saukko (2001)
Mexico, 1988	–	–	–	17.45	–	–	–	–	Waliszewski et al. (1996)
Mexico, 1991	–	–	–	14.60	–	–	–	–	Waliszewski et al. (1996)
Northern Italy, 1989	0.395	–	0.064	0.459	–	0.213	0.104	0.317	Gallelli et al. (1995)
Poland, 1990	√	√	√	15	√	√	√	0.25	Tanabe et al. (1993)
Poland, 1997–2001	0.770	–	0.072	0.842	–	0.064	–	–	Strucinski (2002)
Spain, 1991	√	–	√	4.4	–	√	–	1.53	Gómez-Catalán et al. (1995)
South Vietnam, 1991	√	√	√	4.9	√	√	√	0.03	Nakamura et al. (1994)
Korea, 1994–1995	1.0	0.007	0.056	1.1	0.002	0.18	0.0003	0.182	Kang et al. (1997)
Belgium, 1996–1998	0.471	0.019	0.097	0.587	–	0.004	0.0052	0.0045	Pauwels et al. (2000)
Singapore, 2003–2004	0.789	0.045	0.143	0.977	0.033	0.214	0.025	0.272	Li et al. (2005)

Notse: – = not target compounds; √ = no value reported; mean concentrations (μg g^{-1} on a lipid weight basis).

for Europe and Greenland ~3.3 $\mu g\,g^{-1}$ and 4.0 $mg\,kg^{-1}$, respectively. The highest levels of ΣDDT, with a mean of 84.3 $\mu g\,g^{-1}$ in 1989 and 25.7 $\mu g\,g^{-1}$ in 1991 respectively, were found in persons living in a Veracruz city, Mexico (Waliszewski et al., 1996). Statistical analysis showed that age was positively correlated to levels of several OCPs in adipose tissues of persons living in British Columbia (Gallelli et al., 1995), but no statistically significant differences were found between sexes (Teschke et al., 1993).

Reporting on the storage of the separate isomers in fat tissue among the hexachlorocyclohexanes (HCHs) group of pesticides, investigators found that beta-HCH was the predominant isomer. Due to its greater stability and lipophilic properties, beta-HCH is metabolized only slowly and thus eliminated from the human body at a lesser rate than other HCH isomers (Greve and van Zoonen, 1990). Eighteen years of monitoring data from Holland between 1968 and 1986 showed that beta-HCH concentrations were persistent over time, with little evidence of a marked decline (Greve and van Zoonen, 1990).

Hexachlorobenzene (HCB) is another important pesticide contaminant in human tissues. HCB enters the environment via its agricultural use as a fungicide, and as an industrial byproduct. It is chemically stable and highly recalcitrant in the environment. Due to its persistence, specifically in the tissues of animals of a higher trophic status, HCB continues to pose a threat to public health. In the early seventies, in the Netherlands, an increase of HCB in human adipose tissues was associated with an increase in HCB concentrations in consumer products of animal origin (Greve and van Zoonen, 1990). Following a ban by some EU countries in the 1970s, there has been a gradual decrease of HCB concentrations in biota. In the adipose tissues of Dutch citizens, the concentration of HCB (0.7 $mg\,kg^{-1}$) in 1986 was half (1.3 $mg\,kg^{-1}$) of that reported in 1968–69 (Greve and van Zoonen, 1990).

16.3. Dioxins, furans, and polychlorinated biphenyls

Dioxins (PCDDs) and furans (PCDFs) are polyhalogenated aromatic hydrocarbons of high toxicity. There are a total of 210 different congeners; 75 dioxin congeners and 135 furan congeners, of which 17 are potentially toxic. Dioxins and furans are now found prevalent in air, water, and soil in almost all natural environments. PCDD/Fs are strongly bound to organic matter, where half-life in soil has been estimated at 10–20 years (Ryan et al., 1987). PCDD/Fs enter the environment primarily as unintentional byproducts of combustion and chemical processes.

Waste incinerators have been identified as one of the major sources in the urban environment, and others include uncontrolled combustion. Car-exhaust emissions, especially from cars using leaded gasoline with halogenated scavengers also contain considerable levels of PCDD/Fs.

From studies conducted in the 1980s, persons inhabiting industrial areas were found to have higher tissues dioxin levels in adipose tissue (Schecter et al., 1994). For example in rural China, values of 0.142 ng g^{-1} of dioxin were reported in 1984—almost 10 times less than levels reported for the industrialized areas of Japan, Canada, and New York, USA (Table 16.2). PCDD/F levels at 1.75 ng g^{-1} were measured in adipose tissues samples from certain areas of South Vietnam in 1984—10 times higher than concentrations measured in the north of the country. Over 170 kg of 2,3,7,8-TCDD, a congener of PCDD, was sprayed onto vegetation as a defoliant from fixed-wing airplanes or helicopters to certain areas in the south of Vietnam during the war between 1962 and 1970 and is the direct cause of the high PCDD/F levels found in human adipose tissues (Schecter et al., 1986).

The National Human Adipose Tissue Survey (NHATS) was first conducted by the United States Environmental Protection Agency in 1987. An average concentration of 5.38 pg g^{-1} (wet weight) of 2,3,7,8-TCDD was reported in the adipose tissue of the US population, increasing from 1.98 pg g^{-1} in children under 14 years of age to 9.40 pg g^{-1} in adults over 45 years. Due to the different health risks associated with individual PCDD/F congeners, the International Equivalency (I-TEQ) factor was established by the North Atlantic Treaty Organization (NATO) in 1989. More recently, in 1998, the World Health Organization specified Toxic Equivalency Factor (WHO-TEQ) values with slightly different weighting coefficient for PCDD/Fs toxicity compared with those from I-TEQ, and as such is not directly comparable for risk evaluation in human health.

A mean level of PCDD/PCDFs has been reported at 35.6 pg I-TEQg^{-1} lipids in adipose tissue of citizens of France. Samples analyzed in 1999 were found to have similar levels to those reported for other European countries and the USA. No relation to sex or age of the tissue donor was apparent, and levels can be considered as representative of prevailing concentrations of these compounds in most industrialized countries (Schecter et al., 1994). There was no obvious trend of PCDD/F levels found in adipose tissue in citizens of Japan between 1970 and 1999 (Choi et al., 2002; Takenaka et al., 2002) (Table 16.2). However, in 2000, the concentration of PCDD/Fs was reported as only one-third of the amount in 1999 (Choi et al., 2002). This magnitude of decline seems unlikely over such a short time interval, but a longer term reduction is supported by the downward trend in emission levels of PCDDs and PCDFs following

Table 16.2. Levels of PCDDs, PCDFs, and PCBs in human adipose tissue from various countries

Country and sampling time	PCDD/Fs	PCBs	References
Korea, 1994–1995	19^{a} (males) 16.5^{a} (females)	– –	Kang et al. (1997)
France, 1999	35.6^{a}	–	Arfi et al. (2001)
Japan, 1970–1971	31.6^{a}	–	Choi et al. (2002)
Japan, 1994–1996	31.5^{a}	35.4^{a}	Choi et al. (2002)
Japan, 1998–1999	49^{b}	17^{b}	Takenaka et al. (2002)
Japan 2000	11.9^{a}	15.3^{a}	Choi et al. (2002)
India	14–46^{b} (males) 16–56^{b} (females)	 –	Kumar et al. (2001)
Spain, 1997–1998	31^{a}, 36.3^{b}	25.2^{b}	Schuhmacher et al. (1999); Wingfors et al. (2000)
Spain, 2002	9.2^{a}, 11^{b}	10.8^{b}	Agramunt et al. (2005)
Italy	2.81–13.2	–	Baldassarri et al. (2002)
North of Vietnam, 1984	0.142	–	Schecter et al. (1986)
South of Vietnam, 1984	1.749	–	Schecter et al. (1986)
China, 1984	0.113	–	Ryan et al. (1987)
Japan, 1984	1.667	–	Ryan et al. (1987)
Canada, 1976	1.017	–	Schecter et al. (1986)
Canada, 1980	0.915	–	Schecter et al. (1986)
USA, New York, 1982–1983	1.047	–	Schecter et al. (1986)
Finland, 1984	<0.002–7.70	–	Koistinen et al. (1995)
Belgium, 1996–1998	–	373.1 (7 congeners)	Pauwels et al. (2000)
Belgium, 2000	–	879.7 (35 congeners)	Covaci et al. (2002)
Poland, 1979	–	1200^{c}	Tanabe et al. (1993)
Poland, 1990	–	1500^{c}	Tanabe et al. (1993)
Japan, 1980	–	3000^{c}	Loganathan et al. (1990)
Japan, 1981	–	3100^{c}	Mori et al. (1983)
Japan, 1986–1987		775^{c}	Kashimoto et al. (1989)
Singapore, 2003–2004	–	34 (40 congeners)	Li et al. (2005)

Note: Mean concentrations (ng g^{-1} on a lipid weight basis).

[a]PCDD/F and PCB toxic equivalents (TEQ) are given as I-TEQ.

[b]PCDD/F and PCB toxic equivalents (TEQ) are given as WHO-TEQ.

[c]Numbers of congeners not specified.

implementation of strict emission regulations and associated abatement technologies (Papke, 1998).

Polychlorinated biphenyls (PCBs) are a family of 209 congeners for which there are no known natural sources. PCBs were widely used as coolants and lubricants in electrical components and paint additives until they were widely banned in the 1970s by most developed nations. During their manufacture and use, PCBs were released into the atmosphere via industrial emissions, weathering of PCB containing materials, and the incineration of PCB-containing products. However, PCBs continue to be released into the environment from leakage of defunct equipment, leaching from landfills, and from previously contaminated soils and sediments. Recent reports have shown that oily fish and Scottish-farmed salmon contain particularly high levels of PCBs (The Sunday Times Magazine, 2004). PCBs have the potential to affect thyroid hormone functions, thereby impairing mental development (The Sunday Times Magazine, 2004).

In a survey of Dutch citizens, the levels of PCBs did not change over a 10-year period between 1973 and 1983, where the persistence of PCBs in fatty tissues remained at a level of $3\,\mu g\,g^{-1}$ (lipid weight basis) (Ryan et al., 1987). With mean levels of PCBs among Poland's population measured at 1200 and $1500\,ng\,g^{-1}$ (lipid weight basis) in 1979 and 1990 respectively, the data indicates the potential of PCBs to persist in human adipose tissue over time (Shinsuke et al., 1993). Although a ban ended the use of PCBs in Japan in 1976, high levels of PCBs of up to $3000\,ng\,g^{-1}$ (lipid weight basis) were detected in human adipose tissue in 1981. However, the concentration of PCBs was reduced to a mean level of $775\,ng\,g^{-1}$ (lipid weight basis) within 36 human adipose tissue samples analyzed in Japan in 1987 (Kashimoto et al., 1989).

Due to similar mechanisms of toxicity to dioxins for some PCB congeners, including non-*ortho*, mono-*ortho* chlorine substituted biphenyls, these compounds are also referred to as "dioxin-like" compounds and rated in terms of toxic equivalency I-TEQ or WHO-TEQ. As shown in Table 16.2, recent studies conducted in Japan between 1994 and 2000 reported dioxin-like PCB congener I-TEQ or WHO-TEQ values which can be used to compare toxicity profiles with PCDD/Fs and assess exposure risk to human health (Choi et al., 2002; Schuhmacher et al., 2004). An earlier study, conducted in 1994, showed similar I-TEQ values of $31.5\,ng\,g^{-1}$ (or $35.4\,ng\,g^{-1}$ on a lipid weight basis) in human adipose tissues for PCDD/Fs and PCBs, which indicates a similar level of toxicity for PCDD/Fs and PCBs to human health, respectively. In 2000, the levels of PCDD/Fs and PCBs with I-TEQ values were also comparable, but reduced to the levels of $11.9\,ng\,g^{-1}$ (or $15.3\,ng\,g^{-1}$ on a lipid weight basis) in human adipose tissues from Japan, which indicates a declining toxic effect on human health over a period of 6 years. A separate study, conducted from 1982 to 1989, on human adipose tissues obtained from donors in Atlanta, Georgia, showed that dioxin-like PCB congeners in adipose tissue varied greatly between samples whereas PCDD and PCDF profiles were more consistent. Age was positively correlated with the concentrations of PCDDs and PCBs in adipose tissue (She et al., 2002).

16.4. Polybrominated diphenyl ethers (PBDEs)

Rarely has there been so much discussion about a group of chemical products as the flame retardants (www.bsef.com). PBDEs are a specific group of flame retardants widely used in plastics, textiles, electronic circuitry, and other materials to suppress combustion. Three industrial formulations of PBDEs are used widely as flame retardants (BSEF, 2001). Deca-BDE (consisting almost completely of BDE-209) is used mainly in thermoplastics and textiles; octa-BDE (a mixture of hexa- to octa-BDE congeners) is used in acrylonitrile/butadiene/styrene plastics; and penta-BDE (a mixture of tetra-and penta-BDE congeners) is used mainly in polyurethane foam. In 2001, total worldwide demand for these three PBDEs reached 67 MT. Production of all PBDEs has escalated greatly over the last 20 years, and this has been accompanied by their emergence in a diversity of environmental and biological matrices (Cynthia and de Wit, 2002). To date, the toxicology of PBDEs is still under investigation, but it has been established that PBDEs are environmentally persistent, bioaccumulative, and toxic to human health (Watanabe and Tatsukawa, 1990). The critical effects of penta-BDE are associated with neurobehavioral development at low doses (from a dose of 0.6 mg kg^{-1} body weight) and, at higher doses, effects on thyroid hormone levels in rats and mice (Domingo, 2004). Due to concerns over rising levels of contamination in human breast milk and wildlife, as well as associations with thyroid dysfunction, penta- and octa-BDE were banned in the EU in mid-2003 (www.bsef.com). Deca-BDE has been classified as a possible human carcinogen and is known to interfere with brain development in rats (The Sunday Times Magazine, 2004).

PBDE congeners 2,2′,4,4′-tetra-BDE (BDE-47), 2,2′,4,4′,5-penta-BDE (BDE-99), and 2,2′,4,4′,5,5′-hexa-BDE (BDE-153) were detected at high levels in human adipose tissue samples from Sweden in 1999 and, combined, constituted 87–96% and 84–94% of the total sum of PBDEs in liver and adipose tissue, respectively (Meironyté Guvenius and Norén, 1999). BDE-47 has been identified as the predominant congener in the adipose tissue of contemporary California women, where concentrations ranged between 5.2 and 196 ng g^{-1} of lipid, with a median value of 28.9 ng g^{-1} of lipid among 32 breast adipose tissue samples analyzed in 1995. These levels were between 3 and 10 times higher than those measured in similar samples from Japan, Sweden, Germany, and Norway

Table 16.3. Mean levels of PBDEs (ng g^{-1} on lipid weight basis) in human adipose tissue from various countries

Country and sampling time	PBDEs	References
USA, California	28.9 (PBDE47)	Washam (2003)
USA, San Francisco Bay	85.7 (PBDE47, 99, 153, 154)	Petreas et al. (2003)
Belgium, 2000	4.75 (PBDE28, 47, 99, 100, 153)	Covaci et al. (2002)
Sweden	5.36 (PBDE17, 28, 47, 66, 100, 99, 85, 154, 153)	Meironyté Guvenius et al. (2001)
Sweden	11.7 (PBDE47, 99, 100)	Haglund et al. (1997)
Sweden	3.8–16 (PBDE47)	Lindström (1998)
Sweden	5.0 (PBDE28, 47, 85, 99, 100, 153, 154)	Meironyté Guvenius and Norén (1999)
Finland	6.3–22 (PBDE47, 99, 153)	Strandman et al. (1999)
Spain	25.1 (PBDE47, 99, 153)	Meneses et al. (1999)
Singapore, 2003–2004	3.7 (PBDE47, 99, 100, 153, 154)	Li et al. (2005)

Note: Mean concentrations (ng g^{-1} on a lipid weight basis).

(Lindström, 1998; Strandman et al., 1999; Covaci et al., 2002; She et al., 2002; Washam, 2003). The authors speculated that high levels may be due to California's flammability regulations that demand the use of treated polyurethane foam and textiles used in furnishings. A relatively high concentration of BDE-47 in the adipose tissue of a 74-year-old Swedish male was reported at 8.8 ng g^{-1} lipid on a weight basis in 1994 (Haglund et al., 1997), which indicates the strong propensity of PBDE bioaccumulation in the human body over a lifetime. In four Swedish reports, the sum concentrations of PBDEs did not show any clear change in adipose tissue samples between 1997 and 2001 (Haglund et al., 1997; Lindström, 1998; Meironyté Guvenius and Norén, 1999; Meironyte Guvenius et al., 2001).

Reported data on the levels of PBDE congeners in human adipose tissues from various countries are given in Table 16.3.

16.5. POPs in human disease

Diet plays an important role as a source of exposure to many synthetic organic chemicals used in industry, agriculture, or accidentally released to the environment. Among these, OCPs, PCBs, hexachlorobenzene (HCB), and the pesticides including DDT and lindane (γ-hexachlorocyclohexane, HCH) have been classified as possible carcinogens to humans by the International Agency for Research on Cancer (IARC, 1987, 1991). Although initial data for these classifications have been derived from animal experimentation, the evidence for carcinogenesis in humans is accumulating from both non-occupational and occupational exposure studies (ATSDR, 2000, 2002). It is noteworthy that these POPs remain one of the most important groups of persistent pollutants to which humans are exposed to, primarily via dietary intake of dairy products, meat, and fish. Being lipophilic, they are not readily metabolized or excreted and readily accumulate in adipose tissue. Many are semivolatile, capable of traveling in air for thousands of miles before they settle. These compounds resist photolytic, biological, and chemical degradation and persist in the environment, taking as long as a century to degrade.

Concerns over the detrimental effects of exposure to POPs initially arose from investigations of wildlife communities that showed reproductive, developmental, endocrine, and carcinogenic effects. High rates of malformed genitalia, aberrant mating behavior, sterility, cancer, immune, and thyroid dysfunction have been reported for a range of species (Colborn et al., 1993; Johnson, 1998; Tryphonas, 1998; Fisher, 1999). Moreover, hematological, neurodevelopmental, and reproductive effects have been noted in animals at levels of exposure that overlap the range of concentrations and body burdens found in humans (Johnson, 1998). Available epidemiological evidence in humans suggests that they are similar to those in animals affecting neurodevelopment (Lai et al., 1994; Lai, 2001; Ribas-Fito, 2001), thyroid (Brouwer et al., 1998), estrogen (Wade, 2000), and immune functions (Jacobson, 1990a). The developing brain and nervous system in the fetus appears to be most vulnerable. A landmark longitudinal study from Lake Michigan indicated that babies born to mothers who consumed large amounts of fish contaminated with PCBs had lower birth weights, smaller head circumference, and a shorter attention span than those from mothers who did not eat fish (Jacobson, 1990a, b). Follow-up of these children over a time span of 11 years showed that they continued to perform poorly in a range of skills and developmental tests, including deficits in intellectual functions (Jacobson and Jacobson, 1996). Although postnatal exposure to PCBs through breast-feeding was reported to be not clearly related to any effect on neurological development in these children, current understanding of such adverse health effects following exposure to POPs is limited by available research methods and measures of exposure and outcome. Twelve POPs including nine pesticides designated as the “Dirty dozen” have been identified by the United Nations Environment Programme as potential threats to the health of humans and wildlife and have been targeted for elimination (Ritter, 1995).

In addition, residence in close proximity to hazardous waste sites containing POPs has shown to be a risk factor for several cancers (Ozonoff et al., 1994), low birth weights (Baibergenova et al., 2003), and congenital malformations (Geshwind et al., 1992; Marshall et al., 1997) in susceptible individuals. Besides, persons living near the three areas of concern in New York had significant elevations in rates of hospitalization for thyroid and genital cancers (Carpenter, 2001). Marked elevations in respiratory diseases also correlated well with the concentrations of PCBs measured in blood (Nakanishi et al., 1985). Although conventional wisdom dictates that ingestion is the major source of exposure to POPs, the above studies clearly demostrate that living in proximity to POP-contaminated sites could lead to widespread exposure of the population via air transport of contaminants. Either particulates or vapor phase POPs could have been ingested or inhaled.

More recently, it had been reported that prenatal exposure to PCBs and their heat degradation product dibenzofurans resulted in babies born with retarded growth with dysmorphic physical findings, delayed cognitive development, increased otitis media, and more behavioral problems than in unexposed children (Guo et al., 2004b).

Ingestion of rice oil contaminated with PCBs resulted in the ‘‘Yucheng’’ disease in Taiwan in which the patients developed chloracne, hyperpigmentation, and peripheral neuropathy amongst other signs and symptoms. The acneform eruptions were predominantly in the form of open comedones, papules, and pustules which were distinct from acne vulgaris in that they had dark heads and were found not only in the classified sites for acne but also on extremities, axillae, and external genitalia (Guo et al., 2004a). The offspring of Yucheng women after exposure to PCBs and dinitrofurans constitute one of the largest groups (~2000) of humans prenatally contaminated with high levels of these pollutants (Guo et al., 2004b). A more meticulous longitudinal study of this group of toxicants in the second and third generation offspring of affected women could provide more information on dose-response relationship, teratogenicity, and endocrine-disrupting mechanisms of these hazardous chemicals.

16.6. POPs as endocrine disrupters

Recently, Harrison and Sharp and Irvine summarized the hypothesis and status of evidence implicating endocrine disruption and their adverse impacts on human health (Sharp and Skakkebaek, 1993; Harrison, 2001; Sharp and Irvine, 2004). They outlined that exposure of the fetal/developing male to environmental pollutants resulted in hypospadias, cryptorchidism, prostrate cancer, testicular cancer, a global decrease in sperm counts, and decreased male reproductive capacity. Detrimental effects in women include breast cancer, cystic ovaries, and endometriosis.

The hallmark of Harrison and Sharp's proposition is the so-called Sharp-Skakkebaek hypothesis for reproductive abnormalities in men that can be attributed to an increased exposure to estrogens in utero (Sharp and Skakkebaek, 1993), whereby synthetic chemicals in the environment are the prime source of excessive estrogenic stimulation of the male fetus. However, in many instances it is difficult to assign causality because of the complexity of environmental contaminants and the lack of adequate analytical data that document contaminant levels during critical windows of exposure. Nevertheless, there have been several adverse effects in wildlife populations that strongly correlate with POP exposure (Brunstrom and Halldin, 2000). As noted by the recent assessment by the World Health Organization, the clearest available evidence is derived from animal studies including reproductive and immunological effects in marine organisms living in environments contaminated by OCPs PCBs, DDE (WHO, 1978). Egg-shell thinning and embryonic abnormalities in various avian species exposed to DDT and PCBs have been reported (Vos, 2000), as well as the induction of vitellogenin in fish and marine mollusks living near effluent sewage treatment plants (Damstra, 2005). Alligators exposed to organochlorine pesticides spilled into lakes display a host of morphologic and hormonally related abnormalities of the male and female reproductive tracts (Guillette et al., 1994, 1996). Conversely, lower concentrations of POPs in the Great Lakes region have correlated with dramatic improvements in reproductive capacities with significant increases in the populations of cormorants, gulls, terns, herons, and other predatory birds in this region (Tremblay and Gilman, 1995).

In humans, adipose tissue levels of POPs are 200–1000 times higher than in the corresponding concentrations in serum (Kutz and Wood, 1991; Mussalo-Rauhamaa, 1991; Toppari, 1996). Therefore, even small samples of adipose tissue have organochlorine compounds in the detectable range and are more suitable for congener-specific analysis (Wolff, 1983). This tissue also provides a good measure of cumulative internal exposure to these environmental agents. In order to evaluate the abdominal adipose tissue concentrations of POPs, a hospital based control study of pregnant women undergoing elective caesarean section was conducted in Singapore (Li et al., 2005). Our investigations on adipose tissue levels of POPs revealed that DDT and its derivatives were the dominant pollutants present in adipose tissue with a concentration range from 7 to 2928 $\mathrm{ng\,g^{-1}}$, and a mean of 977 $\mathrm{ng\,g^{-1}}$ on a lipid weight basis which is comparable to the value from Finland (Mussalo-Rauhamaa et al., 1984) and Poland 2001 (Teschke et al., 1993). A total of 41 congeners of PCBs were analyzed and ranged in concentration from 7 to 71 $\mathrm{ng\,g^{-1}}$ with a mean of 34 $\mathrm{ng\,g^{-1}}$ on a lipid weight basis. These levels are much lower than reported in Japan in 1980 Mori et al., 1983; (Loganathan, 1990), and Belgium in 2000 (Covaci et al., 2002). A sum of five PBDE congeners (BDE-47, 99, 100, 153, 154) were present at a concentration range of 0.5–12.3 ng g^{-1}, and a mean of 3.6 ng g^{-1} (lipid weight basis) in adipose tissue which is comparable to values obtained from Belgium citizens in 2000 (Covaci et al., 2002).

The concern that organochlorine pollutants in the environment or ingested foods may cause cancer in humans is widespread. Evidence has been accumulating that PCBs are carcinogenic in nature due to the fact that they are weakly estrogenic and some organochlorines have been tested almost exclusively in epidemiological studies in breast (Aronson et al., 2000; Hoyer et al., 2001), prostrate (Hoyer et al., 2001), colorectal, endometrial cancers (Howsam et al., 2004), and in non-Hodgkin's lymphoma (Quintana et al., 2004). Moreover, critical periods of urogenital tract and nervous system development in utero and during early postnatal life are especially sensitive to hormonal disruption with a potential impact on sexual maturation (Krstevska-Konstantinova, 2001) and neuro-developmental retardation (Jacobson and Jacobson, 1996). A delay in pubertal breast development has been linked with dioxin-like compounds in serum samples in girls (Staessen et al., 2001), while DDT/DDE exposure resulted in precocious puberty (Staessen et al., 2001). Early onset of menarche has also been associated with PBB exposure, but no such effect was observed in pubertal girls with regard to PCB exposure (Den Hond, 2002; Vasiliu et al., 2004). It is likely that a different endocrine activity could be ascribed to the different halogenated POPs. Further research is warranted to elucidate the mosaic of putative endocrine disruption effects induced by specific POPs in relation to aberrant sexual maturation and carcinogenicity in humans.

16.7. POPs in typical seafood consumed in Singapore

The routes of exposure to POPs for human beings include inhalation, dermal exposure, and ingestion of water or food contaminated by POPs. Cases of occupational or accidental exposure to POPs have been recorded, particularly during the application of pesticides (Vallack et al., 1998). However, food consumption is one of the most important pathways of exposure for the general population (Dougherty et al., 2000; Stefanelli et al., 2004).

Seafood consumption is a rich source of vitamins, minerals, proteins, and omega-3 polyunsaturated fatty acids that have a wide range of beneficial effects for human health (Sidhu, 2003). However, among food items, seafood has been identified as a major source of POPs (Bocio et al., 2003), particularly in Asian countries, where fish and shellfish account for a significant component of the dietary intake (Kannan et al., 1997; Ohta et al., 2002; Simmonds et al., 2002). As a consequence of high consumption rates, a strong correlation exists between the levels of PBDEs in human breast milk and fish consumption (Meironyté et al., 1999; Ohta et al., 2002). Most controversially, in the USA, it has been shown that 11-year-old children born to women who had consumed contaminated fish from the Great Lakes, i.e., exposed to polychlorinated biphenyls, had memory and attention problems (Jacobson and Jacobson, 1996). Reports of POPs in seafood include xenobiotics such as PCBs (Bjerregaard et al., 2001), organochlorine pesticides (Smith and Gandolli, 2002), PBDEs (Bocio et al., 2003), dioxins, and furans (Schecter et al., 2003). In particular, the impact of consuming farmed fish has recently raised health concerns as elevated levels of POPs have been measured in edible tissues relative to wild fish (Easton et al., 2002; Antunes and Gil, 2004; Hites et al., 2004).

However, although the importance of seafood in the human exposure to POPs, no information is available regarding the human intake of contaminants via seafood consumption in Asian countries, including Singapore. Seafood consumption in Singapore averaged 46.3 and 49.9 g/day for women and men, respectively, in 1998 (Ministry of Health, Singapore, 2001), which is comparable to typical seafood consumption rates in Taiwan (Chien et al., 2003), but more than twice the intake in San Francisco, USA (Greenfield et al., 2003). Most seafood consumed in Singapore is imported—principally from elsewhere in Asia (e.g., prawns from Thailand), but also from Europe (e.g., salmon from Norway) and the Americas (e.g., scallops from USA), (Singapore Trade Development Board, 2001). In this study, the levels of POPs (i.e., PCBs, PBDEs, and organochlorine pesticides) were measured in the edible portions of 20 different seafood types commonly consumed in Singapore and a contaminant risk assessment was conducted based on seafood consumption (Bayen et al., 2005b).

Twenty types of seafood were collected from local supermarkets between June 2002 and June 2003. Details of the samples analyzed are presented in Table 16.4. The selection of the seafood types was based on supermarket sales figures and represents typical consumption patterns in Singapore (personal communication). Levels of α- and γ-chlordane, DDTs (sum of *p,p′*-DDT, *p,p′*-DDD and *p,p′*-DDE), PCBs (sum of congeners 17, 18, 28–31, 33, 44, 49, 52, 70, 74, 82, 87, 90–101, 105, 110, 118, 128, 132, 138, 149, 151, 153, 156, 169, 170, 171, 177, 180, 183, 187, 194, 199, 201, 205, 206, 208, and 209), and PBDEs (sum of congeners 47, 99,

Table 16.4. Sample types and characteristics of seafood

Seafood type	Species	Sample size
Shark steak	Species not identifiable	4 fillets
Shark fin	Species not identifiable	2 × 100 g
Cod fillet	Species not identifiable	2 fillets
Stingray fillet	*Dasyatis kuhlii*	2 fillets
Tuna steak	Species not identifiable	4 fillets
Canned tuna	Species not identifiable	2 cans
Silver pomfret fillet	*Pampus argenteus*	3 fish
Selar fillet	*Selar crumenophtalamus*	3 fish[a]
Kuning fillet	*Selaroides leptolepis*	10 fish[a]
Conger eel fillet	Species not identifiable	2 fillets
Greasy grouper fillet	*Epinephelus coioides*	3 fish
Sea bass fillet	*Lates calcarifer*	3 fish
Song fish fillet	*Aristichthys nobilis*	2 fillets[a]
Salmon fillet	*Salmo salar*	3 fillets
Squid ring	Species not identifiable	140 g[a]
Grey prawn	Species not identifiable	12 prawns[a]
Giant tiger prawn	*Penaeus monodon*	12 prawns[a]
Flower crab	*Portunus pelagicus*	3 crabs[a]
Green mussel	*Perna viridis*	9 mussels[a]
Scallop	*Pectinidae spp.*	10 scallops[a]

[a] Refers to a pooled sample.

and 100) in the edible parts of the 20 types of seafood analyzed are presented in Figs. 16.1a–d. The average concentrations of POPs in seafood, as well as their limit of detection and relative occurrence amongst the seafood types are reported in Table 16.5. Chlordanes, DDTs, and PCBs were detected in 75, 90, and 100% of the seafood types, respectively. On the contrary, mirex and pentachloronitrobenzene (PCNB) were only detected in 10 and 15% of the seafood types, at a concentration two orders of magnitude less than for DDTs and PCBs, respectively. Levels of chlordanes were below $1\,\text{ng}\,\text{g}^{-1}$ wet weight (ww) in all seafood types, except for green mussels ($14.4 \pm 2.0\,\text{ng}\,\text{g}^{-1}$ ww) and salmon fillets ($2.9 \pm 1.7\,\text{ng}\,\text{g}^{-1}$ ww). Levels of DDTs were below $5\,\text{ng}\,\text{g}^{-1}$ ww, except for green mussels ($37.8 \pm 0.7\,\text{ng}\,\text{g}^{-1}$ ww) and salmon fillets ($14.4 \pm 9.1\,\text{ng}\,\text{g}^{-1}$ ww). Levels of PCBs were below $5\,\text{ng}\,\text{g}^{-1}$ ww in all seafood types except for green mussels ($8.2 \pm 2.6\,\text{ng}\,\text{g}^{-1}$ ww) and salmon fillets ($28.5 \pm 14.4\,\text{ng}\,\text{g}^{-1}$ ww). Levels of PBDEs were below $0.1\,\text{ng}\,\text{g}^{-1}$ ww for all seafood types, except salmon fillets ($2.8 \pm 1.8\,\text{ng}\,\text{g}^{-1}$ ww). Amongst the 20 seafood types analyzed, green mussel and salmon fillets samples contained the highest levels of POPs. Green mussels are filter-feeders and therefore readily accumulate POPs. The levels found in market samples were in the upper range of concentrations found in wild mussels in

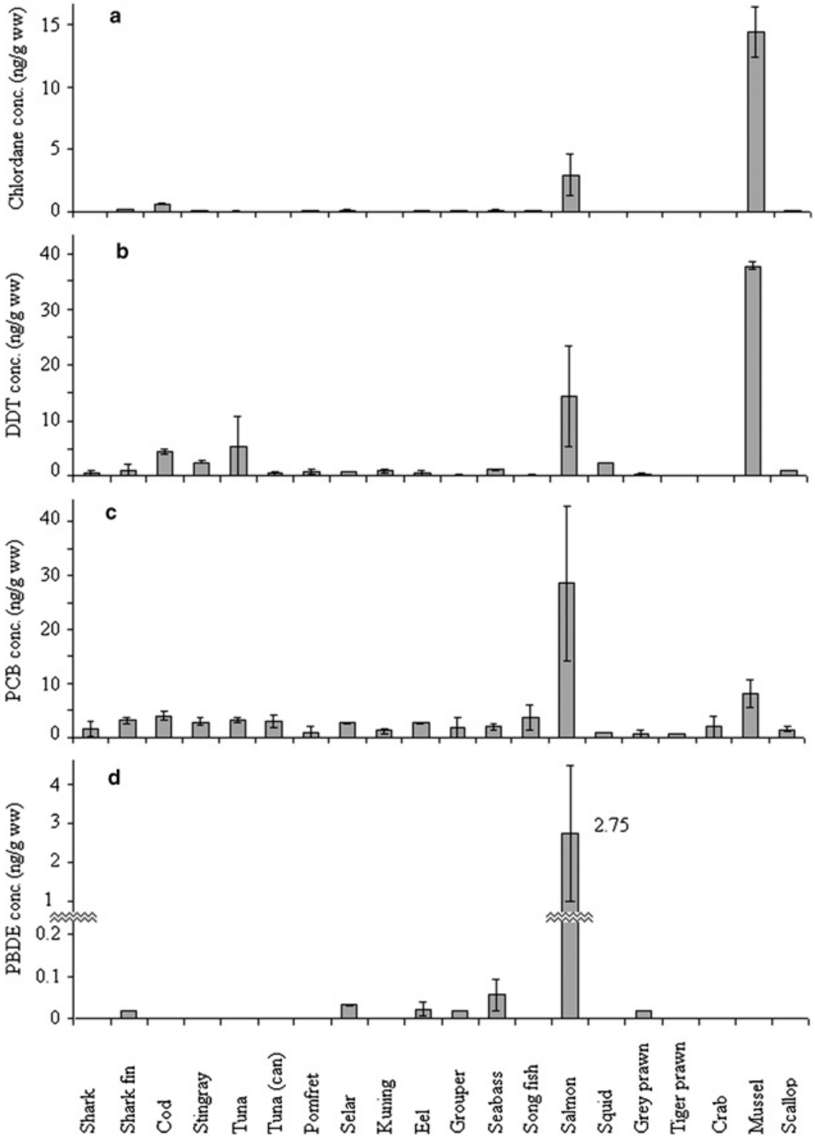

Figure 16.1. Total levels in ng g^{-1} wet weight (ww) of chlordanes (a), DDTs (b), PCBs (c), and PBDEs (d) in the major seafood types commonly consumed in Singapore (mean level ± SD).

Table 16.5. Mean level, occurrence, and mean daily intake of POPs from seafood for a 60 kg person in Singapore

Contaminant	Method limit of detection in ng g^{-1} ww	Mean level (range)[d] in ng g^{-1} ww	Percentage of seafood types with levels above MDL (%)	Mean daily intake (μg kg^{-1} body weight/day)		Oral RfD[e]	Cancer benchmark concentration[f]
				Hypothesis no detect = 0	Hypothesis no detect = 0.5 DL		
Chlordane[a]	0.04	0.95 (BLD–14.39)	75	0.75	0.76	500	1
DDTs[b]	0.04–0.09[c]	3.76 (BLD–37.84)	90	3.00	3.01	500 as *p,p′*-DDT	3
PCNB	0.04	0.03 (BLD–0.13)	15	0.01	0.02	3000	
Heptachlor	0.08	0.39 (BLD–6.52)	35	0.29	0.31	500	0.22
Heptachlor epoxide	0.04	0.16 (BLD–2.13)	55	0.123	0.130	13	
Mirex	0.02	0.01 (BLD–0.04)	10	0.003	0.012	200	
PCBs	0.01–0.2[c]	3.72 (0.61–28.47)	100	2.99	2.99	20 as Aroclor 1254	0.13
PBDEs	0.01–0.03[c]	0.17 (BLD–2.75)	30	0.117	0.134	2000	

[a] Sum of α and γ-chlordanes.

[b] Sum of *p,p′*-DDT, *p,p′*-DDD, and *p,p′*-DDE.

[c] Range for all congeners.

[d] Mean concentration (range between brackets) amongst the various types of seafood for the hypothesis "Nondetect = 0.5 detection limit"—BLD: below limit of detection.

[e] Data obtained from USEPA' Integrated Risk Information System (http://www.epa.gov/iris).

[f] Represents the exposure concentration at which lifetime cancer risk is one in one million.

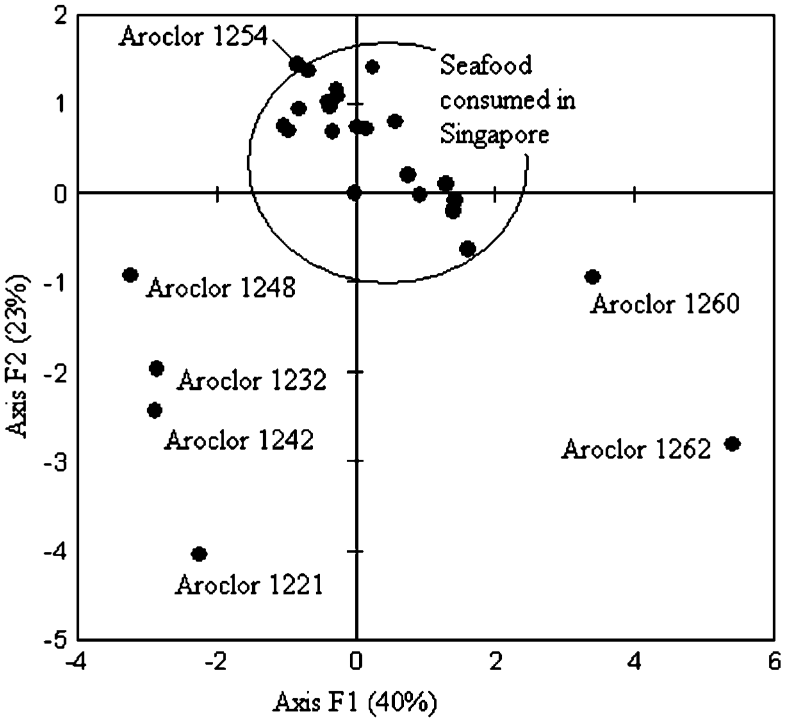

Figure 16.2. Bi-plots showing the first two principal components of relative individual polychlorinated biphenyl (PCB) congener profiles in seafood in relation to congener profiles for Aroclor mixtures 1221, 1232, 1242, 1248, 1254, 1260, and 1262.

Southeast Asia. Several recent studies have revealed that farmed salmon contains higher levels of POPs including PCBs and PBDEs compared to wild specimens (Easton et al., 2002; Ohta et al., 2002; Hites et al., 2004). Concentrations of POPs in typical salmon fillets consumed in Singapore are in the range of values reported for farmed salmon.

Principal component analysis of PCB congener profiles of seafood relative to commercial Aroclor mixtures is shown in Fig. 16.2. PCB congener profiles for Aroclor mixtures 1221, 1232, 1242, 1248, 1254, 1260, and 1262 were determined by Frame (1997). The first principal component, F1, has a positive loading on hepta-CBs and octa-CBs and a negative loading on tri-CBs and tetra-CBs. The second principal component, F2, has a positive loading on penta-CBs and hexa-CBs and negative loading on tri-CBs, hepta-CBs, and octa-CBs. The PCB congener profile of seafood types analyzed reflects the presence of a mixture of Aroclor 1254 and Aroclor 1260 congeners, with the majority of the 20 types closely matching the PCB congener profile of Aroclor 1254. A similar match was observed for a variety of marine organisms elsewhere (Miao et al., 2000). The congener BDE-47 (2,2′,4,4′ tetra-BDE) was proposed as an indicator for PBDE contamination in marine fish (Akutsu et al., 2001). In addition to salmon fillets, BDE-47 has also been detected in selar, seabass, and grey prawn samples in this study—seafood that originates from within Southeast Asia (MFRD, 1996). Little is known about the occurrence of brominated flame retardants in the environment of Asia (Kemmlein et al., 2003). The present data suggest that BDE-47 is present in the marine environment of Southeast Asia and is accumulating in the foodchain.

To undertake a risk assessment on the consumption of food, the first step is to compare the levels with the maximum residue limits (MRLs). MRLs for POPs in Singapore (Government of Singapore, 1990) and the United States (USFDA, 2001) are presented in Table 16.6. Samples were lower than respective MRLs for all POPs.

Periodically, the Ministry of Health in Singapore conducts a survey on the dietary habits of the population. Latest available seafood consumption figures, from 1998 (Ministry of Health, Singapore, 2001), were used for risk assessment calculations using analytical data obtained from this study. In this survey, the mean daily intake (MDI) of fish/seafood for the general population of Singapore is similar for both females and males and approximated to 46 and 50 g/day, respectively. Therefore, an average MDI for seafood of 48 g/day was used in dietary exposure calculations, together with an average body weight of 60 kg. The estimated MDI of contaminants from seafood was calculated as the MDI of seafood multiplied by the mean concentration of contaminants in the 20 seafood types. Using the methodology specified by the US Environmental Protection Agency (Dougherty et al., 2000), the mean concentration of contaminants was calculated according to two hypotheses: "non-detect samples are equal to zero" i.e., contaminant values below the limit of

Table 16.6. Maximum residue limits for POPs in seafood in Singapore and the United States

Contaminant	Singapore ($\mu g\, g^{-1}$)	US FDA ($\mu g\, g^{-1}$)
Chlordane	0.05	0.3
Heptachlor		0.3
Heptachlor epoxide		0.3
Mirex		0.1
DDTs	5.0	5.0
PCBs		2

analytical detection are ascribed a value of zero; and "non-detect samples are equal to half of the limit of detection" i.e., contaminant values below the limit of analytical detection are ascribed a value of 50% of the limit of analytical detection. The first hypothesis tends to underestimate the concentration, and therefore the intake of contaminants. MDIs of POPs in seafood types typically consumed in Singapore are presented in Table 16.5. MDIs were similar (difference $<10\%$) regardless of the value attributed to the non-detect samples (i.e., zero or half of the detection limit), except for PBDEs, PCNB, and mirex. Differences of greater than 10% can be attributed to the low occurrence of contaminants amongst food types (Dougherty et al., 2000). The mean daily intake of DDTs, PCBs, and PBDEs from seafood for a 60 kg person in Singapore reaches 3.0, 3.0 and 0.1 ngkg body weight per day, respectively. Data comparison with human consumption studies conducted elsewhere shows that mean daily intake of PCBs from seafood in Singapore represents only 6% of the total daily intake of a whole diet in Italy (Zuccato et al., 1999). The MDI of DDT from seafood in Singapore is 2.5 times higher than for a seafood diet in Italy, according to a study conducted in 1997 (Stefanelli et al., 2004). Contributions of specific types or groups of seafood to the MDI of POPs were calculated for the hypothesis of "non-detect samples are equal to zero" (See Fig. 16.3). On this basis, it can be concluded that salmon consumption accounts for 19, 38, and 94% of the mean calculated intake of DDTs, PCBs, and PBDEs, respectively, and green mussel consumption accounts for 51, 11, and 77% of the mean calculated intake of DDTs, PCBs, and chlordanes, respectively.

The "oral reference dose" (Oral RfD) is an estimate of the daily exposure of a person to a contaminant that is likely to be without appreciable risk of a deleterious non-carcinogenic effect during a lifetime (USEPA; http://www.epa.gov/iris/). Oral RfD values for POP concentrations in seafood types are presented in Table 16.5, together with the daily intake of POPs from seafood consumed in Singapore. Daily intakes of POPs from seafood are below the oral RfD. The "cancer benchmark concentration" (Dougherty et al., 2000) represents the exposure concentration at which a lifetime cancer risk equates to one excess cancer death in one million persons. This level is defined as the public health protective concentration in the Congressional House Report to the Food Quality Protection Act of 1996 in the USA. Cancer benchmark concentrations were exceeded for DDTs, heptachlor, and PCBs (See Table 16.5). The "cancer hazard ratio" is the ratio of the MDI for a specific contaminant relative to the cancer benchmark concentration. The cancer hazard ratio represents the extent to which average daily exposure exceeds the benchmark concentration. The cancer hazard ratio of seafood consumption

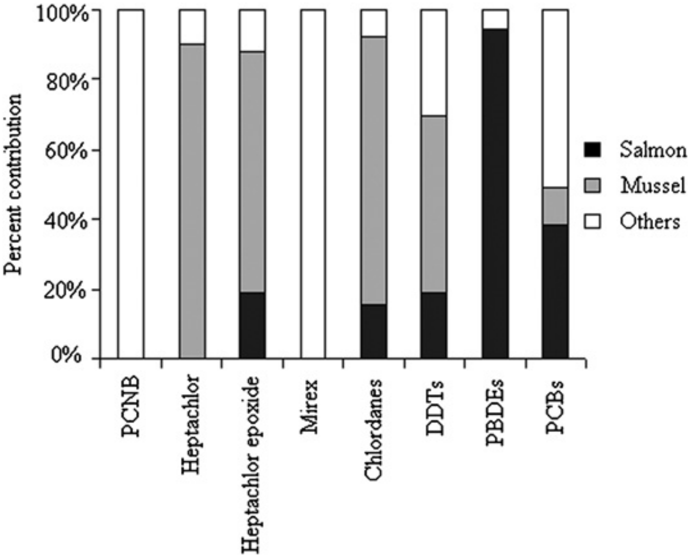

Figure 16.3. Percentage contribution of salmon, green mussels, and other types of seafood to the mean daily intake of POPs via seafood consumption in Singapore.

was equal to 1, 1, and 23 for DDTs, heptachlor, and PCBs, respectively, meaning that, according to Dougherty et al., (2000), a significant number of people are potentially at risk in Singapore over a lifetime of seafood consumption. However, it is important to note that the standard deviation for per capita seafood consumption data in Singapore is large (i.e., 46.3 ± 36.9 and 49.9 ± 40.0 g/day for women and men, respectively), where significant levels of variability exist between ethnic subgroups in the population. As an example, a Malay male adult in Singapore consumes 64.9 g/day of seafood versus 42.8 g/day for an Indian and 48.2 g/day for a Chinese male adult, respectively (Ministry of Health, Singapore, 2001). The risk associated with seafood consumption is therefore up to 51% higher for a male adult in the Malay community.

It is also worth noting that these calculations are derived from raw tissue analysis and more information is required on the effect of seafood cooking in Singapore on the final load of contaminants ingested. Cooking processes, such as baking, frying, or boiling are known to reduce the burden of POPs in fish (Schecter et al., 1998; Zabik and Zabik, 1999). In another study on the effect of cooking on the loss of POPs from salmon (see Bayen et al., 2005a), the initial burden of POPs in the fish steaks decreased by 26 ± 15% after cooking with an additional loss of 9 ± 3% when the skin was removed from the cooked steak. Human health effects associated with the consumption of cooked salmon can be considered to decrease proportionally, and it can be concluded that cooking has a beneficial reduction on the burden of POPs in salmon steaks. Therefore, based on the present results, an average reduction of the POPs load by 26% following cooking would decrease the mean daily intake of POPs proportionally. The consequence is that the mean daily intake of DDT would then be below the cancer benchmark concentration; however, the cancer hazard ratio for PCBs (17) would be still significantly greater than one—even when taking into account the cooking of the seafood.

16.8. Conclusions

Among the pesiticides, DDT group of OCPs are the most prevalent contaminants in human adipose tissues worldwide. Typically, levels of PBDEs are still the lowest amongst the major groups of POPs prevailing in the environment, but levels in biological matrices, including human adipose tissues are rising around the world due to large scale production and usage of these compounds. Clearly, it will remain a challenge for the scientific community to continue to monitor and evaluate the risk of current and emerging POPs in our environment, and ultimately to eliminate the most harmful compounds and identify safer alternatives. Historical data on the known effects of POPs on wildlife and human health clearly advocates the adoption of a precautionary principle prior to the intentional or incidental emission of novel POPs into the environment.

Analysis of local samples in Singapore has demonstrated the prevalence of POPs in human adipose tissues. Our investigations have also shown the ubiquity of POPs in seafood commonly consumed in Singapore. As a result of the use of contaminated fish meals, levels of POPs in farmed salmon were relatively higher than in any other fish commonly consumed in Singapore. Human health risks associated with the consumption of contaminated seafood exist and maximum exposure criteria are exceeded when considering seafood consumption alone. Further investigation should be undertaken to consider exposure through the whole diet for the Asian population. Although concentrations are comparable to those observed elsewhere, longer term monitoring of a larger cross section of the popluation is warranted in order to establish temporal trends and potential long-term risks to human health.

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Chapter 17

Persistent Organic Pollutants: Occurrence and Health Risks in Australia

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Abstract

The major persistent organic pollutants (POPs) in Australia are the persistent organochlorine pesticides (OCPs). The adverse effects of DDT were first recognised in Australia in the late 1960s. Subsequently, the Australian Government introduced a policy of phasing out the registered uses of this major pesticide and related substances so that their use in agriculture ceased by 1987.

Australian foods are monitored on the basis of the National Residue Surveys and Australian Market Basket Surveys (now Total Dietary Survey). Only a low percentage of OCP residues have been detected in animal fats since 1996 and none in grains since 1992. Elevated intakes of residues (e.g. dieldrin and HCB) occurred in the early 1970s, which have since declined at approximately first-order kinetics to much lower and generally acceptable levels of intake in the 1990s.

Total intakes of OCPs from the Australian diet and environment have been estimated from the 1970s to the 1990s and used to evaluate human health risks for the Australian population. The Hazard Index (HI) was estimated for the general Australian population for the OCPs for 1996 at <1.0 in all cases. In addition, the USA-EPA model for occurrence of cancer has been applied to some of the persistent OCPs and found to be in the range of $>1\times10^{-6}$ to 4×10^{-5}. The level of health risk for the general Australian population was considered to be acceptable in 1996.

Some scenarios for high-risk groups in the Australian population were examined. These indicated that dieldrin intake from contaminated fish, contaminated soils, or in indoor air following termiticide treatment was a potential risk for exposed persons. Also the exposure of breast-fed infants to DDT during 1996 with a HI of 0.9 was questionable. However, extrapolation to 2005 using first-order

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*Corresponding author: E-mail: d.connell@griffith.edu.au kinetics indicated that the HI for all OCPs was below 0.1 and thus not a hazard to health of the Australian population.

The National Dioxin Program has extensively surveyed the levels of dioxins in Australian foods, human milk and the natural environment as well as identifying sources. As a result of this the risks to human health and the natural environment are considered to be minimal. Human health risks from exposure to POPs may continue to be an issue, because of increasing concerns about endocrine disruption and also the possible relationship between residues and specific cancers such as breast cancer.

17.1. Introduction

During the 1960s and 1970s, semivolatile and persistent chlorohydrocarbon pesticides, such as DDT, HCHs, dieldrin and chlordane, and industrial chlorohydrocarbons such as the PCBs and hexachlorobenzene (HCB), were detected throughout environmental compartments and were found to be bioaccumulative in lipid-containing tissues (Woodwell et al., 1971). These lipophilic substances, having environmental persistence and occurring widely in ecosystems, have been generally described as persistent organic pollutants (POPs). In addition, combustion products have been detected consisting principally of the polychlorodibenzodioxins (PCDDs) and the polychlorodibenzofurans (PCDFs), which share the persistent, lipophilic and bioaccumulative properties of the chlorohydrocarbons (Rappe et al., 1978). Thus, currently the following substances are usually considered to be globally important POPs: aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, HCB, hexachlorocyclohexane (HCH including lindane), mirex, toxaphene, polychlorobiphenyls (PCBs), PCDDs, and PCDFs. The first nine substances in this list (from chlordane to toxaphene) are commonly referred to as the organochlorine pesticides, the OCPs. In this paper the term OCPs refers to the chlorohydrocarbon group alone and does not include such substances as 2,4,5-T and 2,4-D, which are not considered to be persistent in the environment.

In Australia several landmark reports were published regarding adverse affects of OCPs including major reviews by the Australian Academy of Science (1972) and the Victorian Government in 1966 (Victorian Pesticides Committee, 1966), and papers by Butcher (1965) and Bacher (1968). These publications have had a major influence in that they initiated a large monitoring program in Australia. As a result there have been many scientific and governmental enquiries into the usage of DDT and other chlorohydrocarbons. It is now clear that the use of DDT has caused a range of problems including direct lethal effects and sublethal effects such as eggshell thinning in certain species of birds (Olsen & Olsen, 1979).

The OCPs have been the major POPs in the Australian environment and were introduced to Australia in the mid-1950s. The major uses of OCPs were crop and livestock protection from insects and parasites. Meaningful data on the actual amounts of OCPs that were used in Australia are not readily available. A steady increase may be assumed from Australian pesticide sales, which increased from a value of 15 million dollars in 1975 to 130 million dollars by 1990 (Short, 1994). Herbicides, however, account for the largest proportion of pesticides sold in Australia (Rayment & Simpson, 1993). The use of OCPs in Australia spans approximately 40 years from the 1950s to 1990s. By 1975, there were many pesticide products containing DDT, HCH and dieldrin, a lesser number for lindane and chlordane, and some for aldrin. During this period, one or more of these pesticides was registered for use against pests in a broad range of crops. OCPs were also used for termite control and around livestock quarters.

These chemicals were most widely used during the mid-1970s but were largely phased out by 1990. The first restrictions occurred in 1961/1962 when OCPs were deregistered for use on food producing animals. Monitoring of residues in table ready foodstuffs was introduced in 1970. During the early 1970s, the Standing Committee on Agriculture introduced a policy of deregistering persistent OCPs in all agricultural uses as soon as alternatives became available.

Significant reductions in registered OCPs occurred during the late 1970s due to scrutiny by registration authorities and pressure from technical committees on agricultural chemicals including the National Occupational Health and Safety Committee, Australian Agricultural Council, National Health and Medical Research Council (NHMRC) and the Australian Environment Council. By the end of 1985, most pest/crop/chemical combinations in agricultural applications were deregistered. During 1987, the States and Territories commenced recall programs of OCP stocks and import of OCPs into Australia was prohibited. However mirex and lindane were registered for strictly restricted usage. In 2002, Connell et al. (2002) published a report on the environmental occurrence of the OCPs in which they report that the levels of these substances had fallen to low to negligible levels in the human diet, sewage inputs to the environment and in the environment in general.

In Australia there was little coordinated information on the dioxins and furans up until 2001. In that year a National Dioxins Program was set up by the Australian Department of the Environment and Heritage which carried out an extensive program of investigations of sources, air, soils, aquatic fauna, human foods, blood and milk. The findings were released in 2004 and indicated that the levels of risk to human health and the natural environment were low (National Dioxins Program, 2004).

17.2. Sources of POPs in Australia

DDT had been imported or manufactured in Australia since 1966, but in early 1971, manufacture within the country ceased and all DDT since then was imported. The early use of DDT in Australia was summarised by the Australian Academy of Science (1972) in *The Use of DDT in Australia*. At that time it was estimated that about 900 tonnes of DDT were used annually. Total DDT annual imports or production in Australia peaked in 1973 at 3625 tonnes (Olsen et al., 1993). The cumulative total DDT usage in Australia up to 1993 was estimated to be 10,000 tonnes (Connell, 1981; Connell et al., 1999).

There are no clear estimates of the quantities of cyclodiene insecticides used in Australia. Investigations by Greenpeace indicated that Australia imported 272 tonnes of heptachlor and 95 kg of chlordane during 1987–1989 (Short, 1994). Estimates for aldrin indicate 364 tonnes were imported between 1989 and 1991. The lindane and the HCH group of perisistent-chlorinated pesticides have been extensively used in the Australian environment but data are not available on the quantities involved. However, the total lindane usage in Australia up to the end of 1993 was estimated to be 900 tonnes (Connell et al., 1999). HCB had limited manufacture as a fungicide the 1960s (Connell et al., 1996). However, its major sources are as a contaminant in a range of chlorinated compounds including pesticides and solvents, and as a waste product in a wide variety of chemical manufacturing processes.

Dioxins (PCDDs) occur as contaminants in many agricultural pesticides and can occur in the environment as a result of pesticide usage, although many other industrial sources and natural sources have been identified. The National Dioxins Program (2004) has revealed that major sources of dioxins in the environment are uncontrolled combustion sources such as bush fires and accidental fires which contribute 70% of the total to the air and 80% to the soil whereas waste disposal and land filling contribute 75% of the total to water.

17.3. Physicochemical and environmental properties

These substances share a set of common physicochemical properties that can lead to undesirable effects on living systems. There is a limited range of bond types present in the POPs group. These are the C=C (aromatic) C=C, C–H, C–Cl with lesser numbers of C–C, C–O which all have zero or very low polarity. This means the compounds in this group tend to have low polarity and dipole moments. These properties result in compounds in this group being *fat soluble* or *lipophilic* and having a low solubility in water. While the solubility in lipid of these compounds lies in the order of grams per litre, the aqueous solubility ranges from 4.7 mg L^{-1} for lindane to 0.0032 mg L^{-1} for p,p^1-DDT and lower for some PCDDs. The lipophilicity of these compounds is indicated by the octanol/water partition coefficient (K_{OW}) which lies between 4100 (log K_{OW} 3.61) for lindane and 3,200,000 (log K_{OW} 6.5) for aldrin and higher for some compounds. Lindane is the lowest molecular weight compound in this group and tends to fall at the extreme end of the properties of the group with properties such as the highest water solubility and lowest octanol/water partition coefficient.

The limited ranges of bond types present in the POPs are generally relatively resistant to attack by abiotic or biotic agents in the environment. As a result environmental degradation proceeds at a relatively slow rate. Most compounds in this group persist for long periods in the environment and often exhibit half-lives of many years as illustrated by the data in Table 17.1.

Bioconcentration in aquatic organisms occurs as a result of partitioning between the organism lipid and the surrounding water. If a substance is *lipophilic*, then equilibrium occurs with a relatively high *Bioconcentration Factor* (K_B), or the organism/water partition coefficient. For example, the K_B value of p,p^1-DDT is 79,400 (log K_B 4.9), heptachlor, 7900 (log K_B 3.9)

Table 17.1. Properties of some persistent organic pollutants

Substance	Log K_{OW}	$T_{1/2}$ (days) (freshwater)	Log K_{OC} adsorption sediments	Aqueous solubility (mg L^{-1})	Log K_B
p,p'-DDT (4,4)	6.2	7–350	4.8 (est)	0.0032	4.9 (est)
Total chlordane	5.54	< 1400	2.4–4.2	0.08	4.22 (est)
Dieldrin	4.32	175–1100	3.87–4.08	0.17	4.1
Heptachlor	5.27	0.9–5.4	4.48	0.18	3.8–3.9
γ-BHC (lindane)	3.61	22–692	3.34 (est)	4.7	2.3 (est)
Hexachloro-benzene (HCB)	5.86	31–41	NA	0.006	4.1
Dioxins and furans	3.7–8.2	~720	NA	$4.4 \times 10-2$ to $1.3 \times 10-9$	2–6

Sources: Chemical Evaluation Search and Retrieval System (1995); Howard (1991); Howard (1991).

dieldrin, 13,600 (log K_B 4.1), lindane 200 (log K_B 3.3). The K_{OW} value and lipophilicity of various compounds are outlined in Table 17.1. Mammals have the capacity to induce oxidative enzyme systems particularly the Mixed Function Oxidase system including Cytochrome P-450, which reduces the bioaccumulation of the OCPs. Thus the concentrations observed in mammals is relatively low. The cyclodiene subgroup, e.g. dieldrin and aldrin, tend to have higher mammalian toxicity than other members of the chlorohydrocarbon family.

17.4. Occurrence of POPs in human foods

In the early 1960s, the Commonwealth (Australian) Department of Primary Industry began testing agricultural products, such as meat, for organochlorines to meet international trade requirements. This program has continued to the present as the National Residue Survey (NRS) now controlled by the Bureau of Rural Resources.

In the case of domestic foodstuffs, State Health and Primary Industry authorities have followed up with testing of selected food groups and the NHMRC initiated market basket surveys of residues in foods based on the normal Australian diet. Since 1990, these surveys have been managed by the Australian New Zealand Food Authority.

The NRS results show that Australian produce has relatively few samples that contain chemical residues above acceptable limits. In 1997, out of 26,161 samples analysed, 64 contained residues above the relevant maximum residue level (MRL) for POPs. Within the meat-testing program, only one sample in 5895 tested for organochlorines was above the MRL. This was a residue of dieldrin in a cattle sample (beef fat). In the other programs (egg, grains and horticulture), organochlorine residues were negligible. From 1993 to 1997, the NRS has detected a low incidence of organochlorine residues in raw food groups. There has been a progressive decline in the percentage of organochlorine residues found in animal fats during the 1990s as shown in Fig. 17.1, while organochlorine residues have not been detected since 1992 in grains. However, there remains continued surveillance of sheep and cattle by National, State and Industry Programs such as the National Organochlorine Residue Management Program. No organochlorine residues have been detected in selected seafood samples (abalone, scallops and southern bluefin tuna) taken in 1995 or freshwater crayfish (yabbies and marrons) sampled in 1996.

An extensive array of foods have been analysed for the dioxins and furans. As expected foods high in lipids were the highest in the lipophilic dioxins and furans which were estimated as one value based on a

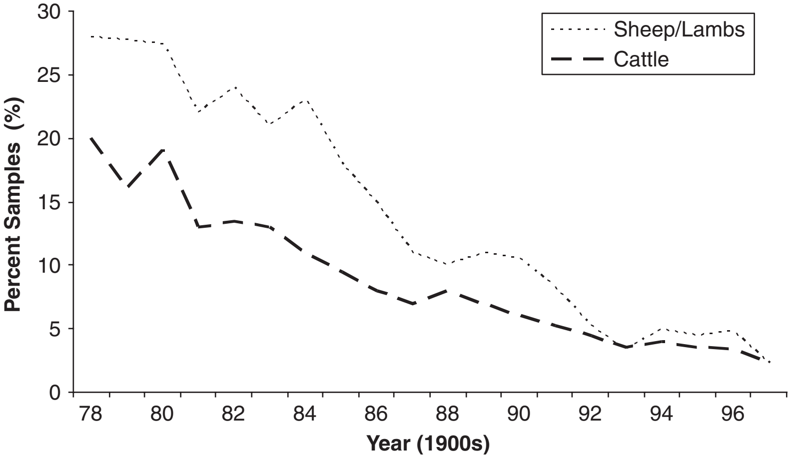

Figure 17.1. Sheep and cattle samples with detectable DDT and organochlorine residues.

summation of the toxicity of the individual components, as toxicity equivalents (TEQ). For example fish fillets, 0.59–0.64 pg TEQ g^{-1} and butter, 0.028–0.270 pg TEQ g^{-1} were the highest observed (National Dioxins Program, 2004).

17.5. Australian market basket survey (now known as Total Dietary Survey)

The Australian Market Basket Survey (AMBS) was set up to monitor pesticides and contaminants in food and estimate their intakes in diets of Australians (ANZFA, 1998). The first total diet survey was conducted by the NHMRC in 1970 and surveys have occurred regularly since then. Currently, it is a biennial survey organised and published by the Australia New Zealand Food Authority (ANZFA, 1998).

Few foods contain residues of organochlorines. However some other pesticide residues (organophosphorus and synthetic pyrethroids) have increased in prevalence relative to organochlorines. Detectable levels of deregistered OCPs arise as a result of ongoing environmental contamination (ANZFA, 1998). A marked decline in residue levels (and intakes) occurred during the 1980s to 1990s as restricted uses, deregistration and regulatory controls on organochlorines progressed. Less persistent endosulfan and dicofol residues are evident in several foods (e.g. fruit and vegetables) in more recent surveys. No residues of 2,4-D and 2,4,5-T herbicides have been detected in targeted food surveys.

17.6. Occurrence of POPs in humans

17.6.1. Human lipid

The earliest Australian survey of human fats was published by Bick (1967). Biopsy specimens of human body fat were collected from 53 individuals of the general population. In this sample, the mean concentrations of total DDT equivalent and dieldrin stored were 1.81 mg kg^{-1} (ppm) and 0.046 mg kg^{-1} (ppm), respectively (100% positive).

Significantly higher levels of DDT and dieldrin were reported by Brady and Siyali (1972) in a survey of 75 human fat specimens. All the samples contained DDT and also HCB, which had not been previously reported in other surveys. An extensive NSW survey in 1988 was conducted by Ahmad et al. (1988) on 290 samples of human body fat obtained from the Westmead Hospital, Sydney. Western Australian levels of total DDT and dieldrin in body fats were shown to be elevated in the late 1960s. However by 1991 total DDT and dieldrin levels had decreased substantially (Stevens et al., 1993).

As well, HCH isomers, including lindane, occur infrequently in human fats. Levels of up to 2.6 mg kg^{-1} were reported in 1972 by Siyali (1972). More recently, Quinsey et al. (1995) detected low median levels (~0.1 mg kg^{-1}) of HCH isomers, with a measure of 4.4 mg kg^{-1}, in human milk fats for Victorian women. The presence of HCH isomers in all of the milk fats suggests a persistent 'background' level of contamination in body fats consistent with POPs profiles for total HCH.

17.6.2. Blood

In Australia, the most extensive set of data involves 4640 blood samples analysed for OCPs at the New South Wales Workcare Authority from 1987 to 1989. The vast majority of samples contained less than the occupational limits 50 ppb (μg L^{-1}) of dieldrin and less than 20 ppb (μg L^{-1}) of heptachlor. Of the 49 samples above the occupational limit 44 of these were from pest control operators (NHMRC, 1992). An earlier NSW study by Siyali (1972) compared whole blood levels of organochlorine insecticides from persons with and without industrial pesticide exposure. Levels of HCB, total DDT, dieldrin and HCH (BHC) were substantially higher in the exposed group, particularly for dieldrin.

DDT levels were tested in the whole blood of an agriculture usage area and unexposed residents during 1973 in NSW. The mean DDT levels in the exposed and non-exposed groups were 21.9 ppb and 16.7 ppb, respectively. The DDT levels in the unexposed groups from NSW were comparable with UK and USA figures for blood levels of DDT and DDE (Ouw & Shandar, 1974).

Blood levels of aldrin in persons exposed to airborne aldrin in dwellings treated for white ants was investigated by Gun et al. (1994). The mean blood dieldrin (ppb or μg L^{-1}) increased from 0.75, prior to treatment, to 1.2; 3 months after treatment.

A survey of the occurrence of dioxins in 9000 human blood samples collected from individuals resident over the major parts of Australia was carried out in 2001–2003. Levels were found to increase consistency with age with adult of age >60 years having almost three times the levels of those of age <16 years. The mean level was 10.9 pg TEQ g^{-1} of lipid which is among the lowest recorded in the world.

17.6.3. Human milk

The excretion of organochlorine insecticides in human breast milk has raised questions about the safety of breastfeeding for infants. Human milks usually contain much higher levels of organochlorines than cow's milk. The main interest in breast milk studies emerged during the 1970s to early 1980s when food residue levels in Australia peaked and later declined following Federal Government phasing out of the OCPs. Nevertheless, follow-up studies appear to be limited (see Quinsey Some breast-fed infants have had daily intakes of organochlorine insecticides (e.g. total DDT, dieldrin and heptachlor) above acceptable daily levels for these insecticides during the early 1990s (Stevens et al., 1993; Quinsey et al., 1995).

Australian health authorities and researchers have conducted a number of studies into organochlorine insecticide residues and human milk that span three decades of organochlorine use, from 1969 to the early 1990s. Early Australian studies of human milk contamination (e.g. HCB, DDT and metabolites, HCH isomers and cyclodienes) cover the period from 1969 to 1972 and include Western Australia (Stacey & Thomas, 1975), New South Wales (Siyali, 1973), Victoria (Monheit & Luke, 1990) and Queensland (Miller & Fox, 1973). Total DDT was shown to occur in the parts per billion range (μg kg^{-1}) in whole milk and in the parts per million range (mg kg^{-1}) in milk fats.

A useful indication of the long-term changes in organochlorine pesticide residues in human milk is obtained from a summary of Western Australia levels from 1974 to 1991, as presented by Stevens et al. (1993) in Table 17.2. The results indicate that mean DDT and dieldrin levels have fallen to 20% or less of 1974 values with substantial decreases occurring between 1982 and 1990. HCB levels fell rapidly in the mid-1970s to 1980.

Table 17.2. Mean concentrations of organochlorine pesticides in breast milk fat, Western Australia (μg kg^{-1})

Pesticide	Years					
	1974	1978	1980	1982	1990	1991
DDT	3600	2000	1200	1100	360	800
Dieldrin	240	240	170	160	40	50
HCB	2600	750	150	NA	30	100
Heptachlor	NA	NA	140	80	20	20

Source: Stevens et al. (1993).

A low residual level appears to remain. Heptachlor levels were relatively low but have decreased further to under 20% of the 1980 value. Similar trends have been observed in other investigations, e.g., Quinsey et al. (1995).

During 2003 the National Dioxin Program (2004) carried out a survey of human breast milk using the WHO design which was used by that organisation during previous investigations. A range of metropolitan and rural regions throughout Australia was surveyed giving a mean of 9 pg TEQ g^{-1} lipid and no differences between regions. This was among the lowest reported by WHO for human breast milk.

17.7. Dietary exposure of the Australian population to POPs

The dietary intake of OCPs is considered the main source of exposure for the general population in Australia and in many other countries. Estimates of dietary intakes of OCPs from AMBS are summarised in Tables 17.3 and 17.4 for the years 1971 to 1996. The initial survey in 1970 estimated that excessive intakes of dieldrin and HCB could occur in the diets of 15–18 year old males. Dieldrin and HCB had estimated daily intakes from 0.4 to 1.8 (0.1) and 0.7 to 1.4 (0.6) μg kg^{-1} bw, respectively. For comparison the accepted daily intake (ADI) at the time is shown in parenthesis (NHMRC, 1971). By 1976, the estimated daily intake of dieldrin remained relatively high, particularly for infants (e.g. 0.1 μg kg^{-1} bw), while HCB residues in foods were too low to estimate a dietary intake.

Since the 1970s, the intake levels of DDT have decreased by a factor of 10 to 100 in the case of adults and children aged 12. However the levels in the diet of infants were a significant fraction of the ADI although below the ADI. Also the levels of the lower concentration pesticides, such as heptachlor and the HCHs were a small fraction of the ADI by the late 1990s. In contrast to OCPs, total endosulfan intakes increased between 1992 and

Table 17.3. Total DDT—estimated daily dietary intake ($\mu g\,kg^{-1}$ bw) for six age-sex categories

Year	Adult male	Adult female	Boy aged 12	Girl aged 12	Child aged 2	Infant 9 months
1976	0.457	0.345	0.543	0.506	0.898	0.737
1977	0.371	0.396	0.617	0.483	0.898	0.947
1979	0.286	0.241	0.444	1.368	0.653	1.158
1987	0.026	0.022	0.033	0.024	0.027	0.016
1990	0.001	0.001	0.001	0.001	0.003	0.546
1992	0.007	0.0054	0.0053	0.0051	0.0152	1.1035
1996	0.0063	0.0047	0.006	0.0167	0.0063	1.748

Table 17.4. Dieldrin—estimated dietary intake ($\mu g\,kg^{-1}$ bw) for six age-sex categories

Year	Adult male	Adult female	Boy aged 12	Girl aged 12	Child aged 2	Infant 9 months
1976	0.043	0.0345	0.0494	0.046	0.082	0.102
1977	0.039	0.034	0.05	0.04	0.065	0.063
1979	0.038	0.034	0.0666	0.053	0.0898	0.105
1987	0.007	0.007	0.009	0.008	0.008	0.001
1990	0	0	0	0	0	0
1992	0.0048	0.005	0.0048	0.0048	0.0068	0.0041
1996	0.0015	0.0023	0.0017	0.0001	0.0019	0.0043

1996 surveys, which is a trend reflecting use. However the intake estimates do not take into account variation in consumption among localities, socioeconomic, ethnic or other groups. Whole dietary patterns may vary for the 'hypothetical diets' used in the AMBS (Harvey et al., 1998).

The dietary trends plotted for the AMBS data are illustrated in Fig.17.2 (dieldrin) and Fig. 17.3 (DDT). Since 1976, there has been an exponential decrease in DDT and dieldrin intake in the diet. However it is interesting to note that the pattern of decline with dieldrin is different for the different population groups of adult males, adult females and infants as shown in Fig. 17.2. The rate of decline in the adult males follows first-order kinetics ($r^2 = 0.90$) with a half-life of about 3 years as shown in Fig. 17.3.

For all age groups the monthly dietary exposure to the dioxins ranged from the highest for infants and toddlers at an average of 15.6 pg TEQ kg^{-1} bw $month^{-1}$ to 3.7 pg TEQ kg^{-1} bw $month^{-1}$ for adults. This is similar to the levels of dietary exposure in New Zealand at a median value of 11.1 pg TEQ kg^{-1} bw $month^{-1}$ but lower than that observed in other countries such as the United Kingdom.

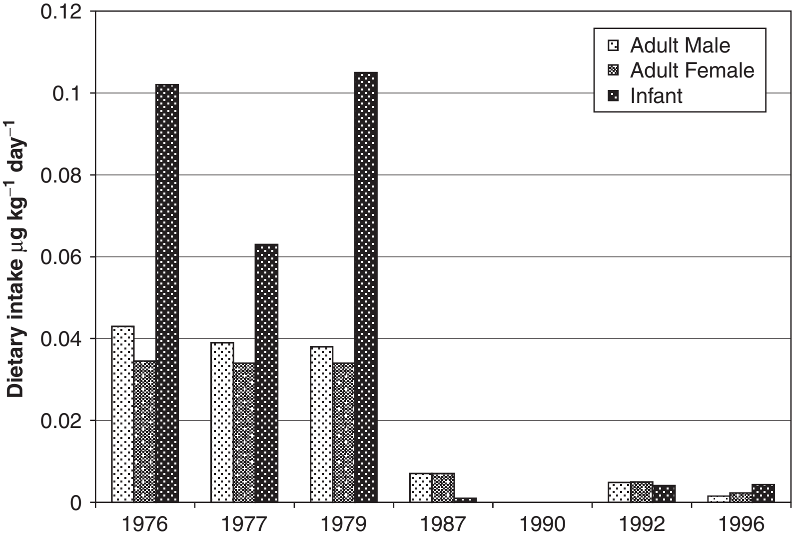

Figure 17.2. Estimated dietary intake of dieldrin for Australian adults and children (1976–1996).

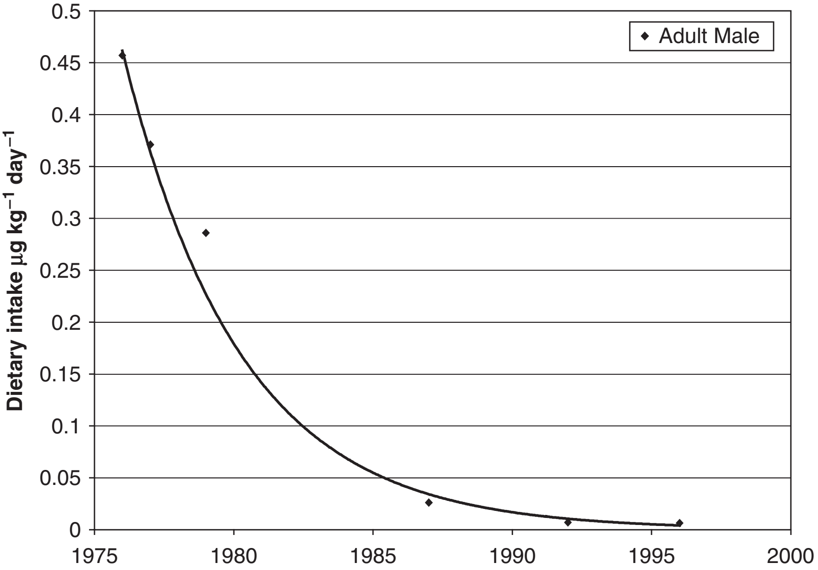

Figure 17.3. Trend in estimated dietary intake of total DDT for Australian adult males (1975–2000).

17.8. Risks to human health in Australia

Most POPs are readily absorbed (via the digestive system and inhalation) and accumulate in fatty tissue, including brain and adipose tissue and human milk. These substances can induce neurological effects and cause altered functioning of the nervous system as well as acting as endocrine disruptors.

ADIs are based on experimental data, which allows an intake level to be set below which adverse effects are not expected. The ADIs are recommended by the WHO/FAO Joint Meeting and Pesticide Residues (see Table 17.5). ADIs are not necessarily set values and can change based on reviews of toxicological information by WHO/FAO and Australian authorities. For example, the ADI for DDT and analogues has reduced by a factor of 10, from 20 to 2 $\mu g\ kg^{-1}$ bw day^{-1} (see Table 17.5) and in some cases where detection has not occurred in many years the residue limit has been cancelled, e.g. BHC and HCB.

To enable a comparison of hazards from chemicals a Hazard Index (HI) can be calculated as the ratio to the ADI. In addition to dietary uptake the possible pathways of entry of POPs for humans are

1. eating foods—dietry
2. contact with dusts or soils
3. drinking water
4. breathing air
5. absorption through skin—considered to be minor here but important for occupational or workplace exposures.

The amount of certain POPs which could enter the human body through contact with dusts or soils, drinking water and breathing air was calculated for the general population in Australia. Thus the total intake for POPs was calculated for 1996 and the risks to the general Australian population have also been calculated and the results are shown in Table 17.6. In addition the risks for specific population groups have been evaluated. These groups are breast-fed infants, high intake consumers of seafoods, persons living in houses treated for termite control, residents living on former livestock sites, persons consuming vegetables from gardens treated with biosolids and rural residents consuming tank drinking water.

From the selection of specific population groups as identified above, it was clear that the risks from being exposed to OCPs can vary for different groups of individuals in the community. In 1996 a variation of a HI of 3.3 for dieldrin for a hypothetical group of high intake seafood consumers to a small fraction for the other pesticides was estimated. Many persons

Table 17.5. Acceptable daily intakes for organochlorine pesticides

Pesticide	ADI μg kg^{-1} bw day^{-1}	
	NFA (1992)	ANZFA (1998)
Aldrin	0.1	0.1
Chlordane	0.5	0.5
Dieldrin	0.1	0.1
BHC (HCH)	20	No Australian ADI
DDT and analogs	20	2
Dicofol	2	1
Heptachlor and epoxide	0.1	0.5
HCB	0.6	No Australian ADI

Source: ANZFA (1998).

Table 17.6. Risks from total intake of organochlorine pesticides for the Australian population in 1996

Pesticide	Period	Persons	Daily intake (μg kg^{-1} bw day^{-1})	ADI (μg kg^{-1} bw day^{-1})	Hazard index	Lifetime risk estimate
Total DDT	1996	Adults	0.007	2	<0.1	$<1 \times 10^{-6}$
		Children	0.009		<0.1	$<1 \times 10^{-6}$
		Infant	1.7		0.9	
Dieldrin		Adults	0.003	0.1	<0.1	3.7×10^{-5}
		Children	0.004		<0.1	3×10^{-5}
		Infant	0.004		<0.1	
Total heptachlor		Adults	0.0006	0.5	<0.1	1×10^{-6}
		Children	0.002		<0.1	1×10^{-6}
		Infant	0.02		0.04	4×10^{-5}
Heptachlor epoxide		Infant	0.02	0.5	<0.1	

living in homes previously treated with organochlorine termiticides are likely to have been exposed to abnormal or excessive levels in indoor air (and household dusts) in the short term (months to years) with the HI for dieldrin up to 1.25. However for most people, intakes during 1996 indicate a safe level in terms of acceptable daily intakes. Lifetime carcinogenic risks (US-EPA model) were also estimated to be conservatively low (see Table 17.6), although uncertainties exist for persons exposed to higher intakes in the 1960s and 1970s.

Breast-fed infants were an unusually exposed group to DDT, with a HI of 0.9, and dieldrin at 0.04 in 1996. Human milk studies in Australia have shown a marked decline in residues but a significant proportion of breast-fed children have been exposed to levels above the Acceptable Daily Intakes for total DDT and dieldrin and occasionally, heptachlor epoxide.

Similarly, a report produced by the NHMRC (1992) on cyclodiene insecticide use in Australia provides a summary of the toxicological and chronic health effects of aldrin, dieldrin, chlordane and heptachlor.

The levels of total DDT in the Australian environment can be considered to be represented by the data in Fig. 17.3 since this represents a number of food groups including fish, which are usually the most contaminated group with lipophilic substances. This data measured during the 1970s to 1990s follow first-order kinetics ($r^2 = 0.90$) with a half-life of about 3 years (Connell et al., 2002). This decline is due to cessation of usage, environmental distribution characteristics as well as degradation. Extrapolating from the 1976 to 1996 data indicates that the HI for breast-fed infants would be <0.1 and thus a low order of health hazard. Dieldrin in the Australian environment has been suggested to have a half-life of 1.1 to 1.5 years (Connell et al., 2002) and, at this rate of decline the levels present in 2005 would be 0.02 to 0.005 of the levels present in 1996. Thus breast-fed infants, high intake seafood consumers and residents of homes treated with dieldrin would be expected to have low levels of HI, <0.1, in 2005.

The National Dioxin Program (2004) estimated that the dietry intake of the substances as the TEQ value and then estimated the HI against the Australian Tolerable Monthly Intake (TMI) of 70 pg TEQ kg^{-1} bw month^{-1}. These values showed an increase with age with toddlers 2–4 years having HI of 0.1 to 0.5; individuals 4 to 15 years HI 0.05 to 0.35 and adults HI 0.05 to 0.25. This suggests that the dioxins are a low health hazard in the Australian environment.

Some toxicological effects, such as endocrine disruption, continue to be uncertain. For example recent studies of breast cancer patterns in women (e.g. USA and The Netherlands) have shown a statistical association with organochlorine residues, such as dieldrin (see Høyer et al., 1998). Again, there is considerable scientific and medical debate with other studies indicating no significant association (e.g. Krieger et al., 1994; Zheng et al., 1999). Plausible toxicity mechanisms exist (Shekhar et al., 1997) to the extent that this issue may be important for long-term health risks in Australian women, given a past history of elevated DDT, DDE and dieldrin exposures in the 1970s and 1980s.

In a preliminary Australian study, Taylor et al. (1999) found the levels of OCPs were higher in breast adipose tissue taken from women with breast cancer compared with women with benign breast conditions. DDE levels were significantly different between malignant and benign tissues. Studies of plasma levels of organochlorines and breast cancer risks have not supported the hypothesis that exposure to DDT (or DDE) and PCBs increases the risk of breast cancer (e.g. Hunter et al., 1997).

17.9. Conclusions

The dioxins are considered to be at a low level in the Australian environment and constitute a low hazard to human health. The dietary intake of OCPs is considered the main source of exposure to POPs for the general population in Australia and in many other countries. From the 1970s, the AMBS of foods has shown a progressive decline in OCPs detected in food. This has occurred as a result of the banning of the OCPs in Australia, which was effectively complete by 1985. Between 1976 and 1996 the OCPs have declined in the environment in accord with first-order kinetics allowing extrapolations to 2005. The HI from all sources, dietry and others, was used to evaluate the level of risk to human health. This was estimated at <0.1 for all the individual OCPs in 2005.

However several POPs, particularly the OCPs and dioxins, remain at low levels in the Australian environment and several remain persistent at low levels in body fats and fluids of Australians. The levels reflect the past use and persistence of OCPs in the Australian environment, contamination of the food chain and the capacity of the body to metabolise and store in body fats. The dioxins remain due to the ubiquitous nature of their sources with combustion as a major source and their persistence. Future trends are likely to mean very low-level residues in human fats of DDE, cyclodienes, HCB, HCHs and dioxins in the long term. Their rate of decline will probably depend on removing HCB from chlorinated industrial chemicals and OCPs from the environment (e.g. remediation of contaminated soils) by hazardous waste treatment methods (e.g. physical, chemical and biological degradation or fixation) or secure landfill.

Some possible toxicological effects such as endocrine disruption continue to be uncertain, particularly for DDT, DDE, dieldrin and dioxin exposures. The history of environmental health shows that safe levels are uncertain and vary as knowledge improves. The long-term trend is often towards lower levels as uncertainties decrease. This should be considered when accounting for the public benefits of further reducing POPs residues and wastes in the Australian environment.

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Chapter 18

Contamination by Persistent Toxic Substances in the Asia-Pacific Region

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Abstract

This chapter reviews studies conducted in our laboratory at CMES, Ehime University on various aspects of contamination by persistent toxic substances (PTS) in Asia-Pacific region. The sources, distribution, environmental fate, temporal trends and toxic impacts of PTS on wildlife and humans were examined using archived samples from our environmental specimen bank (*es-BANK*). The hot spots of PTS pollution were found in the areas where they have been heavily used, e.g., elevated HCH residue levels were found in samples from India and South China, while pollution by DDTs was found to be high in China and Vietnam. PBDEs exhibited higher concentrations in coastal waters of Korea and Hong Kong and areas around East China Sea, suggesting the presence of PBDE sources in highly industrialized zones. Our recent study on temporal trends of PBDEs in this region clearly demonstrated a substantial increase in PBDE levels in small cetaceans collected from Hong Kong coastal waters. The role of extensive manufacturing of computers and other electronic appliances as well as dumping of e-waste in some East Asian countries as substantial sources of brominated flame retardants such as PBDEs should be elucidated in future. Based on our monitoring surveys involving different environmental media and biological samples, the transport behavior of PTS could be characterized as "local" and "global". DDTs and PCDD/Fs have less potency for long range atmospheric transport, and their sources are, therefore, located in the proximity of areas where they are used/released. On the other hand, HCHs and, to a lesser extent, PCBs and PBDEs exhibit relatively high ability for transport through atmosphere and their contamination may extend globally in future. As far as toxic impacts of PTS are concerned, the open dumping sites for municipal wastes

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in Asian developing countries are potential sources of various chemical contaminants. Residue levels of dioxins and related compounds were higher in soils, human breast milk and bovine milk from dumping sites when compared to reference sites. Possible impacts of PTS on health of people, especially those living in and around these dumping sites, are of great concern and deserve systematic and long-term investigations. Considering these critical issues of PTS pollution, it is clear that continued and constant efforts should be made to deal with the environmental problems caused by the contaminants not only in developed nations but also in developing countries.

18.1. Introduction

As a closing chapter of the book dealing with various important issues on persistent organic pollutants (POPs), this article reviews the outcomes of comprehensive investigations conducted in our laboratory at CMES, Ehime University over the last three decades on the distribution, sources, transport behavior and fate, pollution trends and toxic impacts of the bioaccumulative persistent toxic substances (PTS) in Asia-Pacific region with a particular emphasis on the developing countries. Results of multimedia monitoring studies were complied and discussed to provide in-depth understanding on the various issues of PTS contamination in both ambient environment and animals, including humans. The prominent contamination by PTS was found in the region where they have been heavily used. The East Asian region is probably a potential source of pollution, particularly by the new contaminants such as polybrominated diphenyls ethers (PBDEs). This group of contaminants, together with polychlorinated biphenyls (PCBs), exhibited slow decreasing or even increasing trends in some highly industrialized areas in Asian developing countries, suggesting the necessity for long-term monitoring. The open dumping sites for municipal wastes in major cities are significant sources of many toxic chemicals, and these areas are probably one of the challenges for future research due to the long-term impacts on the environmental quality and human health. The formation of dioxins and related compounds (DRCs) in such dumping sites and their elevated residue levels found in breast milk of residents living in and around the sites warrant long-term impacts of dioxins on the next generations. Comprehensive and long-term monitoring programs are urgently needed with close collaboration and proper capacity building in the local areas in developing countries in order to mitigate the PTS emission and their risk on ecosystems and human health.

The last decades of the 20th century have witnessed a steady increase in the pace and extent of various environmental problems such as biodiversity loss, changes in water quality, land use and climate. Among these, the issue of environmental pollution caused by PTS has become increasingly important because their usage in large quantities have resulted in many negative impacts including environmental deterioration and health effects on wildlife. In particular, many PTS are known to pose endocrine disrupting effects, which are probably the cause for various reproductive abnormalities observed in wildlife species (Colborn et al., 1996). Among a variety of endocrine disrupters, chemicals with severe toxicity, high accumulation potential in the body and persistence in the environment are the most hazardous for wildlife. Organochlorine (OC) compounds—the typical class of chemicals meeting the above conditions—such as DDTs, hexachlorocyclohexanes (HCHs), chlordane related compounds (CHLs) and PCBs have received considerable attention due to their potential to degrade the environmental quality and to pose ecological risk. Mass production and consumption of these OCs started after the Second World War. DDTs, HCHs and CHLs have been heavily used as insecticides for agriculture and public health purposes including malaria eradication. PCBs are mainly used for industrial purposes such as dielectric fluids in transformers and capacitors. Although many developed nations prohibited production and usage of certain OCs in the 1970s and 1980s due to a deep concern regarding their toxic impact on humans and wildlife, they are still in use in some developing countries.

Dioxins and related compounds including polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and coplanar PCBs should also be paid particular attention due to their highest toxicity among the OCs investigated. They are "unintentionally" generated by refuse incineration and/or byproducts during the manufacturing processes of some other chemicals. According to a comprehensive national survey by the Japanese Ministry of Environment (1999), elevated contamination of DRCs were widely detected in fish-eating animals such as kites and cetaceans collected throughout Japan. In developed countries, residue levels of DRCs in human breast milk have been reported to decrease recently due to the implementation of highly efficient incinerators and strict regulations on the production and usage of hazardous chemicals (LaKind et al., 2001). On the other hand, in developing countries, environmental pollution by DRCs may still increase because of improper management controlling the release of these contaminants. Although it has been suspected that the residents in Asian developing countries have been exposed to relatively high levels of DRCs, there is a lack of information on human exposure to these contaminants.

In addition to OCs, PBDEs, the popular brominated flame retardants, are now a worldwide problem even in remote areas, and Asia-Pacific region is surely no exception (Ikonomou et al., 2002; Birnbaum and Staskal, 2004; Ueno et al., 2004). PBDEs are structurally similar to PCBs and DDT and, therefore, their chemical properties, persistence and distribution in the environment follow similar patterns. Studies on the environmental behavior of PBDEs are chiefly derived from Europe, North America and the Arctic. Despite the usage of vast amounts of these compounds in Asia-Pacific region, there is a paucity of data on the prevalence of PBDEs in Asian environment. Studies are necessary to identify Asian sources of PBDEs as well as to quantify emissions and document their potential environmental fate in this region.

In the previous chapters, various issues of PTS contamination such as magnitude of pollution, environmental transport and fate, features of bioaccumulation in organisms as well as trends of contamination have been discussed with in-depth examples of case studies conducted in particular countries in the Asia-Pacific region. These chapters have provided both general and concrete concept of the ultimate fate of PTS in local perspectives and addressed a number of issues of PTS contamination that specifically exist in each country/area.

Results of multi-media monitoring surveys conducted in our laboratory in collaboration with Asian environmental scientists were compiled in this chapter to discuss the fate of PTS in both ambient environment and biota, including humans, from regional and global point of view. The Asia-Pacific region comprises a number of developing and under developed countries, where considerable quantities of PTS are currently used or have been used until very recently. Therefore, the issue of temporal trends of PTS pollution in this region is critically important. This chapter also provides in-depth analysis of temporal trends of PTS residues in various environmental compartments with the purpose of tracing history, predicting future trends of PTS pollution and exploring new clues for understanding their toxic impacts on environment and human health. We fully utilized archived samples in the Environmental Specimen Bank for Global Monitoring (*es-BANK*) at Ehime University which has a wide array of tissues and organs of about 900 species with 80,000 specimens of wildlife and environmental samples collected throughout the world during the last 40 years.

18.2. Distribution and sources

In addition to the multi-media monitoring of the environmental samples, the use of animal tissues and humans as bioindicators has been proved to be a suitable concept to address various important issues of PTS pollution (Tanabe and Subramanian, 2006). Since bivalves have been suggested as suitable bioindicators for monitoring trace toxic contaminant levels in coastal waters (Goldberg, 1975), we have been using mussel as a sentinel animal to elucidate the pollution sources in the Asia-Pacific region (Sudaryanto et al., 2002; Tanabe et al., 2000; Monirith et al., 2003b; Ramu et al., 2005). The survey conducted by Monirith et al. (2003b) revealed that DDT residue levels were highest in mussel samples from the coastal waters of South China (Fig. 18.1). The higher proportion of *p,p′*-DDT, the main component in the formulation, in mussels may indicate the presence of current emission sources of DDT in China, despite its usage was officially banned in 1983. HCH levels were found to be the

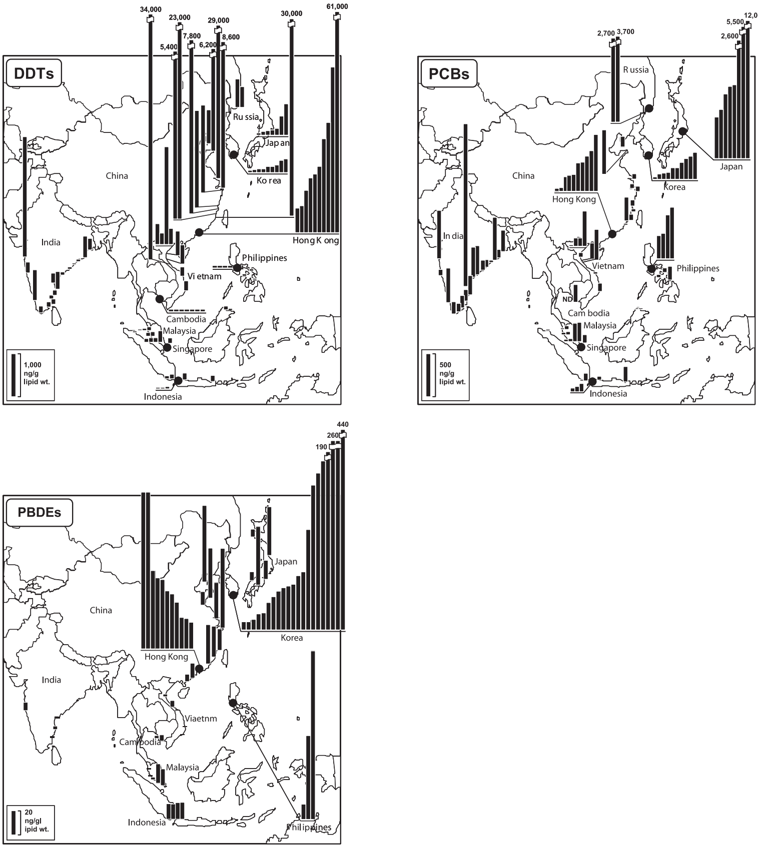

Figure 18.1. DDT, PCB and PBDE concentrations in mussels from coastal waters of some Asian countries.

highest in mussel samples from India, the world's largest consumer of technical HCHs, reflecting continuous usage for public health purposes and on certain food crops (Li et al., 1998; Li, 1999). According to our previous studies on water pollution, considerable contamination by OC insecticides such as HCHs and DDTs was found in developing countries in the Asian tropics (Iwata et al., 1994). On the contrary, PCB levels in mussels in developed nations, including Japan, were clearly higher than those in developing countries (Fig. 18.1). Using resident and migratory birds as bioindicators for monitoring OC contamination, high concentrations of OC insecticides and PCBs were found in birds collected at stopover/wintering areas of tropical Asian developing countries and Russia/Japan, respectively (Tanabe et al., 1998; Kunisue et al., 2002a; Minh et al., 2002). To substantiate our findings with further evidence on pollution sources of OCs, we collected human breast milk from Asian countries and determined residue levels of contaminants. As a result, PCB levels in human breast milk were found to be higher in developed nations like Japan than in developing countries such as China, India, Cambodia and Indonesia (Fig. 18.2). On the other hand, OC insecticides in human breast milk showed apparently higher concentrations in developing countries than in developed nations. Considering all these observations, we can say that, from a global point of view, major emission sources of PCBs are located in developed nations, while that of DDTs and HCHs are in the developing countries.

Noteworthy, widespread contamination by PBDEs in the coastal waters of Asia became apparent with the highest concentration in mussel samples from Hong Kong (Ramu et al., 2005) (Fig. 18.1). Another study focused on cetaceans (Kajiwara et al., 2006) also showed the highest PBDE concentrations in samples from Hong Kong, suggesting that developing nations may also have significant pollution sources of PBDEs (Fig. 18.3). The Pearl River Delta in Hong Kong has a number of electronic and telecommunication industries as well as a number of private manufacturing operations which have transformed this delta into one of the fastest growing industrial manufacturing areas in the world (Zheng et al., 2004). Estimates suggest that one out of three computers manufactured in the world are assembled in this region (Mai et al., 2005). As PBDEs are commonly incorporated into polymers for use in electronic components, the high levels of PBDEs in wildlife from Hong Kong may be due to the discharge of effluents derived from materials used in the production or the dismantling of electronic equipments, the so-called "e-waste". In addition, our recent survey on more than 20 sites along Korean coastal waters (Ramu et al., 2007) revealed that natural blue mussels contained very high concentrations

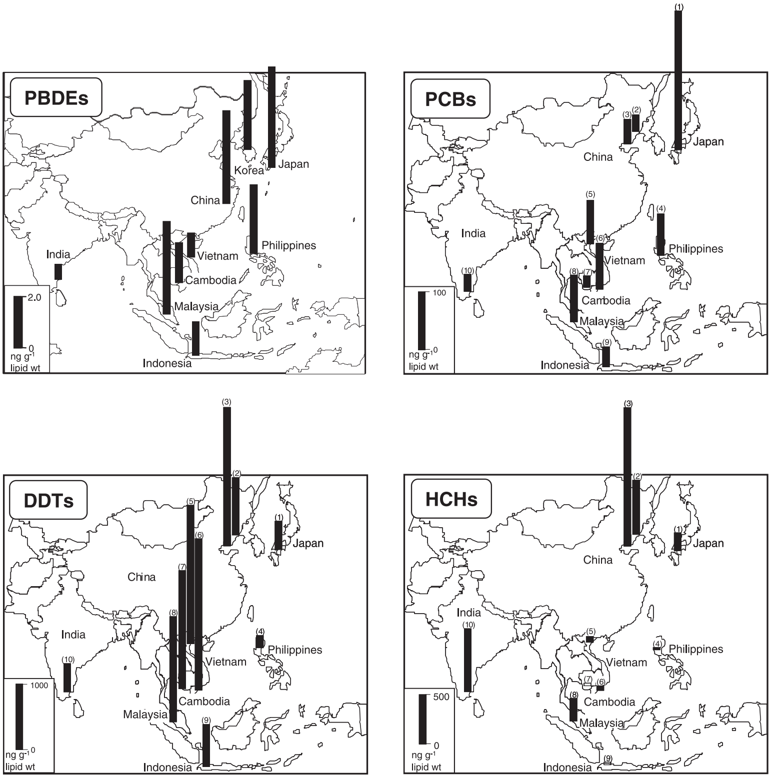

Figure 18.2. Concentrations of PBDEs, PCBs, DDTs and HCHs in human breast milk collected from general public in Asian countries. (1) Ehime, Japan (Kunisue et al., 2004c), (2) Shenyang, China (Kunisue et al., 2004a), (3) Dalian, China (Kunisue et al., 2004a), (4) Quezon, Philippines (Kunisue et al., 2002b), (5) Hanoi, Vietnam (Minh et al., 2004), (6) Hochiminh, Vietnam (Minh et al., 2004), (7) Phnom Penh, Cambodia (Kunisue et al., 2004b), (8) Penang, Malaysia (Sudaryanto et al., 2005b), (9) Jakarta, Indonesia (Sudaryanto et al., 2006), (10) Palaverkadu, India (Kunisue et al., 2002b). Data for PBDEs were from Sudaryanto et al. (2005a).

of PBDEs (mean = 91 ng g^{-1}; range = 6.6–440 ng g^{-1} lipid wt; Fig. 18.1), which are among the highest levels ever reported for the mussels from Asia-Pacific. Elevated residues of PBDEs in mussels from Korea indicate that this region is a potential source of these new chemicals in eastern Asia.

To elucidate whether the DRC pollution sources are also present in developing countries, human breast milk samples were employed for chemical analysis. As summarized in Fig. 18.4, significant levels of DRCs were detected in human breast milk from developing countries,

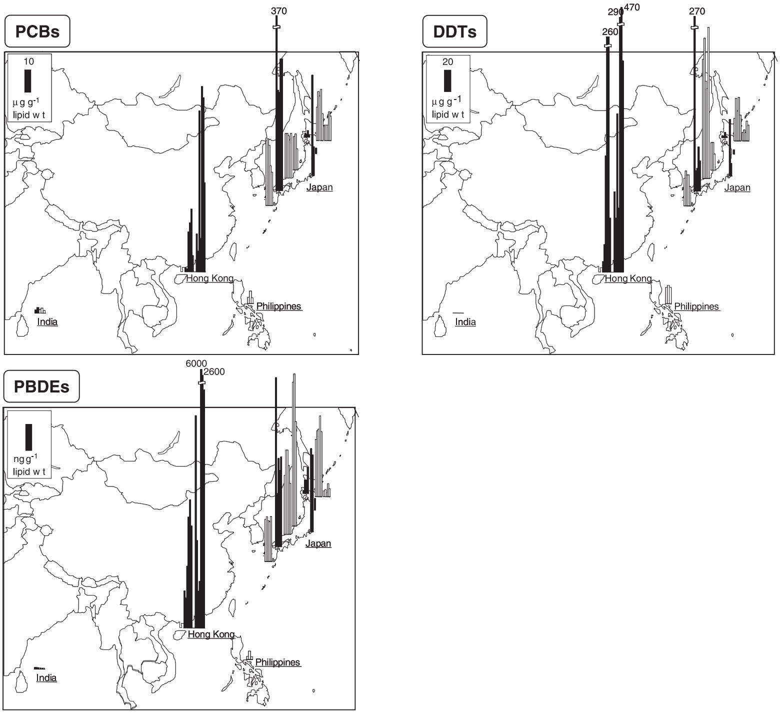

Figure 18.3. Geographical distribution of PCBs, DDTs and PBDEs in Asian cetaceans. Black and white bars indicate coastal and offshore species, respectively.

indicating considerable contamination in some developing countries as well as in developed nations. Our further survey on DRC contamination in soils revealed critical emission sources in the open dumping sites of municipal wastes in Asian developing countries (Minh et al., 2003). A variety of municipal wastes are dumped there continuously and burnt under low temperature spontaneously and/or intentionally generated fire, implying DRCs formation by such uncontrolled combustion with very little waste management. Additionally, PCBs can leach out from old electric appliances dumped there. When comparing PCDD/F levels in various soil types on global terms, open dumping sites in Asian developing countries showed apparently higher concentrations than general background soils and comparable levels to the dioxin-contaminated sites in developed nations so far reported (e.g. de Jong et al., 1993; Lorber et al., 1998). Toxic equivalents (TEQs) concentrations detected in soils from open dumping sites in Asian developing countries exceeded the environmental quality standards set forth by the Japanese

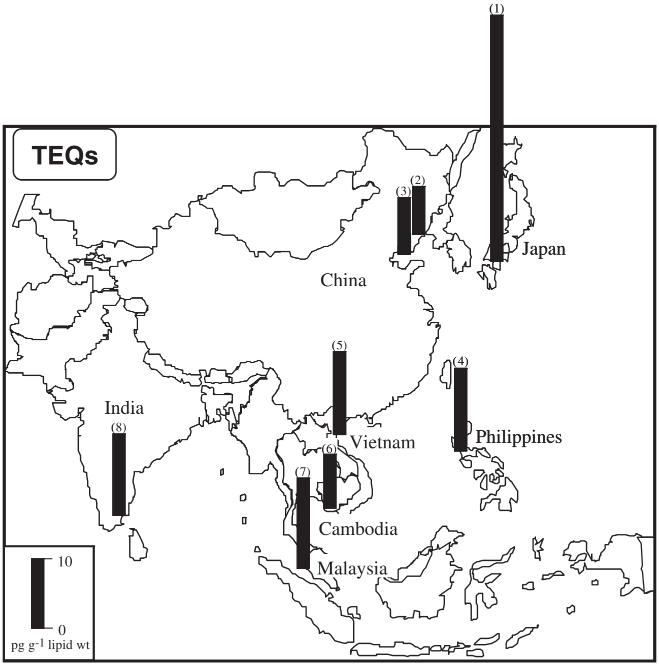

Figure 18.4. TEQs of DRCs (PCDDs, PCDFs, coplanar PCBs) in human breast milk collected from general public in Asian countries. (1) Ehime, Japan (Kunisue et al., 2004c), (2) Shenyang, China (Kunisue et al., 2004a), (3) Dalian, China (Kunisue et al., 2004a), (4) Quezon, Philippines (Kunisue et al., 2004d), (5) Hanoi, Vietnam (Kunisue et al., 2004d), (6) Phnom Penh, Cambodia (Kunisue et al., 2004d), (7) Penang, Malaysia (Sudaryanto et al., 2005b), (8) Palaverkadu, India (Kunisue et al., 2004d).

government and the US Department of Health. More importantly, in Asian developing countries, a stratum of impoverished people earn a living by collecting dumped recyclable and valuable resources and form slums in and around the dumping sites. Since they spend most of the days there, risks on their health through the exposure to significant amount of dioxins and other anthropogenic chemicals are of particular concern. Figure 18.5 illustrates the mean and range concentrations of DRCs in human breast milk collected from residents around dumping sites and reference sites in India, Cambodia and Vietnam (Kunisue et al., 2004d). In these countries, higher levels were observed in dumping sites, particularly, the concentrations in Indian dumping sites were significantly higher than those in control sites, which was not observed in the cases of Cambodia and Vietnam. This result prompted us to consider the presence of extraordinary exposure pathway of DRCs in

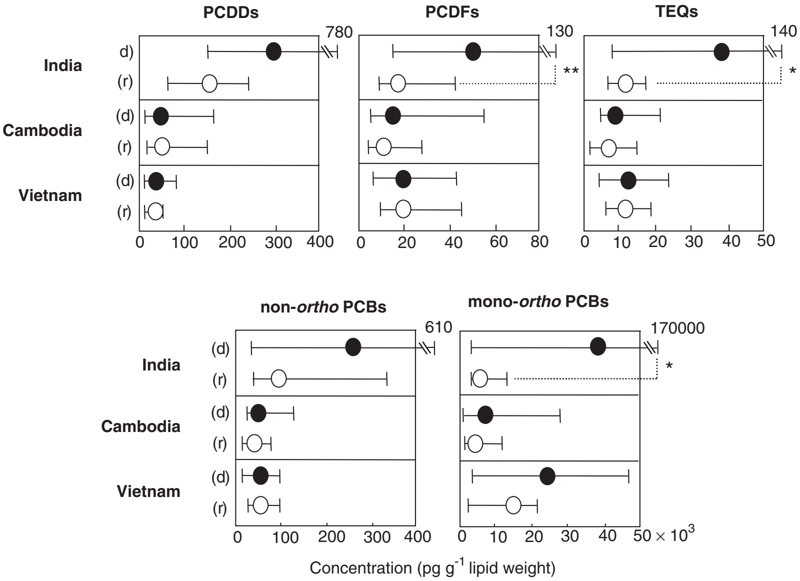

Figure 18.5. Comparison of the concentrations of DRCs in human breast milk from dumping (d) and reference (r) sites. The circles and bars represent mean and range values, respectively. $*p<0.05$, $**p<0.01$, Mann-Whitney *U* test.

the dumping sites of India. Although, in Cambodia and Vietnam, domestic livestock are not reared around the dumping sites, residents around the Indian dumping site consume milk from the buffaloes and cows that graze daily on the garbage in the waste dumping sites. To elucidate whether bovine milk is a potential source of DRCs for the residents around the dumping site in India, residue levels of these contaminants in milk from the buffaloes and cows there were examined (Kunisue et al., 2004d). As expected, concentrations of DRCs in bovine milk collected from the dumping site were significantly higher than those from the reference site (Fig. 18.6), indicating such a dairy operation led to significant accumulation of DRCs in residents around dumping site. For assessing the health risk, we estimated daily intakes by infants based on dioxin, HCH and DDT concentrations in human breast milk (Fig. 18.7). The estimated daily intakes of dioxins by infants in all the four developing countries exceeded tolerable daily intake (TDI) proposed by World Health Organization (WHO) (Van Leeuwen et al., 2000). Epidemiological studies coupled with monitoring of contaminants should be conducted on dumping site populations in developing countries.

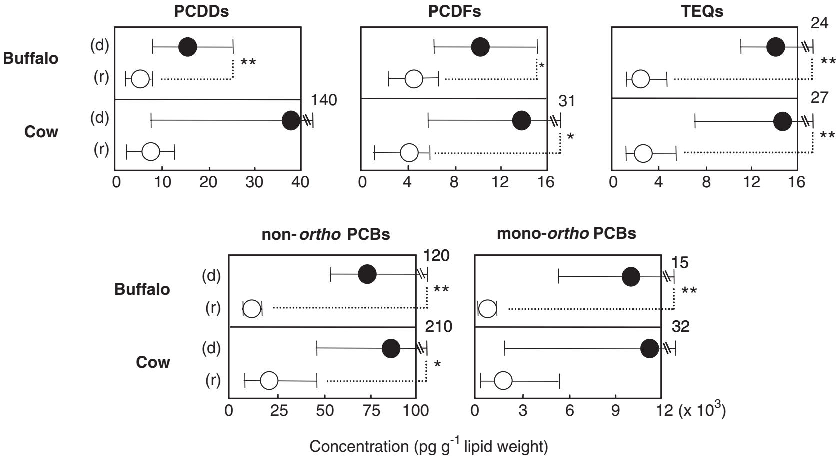

Figure 18.6. Comparison of the concentrations of DRCs in bovine milk from dumping (d) and reference (r) sites. The circles and bars represent mean and range values, respectively. $^*p<0.05$, $^{**}p<0.01$, Mann-Whitney *U* test.

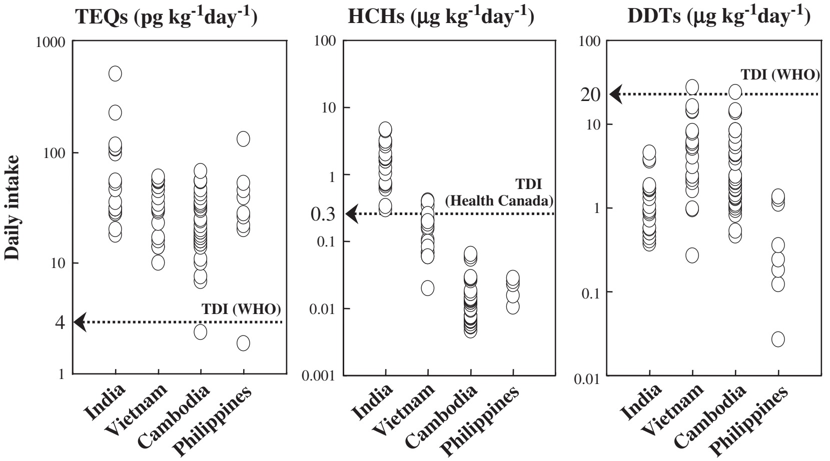

Figure 18.7. Estimated daily intake of OCs by infants in Asian developing countries.

18.3. Transport behavior and fate

Multi-media monitoring studies not only helped increase knowledge of the status of contamination, but also provided in-depth insights into the transport behavior and fate of PTS in tropical ecosystems in Asian developing countries. On a global scale, the fate of persistent OCs in open oceans was different from that in coastal environment (Iwata et al., 1993, 1994; Tanabe et al., 1994). Open oceans play the role as a final sink for PTS, and cold waters from high latitudes like Arctic Ocean, which are located far from pollution sources, serve as significant reservoirs (Iwata et al., 1993). On the other hand, pronounced contamination by OC insecticides was observed in coastal waters of Asian countries as a result of extensive usage for agriculture and public health purposes (Iwata et al., 1994). The latitudinal distribution of persistent OCs such as PCBs, DDTs, HCHs in sediments from the coastal waters of Asian countries is a typical example for understanding the transport behavior of PTS on a smaller scale (Iwata et al., 1994). Iwata et al. (1994) suggested a concept of using the relationship between the concentration ratio of a compound in water phase (concentration in water sample) and in particulate phase (organic carbon normalized concentration in sediment) (S/W ratio) and latitude. The degree of correlation and the ratio (S/W) are indications of the efficiency of their transport.

Analytical results showed relatively uniform distribution of HCHs along with the latitudes, and the ratio (S/W) showed the highest degree of positive correlation with latitude. This phenomenon indicates that HCH isomers pose higher potency for atmospheric transport and global redistribution. Other compounds such as DDTs, CHLs and PCBs with lower correlations and gradients exhibited less efficiency for atmospheric transport.

Another case study conducted by Ramesh et al. (1989) and Takeoka et al. (1991) provided quantitative information on the budget and fluxes of HCHs in the Vellar River watershed, South India, a typical tropical area in Asia. The model showed that 99.6% of the HCH, which was applied to the catchment area, was volatilized and that only 0.4% drained into the estuary. In addition, 75% of the flux to the estuary was volatilized and, thus, only approximately 0.1% of the applied HCH finally reached the Bay of Bengal by aquatic pathways. Despite the fact that HCH was applied into paddy fields in large quantities in India, only very small amounts of this insecticide retained in the aquatic phase due to the extraordinary high degree of volatilization. Elevated temperature in the tropical watershed in South India is favorable factor for the rapid volatilization of highly volatile HCH isomers. Thus, results of this case study on a specific watershed site in South India is consistent with those in the case study on small scale latitudinal distribution of HCHs conducted from various sites along the estuaries of Mekong River Delta, Southern Vietnam (Iwata et al., 1994), which provided insights into the transport and fate of persistent semi-volatile organic compounds.

In general, the degree of usage, the climate and the physico-chemical properties of persistent organic compounds are the major factors controlling the magnitude of contamination in the environment. When comparing the distribution of OCs in different environmental media in Asia-Pacific region, we found that distribution patterns in fish and sediment were relatively similar and showed less spatial variation. The pattern in air and water exhibited greater geographical variability. A recent extensive survey of OC insecticides from Red and Duong rivers, the two largest rivers flowing through the northern delta region of Vietnam, and various lakes in Hanoi has elucidated that DDT and HCH residue levels in rivers are apparently greater than those in lakes (Hung and Thiemann, 2002). This observation suggests different behaviors of semi-volatile compounds in tropical lakes and in rivers, showing shorter retention time in lakes than in rivers. Again, elevated temperatures may enhance volatilization of such compounds, leading to shorter residence time in tropical water phase, lower residue levels and relatively uniform distribution in sediments and aquatic biota. In this context, the role of the tropics in Asia-Pacific region as potential emission sources for higher latitude areas deserves further attention.

In addition to the environmental samples, the use of biological tissues has been proved to be a reliable tool for understanding the distribution patterns and transport behavior of PTS (Tanabe and Subramanian, 2006). Recent studies using the skipjack tuna (*Katsuwonus pelamis*) for monitoring semi-volatile organic compounds in open seas and oceans can be a typical example (Ueno et al., 2003). Skipjack tuna is widely distributed all over the world oceans; its ecology is well studied as it is one of the target species of commercial fishing in Japan. We attempted to make clear the distribution and transport of these compounds using this species as a bioindicator (Ueno et al., 2003). Interestingly, HCH and hexachlorobenzene (HCB) concentrations were higher in the high-latitude areas than in the low-latitude areas (Fig. 18.8). Similar to these insecticides, significant levels of PCBs were detected not only in the samples from coastal waters but also in the open seas. According to various investigations conducted so far, PCBs as well as HCHs and HCB are known to have a highly transportable nature through atmosphere, contributing to global pollution. On the other hand, higher levels of DDTs were found in tunas collected from tropical and subtropical open sea waters, while northern tunas showed much lower DDT levels, which is also similar to the pattern found in dolphins and whales (Prudente et al., 1997). As for DRCs, Ueno et al. (2005) found measurable levels of PCDDs only in the samples from coastal waters around Japan and Korea, but very low levels below detection limit were found in samples from open seas (Fig. 18.9), which is

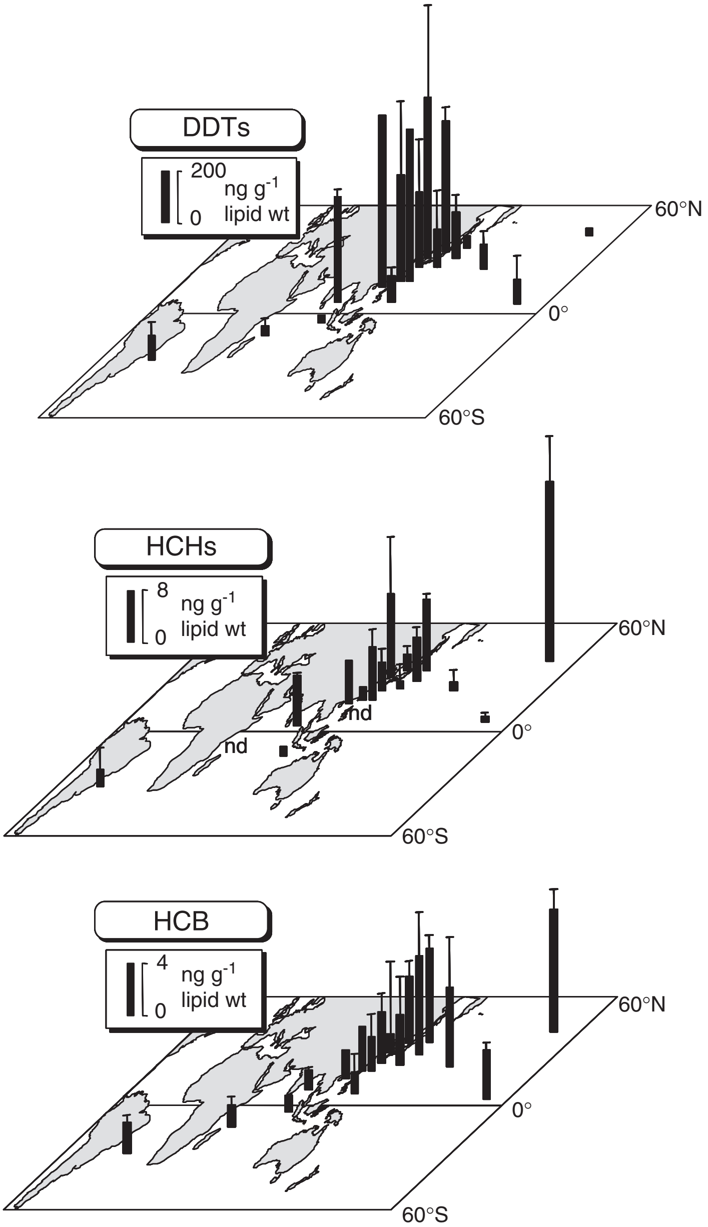

Figure 18.8. Geographical distribution of OC concentrations in the muscle of skipjack tuna. Data from Ueno et al. (2003).

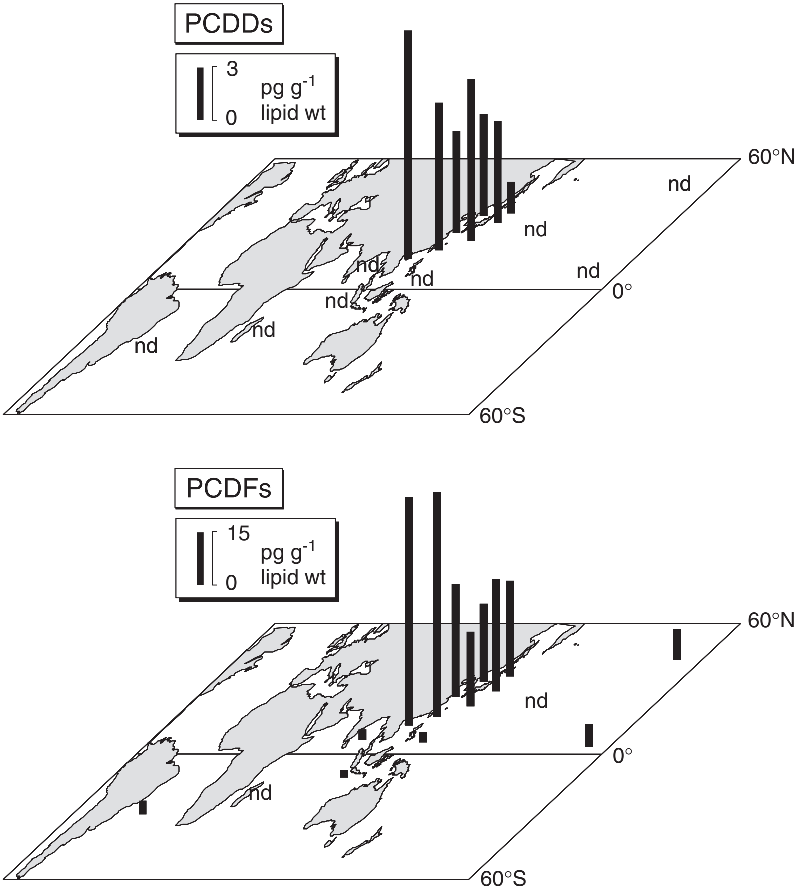

Figure 18.9. Geographical distribution of DRC concentrations in the muscle of skipjack tuna. Data from Ueno et al. (2005). nd: under detection limit.

similar to DDT distribution (Fig. 18.8). These observations on DDTs and dioxins confirm the less transportable and highly localized nature of these contaminants. As a further finding of spatial distribution, PBDEs were also detected in tunas from remote oceans even though their residue levels were relatively low, indicating PBDEs retain transportable nature to some extent similar to PCBs (Ueno et al., 2004). The highest concentration of PBDEs was detected in the sample from off-Taiwan, and relatively higher concentrations of these compounds were observed around the East China Sea and the South China Sea (Fig. 18.10).

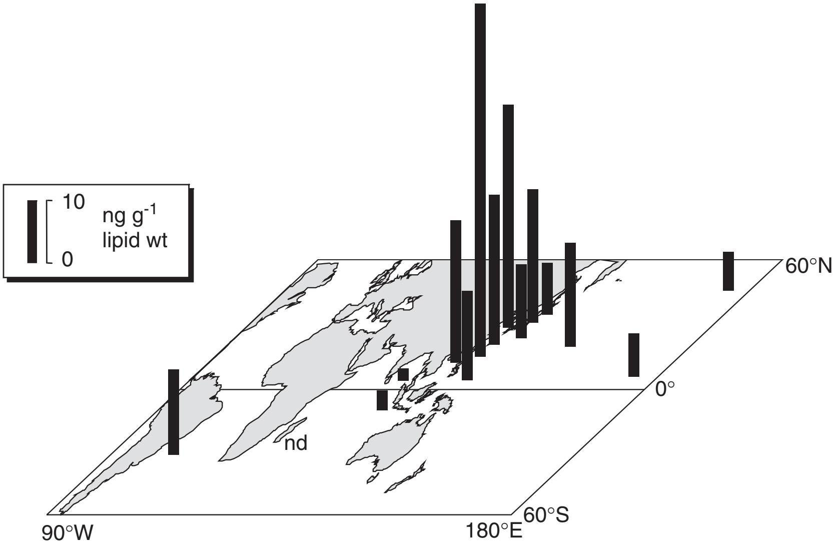

Figure 18.10. Geographical distribution of PBDE concentrations in the muscle of skipjack tuna. Data from Ueno et al. (2004). nd: under detection limit.

The distribution pattern of organohalogen compounds found in skipjack tunas is in association with the long-range atmospheric transport of the compounds. According to Wania and Mackay (1993), chemicals used in developing and developed nations evaporate at different rates, carried out globally by long-range atmospheric transport and eventually deposit mostly in the water phase of open seas, particularly in polar regions. In this context, volatile chemicals such as HCB, HCHs, PBDEs and PCBs are relatively transportable through atmosphere and deposit in open oceans, and significant residue levels were found in skipjack tunas and dolphins from open seas. On the other hand, less volatile contaminants such as DDT and dioxins have low transportability through air, and higher levels still exist in coastal wildlife. Considering these facts, DDTs and dioxins may be designated as regional pollution type contaminants, and PCBs, PBDEs, HCHs and HCB as global pollution type contaminants. In any case, the toxic impacts of POPs affect not only the local ecosystems nearby the emission sources, but also unexpected areas such as the Arctic and the Antarctic regions. Therefore, their influence to the environment should be examined on a global scale as has been done for issues like the ozone depletion by chlorofluorocarbon (CFC) and global warming by carbon dioxide.

18.4. Temporal trends and future prospects of contamination

It is essential to understand the future trends of contamination in order to evaluate forthcoming risks posed by PTS. Hence, we have examined the historical trends in residue levels of organohalogen compounds in some aquatic mammals. We first carried out the investigations to make clear the temporal trends of OC levels in inland areas and open seas. As shown in Fig. 18.11, most OCs in the archived samples of Baikal seals (*Phoca sibirica*), a representative species living in inland water body, were on a declining trend during 1992–2002 (Tanabe et al., 2003; Tsydenova et al., 2004). This result indicates that the regulation of OC production and usage following the recommendation by WHO, Food and Agriculture Organization (FAO), United Nation Environment Programme (UNEP), etc. showed significant effects on inland areas. Recently, Aguilar and Borrell (2005) reported similar decreasing trends of OC contamination in the Mediterranean Sea using striped dolphin (*Stenella coeruleoalba*) as an indicator. In the case of open seas, a study on the archived blubber samples of minke whales (*Balaenoptera acutorostrata*) collected from Antarctic Ocean, a remote area far away from emission sources of pollutants, during 1984–2001, showed that the concentrations of OC insecticides and PCBs did not clearly decline during this period (Fig. 18.12; Aono et al., 1997 with additional data). Considering all these facts, it can be said that the recent contamination by OCs in inland and coastal areas

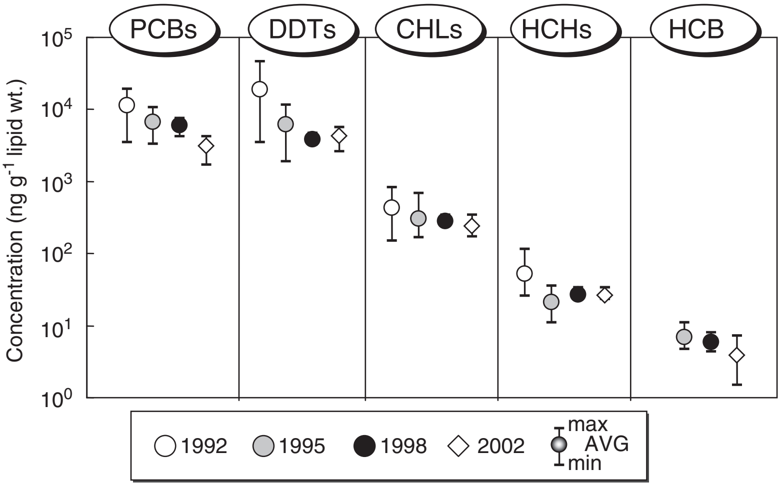

Figure 18.11. Temporal variation of OCs in Baikal seals collected from Lake Baikal in 1992–2002. Data from Tanabe et al. (2003) and Tsydenova et al. (2004).

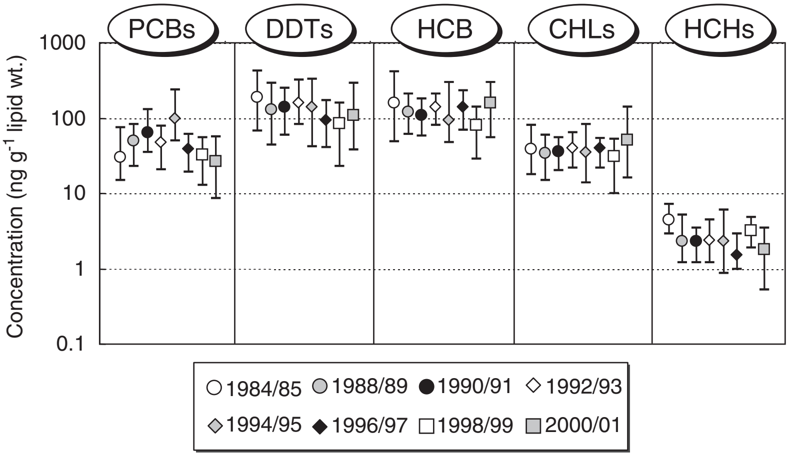

Figure 18.12. Temporal variation of OCs in minke whales collected from the Antarctic in 1984–2001.

have decreased in comparison with their severely polluted status in the 1970s. On the contrary, in remote oceans, their declining trends were very slow in the past several decades. This might be due to the nature of the oceans which are vast reservoirs and act as the final sinks for these persistent chemicals. From these observations we can conclude that the OC pollution and potential risks in marine ecosystems will continue for a considerable period of time in the future, and, hence, long-term monitoring for toxic contaminants is necessary in the marine environment, particularly in open oceans.

Interest in PBDE flame retardants has been as exponential as their apparent increase in the environment over the past 20–25 years in North America (Ikonomou et al., 2002; Norstrom et al., 2002; Rayne et al., 2003) and Europe (Norén and Meironyté, 2000; Thomsen et al., 2002). However, there is still very little information on PBDE contamination and its temporal trend from other regions of the world, including the Asia-Pacific region. Therefore, we have carried out comprehensive investigations to provide an in-depth understanding of the historical trends of contamination by PBDEs since 1972, in the fat tissues of northern fur seals (*Callorhinus ursinus*) inhabiting and migrating in the North Pacific, in comparison to classical OCs (Tanabe et al., 1994; Kajiwara et al., 2004). The lowest PBDE levels were in the fur seals collected in 1972, with the peak concentration around 1991–1994, and then, decreased to about 50% in 1997–1998 (Fig. 18.13). On the other hand, OCs in northern fur seals showed the highest levels in 1970s to early 1980s and then decreased.

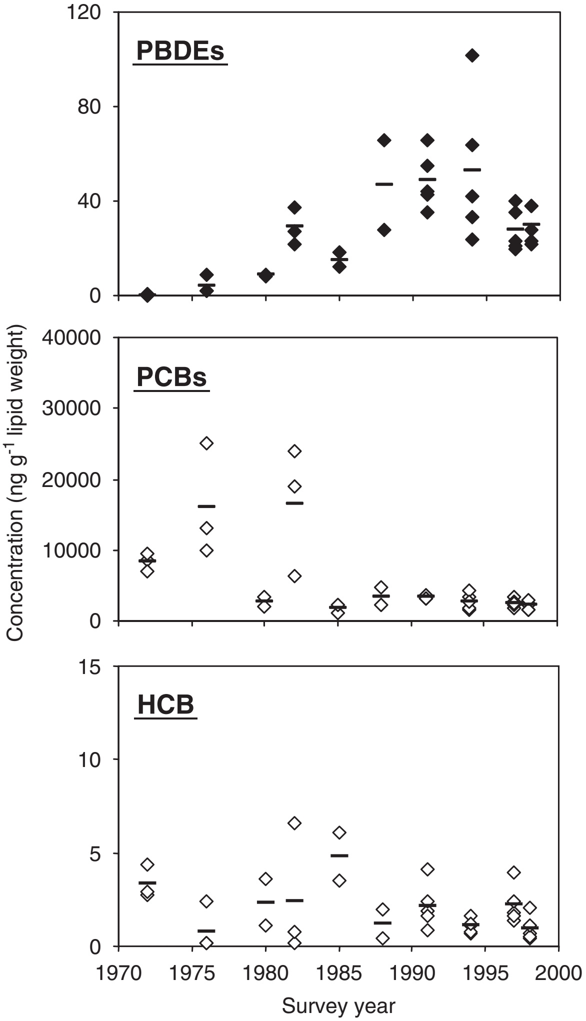

Figure 18.13. Temporal trends in concentrations of PBDEs and OC residue in female northern fur seals collected from 1972 to 1998. Horizontal bars indicate mean values. Data from Tanabe et al. (1994) and Kajiwara et al. (2004).

Compositions of higher brominated congeners increased since 1972, while some lower brominated congeners decreased, implying a change in the pattern of use, particularly the increased usage of highly brominated diphenyl ethers during 1972–1998. In the meantime, PCB compositions in fur seals showed no temporal variation, suggesting a continuous input of

PCBs into the marine environment in significant quantities. As peak concentrations of PBDEs occurred later than OCs, it is essential to follow-up the patterns of PBDE pollution that may be of great concern in the future.

Furthermore, to examine temporal changes in the past 20 years around Japan and 10 years around China, we analyzed PBDEs and OCs in the blubber of melon-headed whales (*Peponocephala electra*) stranded along Japanese coasts in 1982 and 2001 and finless porpoises (*Neophocaena phocaenoides*) from Chinese waters in 1990/91 and 2000/01, respectively. In whales from Japan, PBDE levels in 2001 were significantly higher than 1982, showing an increase of about 10 times (Fig. 18.14). Similarly, finless porpoise from China showed five times increase during the past 10 years, indicating that PBDEs usage in China also increased drastically in the past decade (Ramu et al., 2006). When we compared PBDE congener patterns, higher contributions of hexa-BDEs were observed in whales collected in 2001 than those in 1982. This is similar to the trend found in northern fur seals from the Pacific coast of Japan (Kajiwara et al., 2004), indicating a possible change in the source products. On the other hand, congener profiles in porpoises from China did not shift to higher BDE congeners, implying a continuous discharge of lower BDE commercial mixtures such as Penta-BDE.

Asian countries consumed about half of the annual worldwide consumption of PBDEs in 2001 (Watanabe and Sakai, 2003; BSEF, 2004). In Asia, the major portion of PBDE formulations was estimated to be

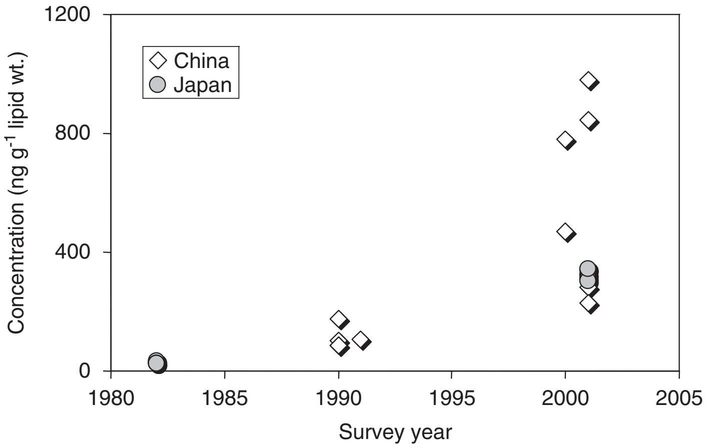

Figure 18.14. Temporal changes in PBDE levels in the cetaceans found stranded along the coasts of China and Japan.

consumed by the countries other than Japan, suggesting that considerable amounts of PBDEs have been also used in some developing countries in Asia, probably in nations with high economic growth rate. The high population and economic growth rate in China (Li and Daler, 2004) undoubtedly accelerated the industrial and human activities involving the usage of modern chemicals including PBDEs. Higher levels of PBDEs in mussels and small cetaceans from Hong Kong, mussels from Korea (Figs. 18.1 and 18.3) and fishes from the East China Sea (Fig. 18.10) as well as the increasing temporal trend of PBDE levels in wildlife from Chinese coasts may suggest their expanding usage in China and nearby countries. Moreover, the export of waste electric products like computers, televisions, etc. used in developed nations to Asian developing countries such as China as trash has been reported (Hileman, 2002; Schmidt, 2002). In some cases, the wastes were burnt in open dumping sites, which may lead to the formation of chlorinated and brominated dioxins. A series of our investigations underlines the need for long-term monitoring of PBDE pollution in Chinese coastal waters as well as other countries in Asia-Pacific region. It is also imperative to find out the pollution sources of PBDEs in the entire Asian region.

18.5. Human exposure and human health implications

18.5.1. Monitoring the status of contamination using breast milk as bioindicator

The presence of PTS in humans is always viewed with concerns because of their potential for various biological effects such as teratogenicity, carcinogenicity, neurotoxicity and immunotoxicity (Nicholson and Landrigan, 1994). Human exposure to toxic chemicals occurs throughout the entire life span of humans, from the prenatal period in the mother's womb and continues until death. Particularly, persistent chemicals such as OC insecticides, PCBs, PBDEs and DRCs with relatively high lipophilicity tend to accumulate in large quantities in lipid rich tissues. Among these, their accumulation in human milk has been of great concern and has received considerable attention during the past four decades. In the previous review, we pointed out that human tissue samples, particularly breast milk, collected in a non-destructive manner, are among the best samples for measuring both spatial and temporal variations of POPs. The advantage of using human tissue samples is that background information such as age, reproduction and possible route of exposure can be accurately obtained from the subjects (Tanabe and Subramanian, 2006).

Recently, we have conducted various studies on the contamination status of PTS comprising PCDDs, PCDFs, PCBs and OC insecticides such as DDTs, HCHs, CHLs and HCB in human breast milk collected from general public and the residents around open dumping sites of municipal wastes in Asian developing countries such as India, Cambodia, Vietnam, Philippines, Malaysia, Indonesia and China during 1999–2003 (Kunisue et al., 2002b, 2004a, b, c, d; Minh et al., 2004; Sudaryanto et al., 2005b, 2006).

Mean lipid-normalized concentrations of POPs and TEQs of DRCs, which were estimated based on human/mammal toxic equivalency factors (TEFs) proposed by WHO (Van den Berg et al., 1998), in human breast milk collected from general public in Asian countries such as India, Cambodia, Vietnam, Philippines, Malaysia, Indonesia, China and Japan during 1999–2003 (Kunisue et al., 2002b, 2004a, b, c, d; Minh et al., 2004; Sudaryanto et al., 2005b, 2006) were illustrated in Figs. 18.4 and 18.15–18.19. In general, relatively high concentrations of DDTs were detected in human breast milk from Asian developing countries, while elevated residue levels of TEQs of DRCs, PCBs and CHLs were observed in Japanese breast milk. This trend of pollution was also observed in the Asia-Pacific Mussel Watch Program of POPs, in which mussels were employed as bioindicators (Monirith et al., 2003b). In Japan, it has been demonstrated in our recent studies on wildlife that TEQs, PCBs and CHLs were predominant (Kunisue et al., 2003, 2006; Kubota et al., 2004).

Among Asian developing countries, concentrations of DDTs in human breast milk from Vietnam, China, Cambodia and Malaysia were relatively higher than those from other countries (Fig. 18.16). It has been previously reported that DDTs were predominant in environmental media, biota and foodstuff from these Asian developing countries. In Vietnam, higher levels of DDTs in sediments from densely populated areas as compared to those from paddy field were reported, indicating recent application of DDTs for public health purposes such as malaria control rather than for agriculture (Nhan et al., 2001). In addition, our previous studies also demonstrated the elevated residue levels of DDTs in wild avian species and foodstuffs from Vietnam (Kannan et al., 1992, 1997; Minh et al., 2002; Kunisue et al., 2003). Although fewer comprehensive investigations on pollution by POPs in Cambodia are available due to lack of monitoring of such pollutants affected by a long-term civil war, it was reported that DDT has been used to control parasites of fish in cage culture (Tana, 1996) and relatively high residue levels of DDTs were observed in fish (Monirith et al., 1999). Higher levels of DDTs were also detected in inland resident avian species (Monirith et al., 2003a). In China, it has been recently reported that not only DDTs but also

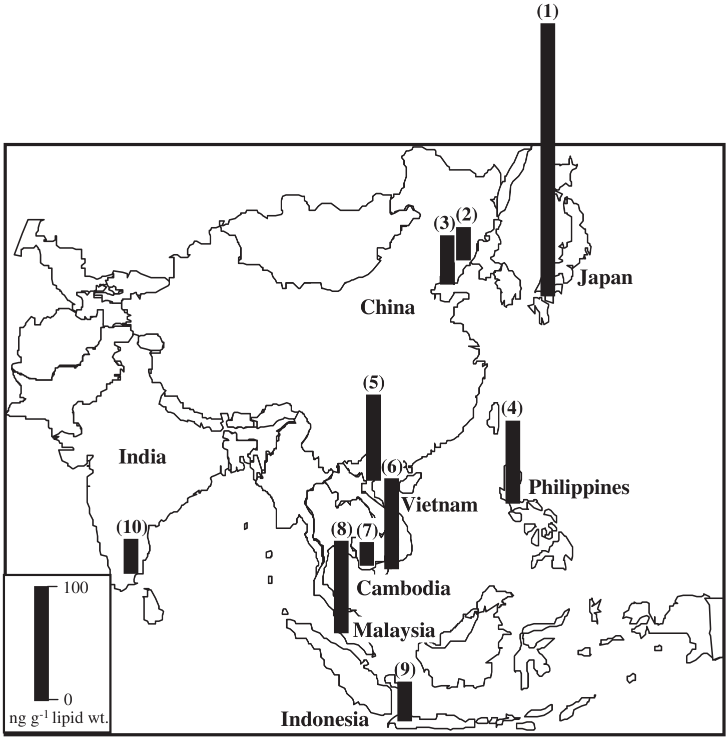

Figure 18.15. Concentrations of PCBs in human breast milk collected from general public in Asian countries. (1) Ehime, Japan (Kunisue et al., 2004c), (2) Shenyang, China (Kunisue et al., 2004a), (3) Dalian, China (Kunisue et al., 2004a), (4) Quezon, Philippines (Kunisue et al., 2002b), (5) Hanoi, Vietnam (Minh et al., 2004), (6) Hochiminh, Vietnam (Minh et al., 2004), (7) Phnom Penh, Cambodia (Kunisue et al., 2004b), (8) Penang, Malaysia (Sudaryanto et al., 2005b), (9) Jakarta, Indonesia (Sudaryanto et al., 2006), (10) Palaverkadu, India (Kunisue et al., 2002b).

HCHs were predominant in various environmental samples along the coastal areas and foodstuffs (Zhou et al., 2001; Chen et al., 2002; Nakata et al., 2002). The investigation on pollution of DDTs and HCHs in sediment cores indicated recent input of these contaminants into coastal areas from inland (Zhang et al., 2002). In addition, the investigation on pollution of DDTs in fish and mussels collected from aquaculture cages in coastal waters showed high proportions of *p,p′*-DDT and also indicated recent releases of this chemical to the environment (Klumpp et al., 2002). Although studies on POPs pollution in Malaysia are limited, Zakaria et al. (2003) reported relatively high levels of *p,p′*-DDT in water and sediments from agricultural areas compared with other POPs.

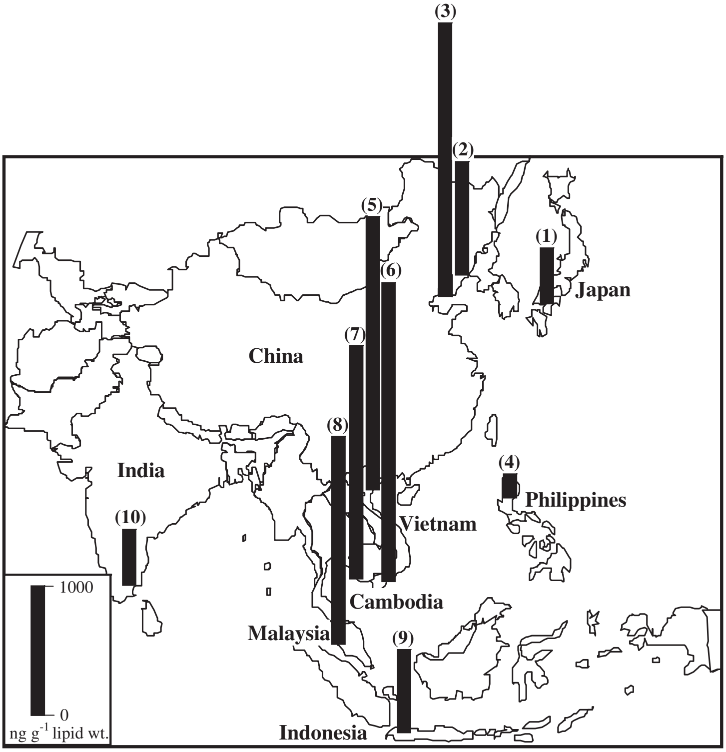

Figure 18.16. Concentrations of DDTs in human breast milk collected from general public in Asian countries. References cited are similar to those in Fig. 18.15.

Considering the above observations, it can be suspected that DDT may be illegally in use in some Asian developing counties and the residents are constantly exposed to this contaminant.

In Chinese and Indian human breast milk, notably higher concentrations of HCHs were observed compared with other Asian countries (Fig. 18.17). It seems that this reflects a huge amount of usage in the past and/or recent illegal use of technical HCH in these two countries. The total usage of technical HCH was estimated as 4.46 and 1.0 million metric tons in China and India, respectively, which are the largest and second largest consumers in the world (Li et al., 1998). As described earlier, relatively high residue levels of HCHs have been recently reported in Chinese environmental media and foodstuffs (Zhou et al., 2001; Chen et al., 2002; Nakata et al., 2002). Our studies revealed elevated residue levels of HCHs in wild avian species and foodstuffs

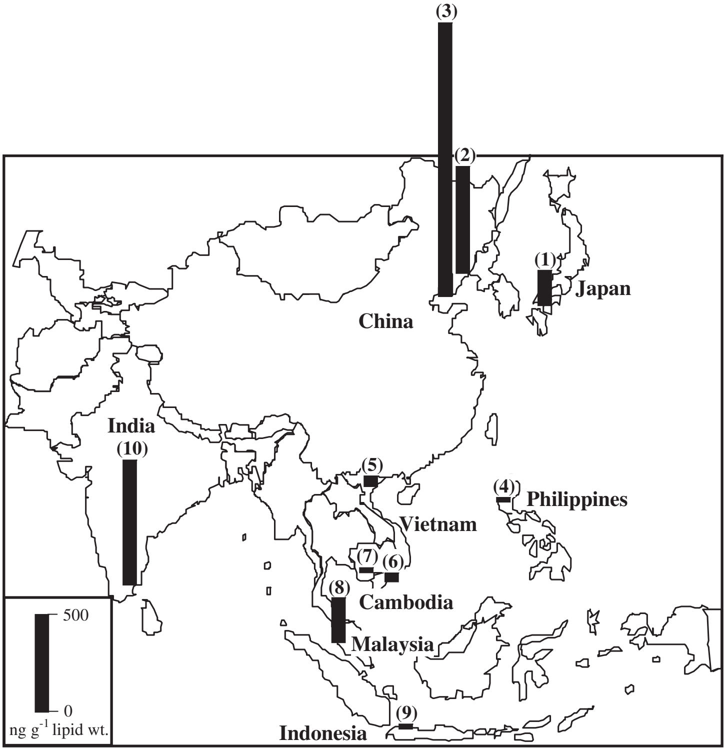

Figure 18.17. Concentrations of HCHs in human breast milk collected from general public in Asian countries. References cited are similar to those in Fig. 18.15.

from India (Kannan et al., 1997; Tanabe et al., 1998; Kunisue et al., 2003). These results indicate that considerable sources of HCHs are still present in the environment of these countries, and that technical HCH may be illegally in use for public health purposes in these two counties and residents are exposed to HCHs.

In human breast milk from China, HCB levels were also higher than other Asian countries (Fig. 18.19). HCB has been produced in a large chemical factory along Ya-Er Lake, which is located in the eastern part of Wuhan, Hubei province, and elevated levels of HCB were detected in soils and sediments from this lake (Wu et al., 1997). In addition, high concentrations of HCB were also detected in tea leaves, indicating recent use of this chemical as a fungicide (Nakata et al., 2002). These results imply that use of HCB is still continuing in China. In addition to being a fungicide and an impurity of pesticides, HCB is known to be formed during waste burning.

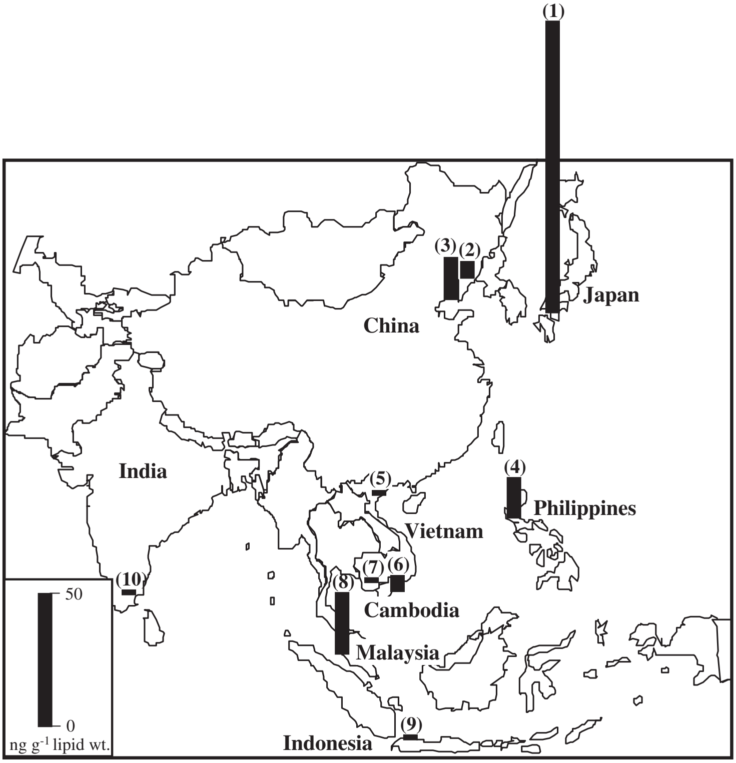

Figure 18.18. Concentrations of CHLs in human breast milk collected from general public in Asian countries. References cited are similar to those in Fig. 18.15.

To understand the magnitude of contamination in human breast milk from Asian countries, levels of PTS were compared to those reported recently in other developed, developing and former socialist countries (Schecter et al., 1990a, b; Dewailly et al., 1992; Hernández et al., 1993; Fürst et al., 1994; Becher et al., 1995; Liem et al., 1995; Gonzalez et al., 1996; Cok et al., 1997, 1999; Hooper et al., 1997; Hansen, 1998; Kinyamu et al., 1998; Schade and Heinzow, 1998; Kiviranta et al., 1999; Newsome and Ryan, 1999; Schuhmacher et al., 1999; Norén and Meironyté, 2000; Paumgartten et al., 2000; Harris et al., 2001; Waliszewski et al., 2001) (Table 18.1). In general, contamination by DDTs in human breast milk is higher in developing and former socialist countries than in developed countries, while levels of TEQs of DRCs, PCBs and CHLs in Asian developing countries were notably lower than those in developed nations. Among human breast milk from Asian developing countries, levels of DDTs in Vietnam, China, Cambodia and Malaysia, HCHs in China and India, and HCB in China were

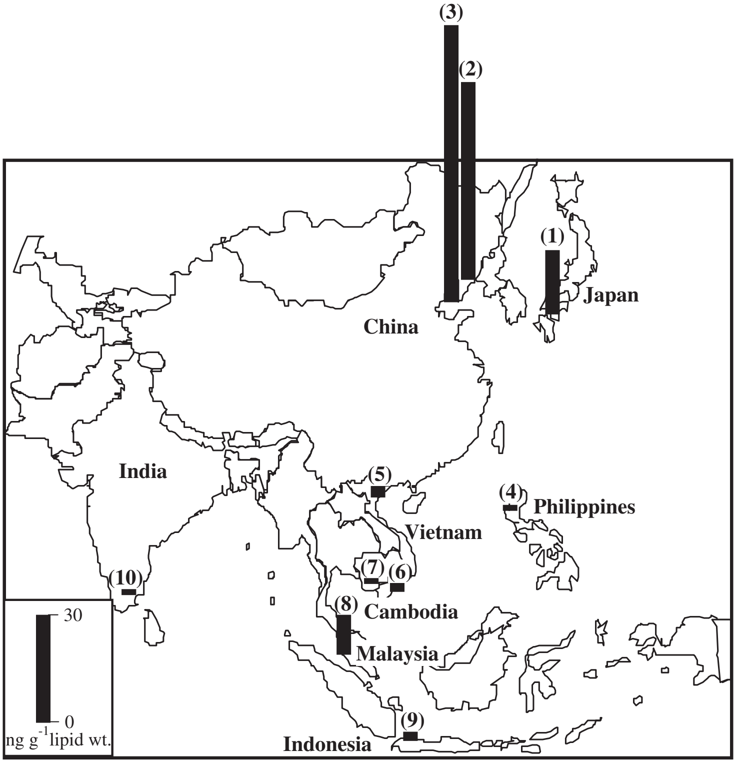

Figure 18.19. Concentrations of HCB in human breast milk collected from general public in Asian countries. References cited are similar to those in Fig. 18.15.

relatively higher compared with other countries, again suggesting recent use of these OC insecticides and fungicides and that these Asian developing countries may be potential sources of these contaminants to the global environment. Moreover, given the uncontrolled and low temperature burning of dumped solid wastes under anaerobic conditions is common in open dumping sites in various Asian countries; the formation of contaminants such as HCB during combustion is another issue that needs particular attention. Further investigations on human exposure and temporal trends of PTS, especially OC insecticides, are needed to elucidate future pollution trends.

18.5.2. Dioxin contamination in open dumping sites in Asian developing countries

In Asian developing countries, the presence of large open dumping sites of municipal wastes in the suburban areas of major cities is the prime

Table 18.1. International comparison of persistent toxic substances in human breast milk

Country	Survey year	TEQs[a]	PCBs[b]	DDTs[b]	HCHs[b]	CHLs[b]	HCB[b]	References
Asian countries								
Japan	1999	36	240	430^{d}	180^{h}	110^{l}	18	Kunisue et al. (2004c)
China	2002	8.2	42	2100^{d}	1400^{h}	16^{l}	81	Kunisue et al. (2004a)
Philippines	2000	12	–	–	–	–	–	Kunisue et al. (2004d)
Philippines	2000	–	72	190^{d}	4.7^{h}	15^{l}	<0.56	Kunisue et al. (2002b)
Vietnam	2000	12	–	–	–	–	–	Kunisue et al. (2004d)
Vietnam	2000	–	74	2100^{d}	58^{h}	2.0^{l}	3.9	Minh et al. (2004)
Cambodia	1999–2000	7.8	–	–	–	–	–	Kunisue et al. (2004d)
Cambodia	1999–2000	–	20	1800^{d}	5.6^{h}	1.6^{l}	1.6	Kunisue et al. (2004b)
Malaysia	2003	13	80	1600^{d}	230^{h}	23^{l}	11	Sudaryanto et al. (2005b)
Indonesia	2001	–	33	640^{d}	14^{h}	2.0^{l}	2.2	Sudaryanto et al. (2006)
India	2000	12	–	–	–	–	–	Kunisue et al. (2004d)
India	2000	–	30	430^{d}	640^{h}	0.91^{l}	1.0	Kunisue et al. (2002b)
Other developing and former socialist countries								
Turkey	1995–1996	–	–	2400^{e}	480^{h}	–	50	Cok et al. (1997)
Iran	1991	–	–	2000^{e}	600^{h}	–	61	Cok et al. (1999)
Brazil	1992	9.7^{c}	150	1700^{d}	280^{h}	–	12	Paumgartten et al. (2000)
Mexico	1997–1998	–	–	4700^{f}	60^{h}	–	30	Waliszewski et al. (2001)
Kenya	1991	–	–	470^{f}	96^{i}	–	–	Kinyamu et al. (1998)
Kazakhstan	1994	–	380	2300^{e}	2300^{i}	–	91	Hooper et al. (1997)
Russia	1996	–	520	2000^{e}	560^{m}	27^{m}	99	Hansen (1998)
Russia	1989	24^{c}	–	–	–	–	–	Schecter et al. (1990a)
South Africa	–	15^{c}	–	–	–	–	–	Schecter et al. (1990b)

Other developed countries								
Sweden	1997	–	320	170[e]	–	–	12	Norén and Meironyté (2000)
Germany	1995–1997		550	240[e]	40[j]	–	80	Schade and Heinzow (1998)
Germany	1986–1991	34[c]	–	–	–	–	–	Fürst et al. (1994)
Canada	1996		250	470[g]	23[h]	140[l]	43	Newsome and Ryan (1999
Canada	1990	24	–	–	–	–	–	Dewailly et al. (1992)
Spain	1991		–	610[e]	280[h]	–	0.6	Hernández et al. (1993)
Spain	1996	14[c]	–	–	–	–	–	Schuhmacher et al. (1999)
UK	1997–1998		–	470[e]	100[k]	–	43	Harris et al. (2001)
USA	1980s	19[c]	–	–	–	–	–	Schecter et al. (1990a)
France	1990	23[c]	–	–	–	–	–	Gonzalez et al. (1996)
Norway	1992–1993	36	–	–	–	–	–	Becher et al. (1995)
Finland	1992–1994	39	–	–	–	–	–	Kiviranta et al. (1999)
Netherlands	1993	47	–	–	–	–	–	Liem et al. (1995)

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[a] pg g^{-1} lipid wt.

[b] ng g^{-1} lipid wt.

[c] PCDD/DFs only.

[d] *p,p′*-DDE + *p,p′*-DDT + *p,p′*-DDD.

[e] *p,p′*-DDE + *p,p′*-DDT.

[f] *p,p′*-DDE + *p,p′*-DDT + *p,p′*-DDD + *o,p′*-DDT.

[g] *p,p′*-DDE + *p,p′*-DDT + *o,p′*-DDT.

[h] α-HCH + β-HCH + γ-HCH.

[i] α-HCH + β-HCH.

[j] β-HCH only.

[k] β-HCH + γ-HCH.

[l] Oxychlordane + *trans*-nonachlor + *cis*-nonachlor.

[m] Total.

source of critical DRC pollution. In those dumping sites, varieties of municipal wastes are burnt under low temperature by spontaneous combustion or intentional incineration, leading to secondary formation of DRCs. We found that the residue levels of DRCs were significantly higher in soils from those dumping sites than the agricultural and urban soils collected far from these areas (reference sites), indicating that the dumping sites are potential sources of DRCs (Minh et al., 2003). To understand the possible toxic impacts of DRCs on humans, we attempted to elucidate the contamination status of DRCs in human breast milk collected from the residents around the dumping sites of municipal wastes in India, Cambodia, and Vietnam and compared with those from the reference sites (Kunisue et al., 2004d).

As already shown previously while discussing the different sources of DRCs, it is noteworthy that the concentrations of DRCs in human breast milk from the dumping site in India were significantly higher than those from the reference site and those from Cambodia and Vietnam (Fig. 18.5), indicating that significant pollution sources of DRCs are present in the dumping site of India and the residents around there have been exposed to relatively higher levels of these contaminants than the other two developing countries. To understand the magnitude of contamination in human breast milk from the dumping sites in India, Cambodia and Vietnam, TEQ levels were compared with the values for human breast milk from general public of other countries since 1990, selected from publications in which concentrations of all the isomers were reported (Fig. 18.20). Because I-TEFs were mainly used to calculate TEQs, the reported data were recalculated by using WHO-TEFs for comparison. The levels of TEQs in human breast milk from India (38 pg TEQs g^{-1} lipid wt.) were comparable to or higher than those from developed countries (Schecter et al., 1990b; Dewailly et al., 1992; Fürst et al., 1994; Becher et al., 1995; Liem et al., 1995; Gonzalez et al., 1996; Kiviranta et al., 1999; Schuhmacher et al., 1999; Kunisue et al., 2004c) and the former Soviet Union (Schecter et al., 1990a). This suggests that the residents around the dumping sites of India have been exposed to comparable levels of DRCs with the general public of developed countries. On the other hand, the levels of TEQs in human breast milk from Cambodia (9.2 pg TEQs g^{-1} lipid wt.) and Vietnam (13 pg TEQs g^{-1} lipid wt.) were lower than those from developed countries and comparable to those from other developing countries (Schecter et al., 1990b; Paumgartten et al., 2000; Kunisue et al., 2004a; Sudaryanto et al., 2005b). In this international comparison, however, there are some uncertainties such as age and parity of the mother, sampling period, sample number and accuracy of the analytical techniques involved. In addition, only very little

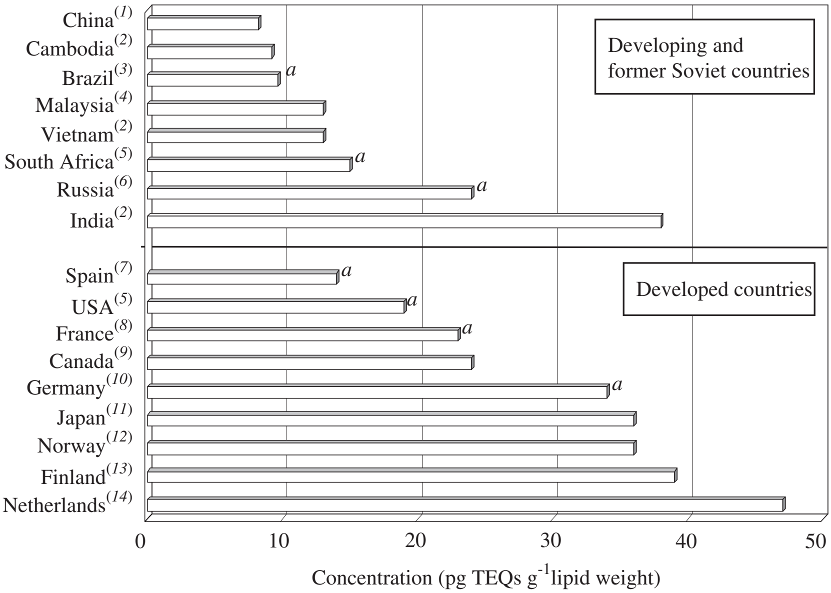

Figure 18.20. Comparison of TEQ levels in human breast milk from the residents around dumping sites in India, Cambodia and Vietnam with those from general public in other countries. [a]PCDD/Fs only. (1)Kunisue et al. (2004a), (2)Kunisue et al. (2004d), (3)Paumgartten et al. (2000), (4)Sudaryanto et al. (2005b), (5)Schecter et al. (1990b), (6)Schecter et al. (1990a), (7)Schuhmacher et al. (1999), (8)Gonzalez et al. (1996), (9)Dewailly et al. (1992), (10)Fürst et al. (1994), (11)Kunisue et al. (2004c), (12)Becher et al. (1995), (13)Kiviranta et al. (1999), (14)Liem et al. (1995).

data is available on non- and mono-*ortho* PCBs in the literature. Because of such uncertainties, it was difficult to draw any firm conclusion. However, the observation that TEQs of DRCs in human breast milk from the dumping site of India were comparable to or higher than those from some developed countries including Japan is noteworthy. In developed countries, it is claimed that the residue levels of DRCs in human breast milk decreased recently (LaKind et al., 2001), because of the installation of highly efficient incinerators and strict regulations on the production and usage of various chemicals. On the other hand, in Asian developing countries, it can be anticipated that the pollution by DRCs may increase further and hence the residue levels in human breast milk may also increase in future, because the release of these contaminants are not at all controlled even now.

Although residue levels of DRCs in soils collected from the open dumping sites in Asian developing countries were apparently greater than those from the reference sites (Minh et al., 2003), the levels of DRCs in human breast milk from the residents around the dumping sites in Cambodia and Vietnam were not significantly higher than those from reference sites. This implies that the residents around the dumping sites in Cambodia and Vietnam have not been greatly exposed to DRCs originating from the dumping sites. However, residue levels of these contaminants in Indian samples around the dumping site were notably higher (Fig. 18.5). In India, buffaloes and cows reared near the waste dumping site mainly feed on dumped leftovers. The residents around the dumping site constantly drink the milk collected from these bovines. On the other hand, in Cambodia and Vietnam, livestock such as buffaloes and cows are not reared around the dumping sites. To elucidate whether bovine milk is a potential source of DRCs for the residents around the dumping site in India, residue levels of these contaminants in the milk of buffaloes and cows collected there were estimated (Kunisue et al., 2004d).

DRCs were detected with elevated levels in the samples from dumping sites in all the bovine milk samples analyzed (Fig. 18.6). This indicates that buffaloes and cows feeding in the dumping site of India consume greater amounts of DRCs through contaminated soils and/or garbage, and that daily intake of these bovine milk by the residents around the dumping site in India is one of the possible reasons why TEQ levels in human breast milk collected from the dumping site were significantly higher than those from the reference site. In India, dietary consumption of dairy products is generally higher than that of other countries, and average consumption of milk in India by a person per day rose from 135 g in 1980 to 176 g in 1990 (John et al., 2001). The residents around the dumping site in India constantly drink the milk collected from reared buffaloes and cows. Assuming that an adult weighing 60 kg drinks 176 g of buffalo or cow milk per day, estimated daily intake of TEQs from bovine milk from the dumping site was from 1 to 4 pg TEQs kg^{-1} day^{-1}, as investigated in our study—the range of TDI proposed by WHO (Van Leeuwen et al., 2000), and only in one buffalo milk sample the value exceeded TDI (Fig. 18.21). Even though the values are within TDI, the residents around the dumping site in India are exposed to considerably high levels of DRCs and hence may be at greater risk of exposure to these contaminants via bovine milk.

18.5.3. Risk assessment for infant

It is realized that the presence of POPs in human breast milk is of great concern because these lipophilic chemicals are readily transferred and

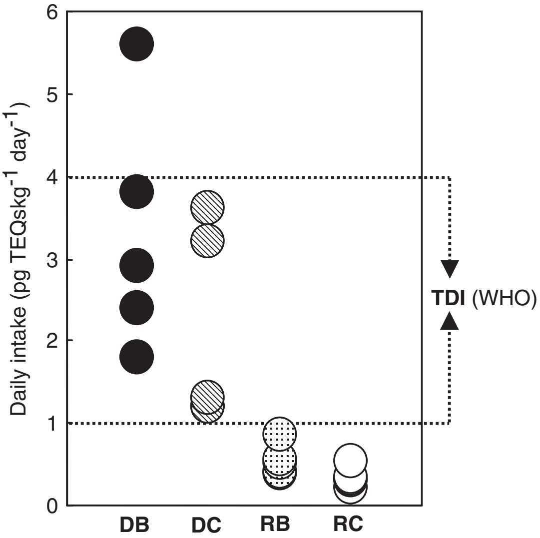

Figure 18.21. Estimated daily intake of TEQs by adults through bovine milk collected from the dumping and reference sites in India. Daily intake was estimated based on the assumption that an adult (60 kg) ingests 176 g of bovine milk per day (John et al., 2001). DB = Buffalo milk from the dumping site. DC = Cow milk from the dumping site. RB = Buffalo milk from the reference site. RC = Cow milk from the reference site.

absorbed to infants. In case of dioxins, it is reported that one to three months old infants absorb above 90% of most dioxin congeners present in their mothers' milk (McLachlan, 1993; Pluim et al., 1993; Dahl et al., 1995), hence they may be exposed to relatively high levels of POPs during this period. To understand the magnitude of exposure to PTS by infants, we estimated daily intake (DI) from the levels of these contaminants in human breast milk observed in Asian countries, based on the assumption that an infant ingests 700 ml milk per day and the weight of an infant is 5 kg (Kunisue et al., 2002b, 2004a, b, c, d; Minh et al., 2004; Sudaryanto et al., 2005b, 2006) and compared to the guideline standards proposed by WHO and Health Canada (Oostdam et al., 1999; Van Leeuwen et al., 2000).

As expected, relatively higher DIs of TEQs were observed in the infants from Japan and the dumping site in India compared with those from other countries and DIs in all the cases exceeded 1–4 pg TEQs kg^{-1} day^{-1}, the TDI (Table 18.2). In addition, DIs of PCBs, CHLs by Japanese, DDTs by Chinese, Vietnamese, Cambodian, and Malaysian, HCHs by Chinese and Indian, and HCB by Chinese infants were relatively high, and the DIs of these contaminants by some individuals exceeded the TDIs (Table 18.2).

Table 18.2. Estimated daily intakes of persistent toxic substances by infants in Asian countries

Country	TEQs[a]	PCBs[b]	DDTs[b]	HCHs[b]	CHLs[b]	HCB[b]
Japan	140 (28–630)	1.0 (0.17–7.8)	2.0 (0.19–22)	0.83 (0.12–6.6)	0.56 (0.038–7.8)	0.069 (0.019–0.34)
China	20 (17–26)	0.075 (0.008–0.45)	3.2 (0.39–18)	1.9 (0.21–15)	0.023 (0.002–0.12)	0.15 (0.029–0.68)
Philippines	29 (1.9–52)	0.14 (0.003–0.30)	0.58 (0.027–1.4)	0.015 (<0.002–0.028)	0.048 (0.003–0.12)	0.002 (<0.002–0.009)
Vietnam	35 (10–60)	0.29 (0.030–1.2)	8.9 (0.78–110)	0.11 (0.010–0.43)	0.018 (<0.002–0.080)	0.012 (<0.002–0.040)
Cambodia	26 (2.4–67)	0.080 (0.012–0.42)	4.5 (0.47–23)	0.016 (<0.002–0.065)	0.006 (<0.002–0.018)	0.006 (<0.002–0.032)
Malaysia	19 (3.3–40)	0.21 (0.022–1.7)	4.0 (0.19–19)	0.43 (0.063–1.8)	0.050 (0.006–0.18)	0.031 (<0.002–0.29)
Indonesia	–	0.080 (0.020–0.32)	1.2 (0.030–8.9)	0.040 (0.005–0.25)	0.010 (<0.002–0.030)	0.010 (<0.002–0.020)
India	28 (18–35)	0.037 (0.012–0.060)	1.0 (0.33–3.1)	1.6 (0.57–4.0)	0.003 (<0.002–0.012)	0.003 (<0.002–0.012)
India (dumping site)	120 (28–500)	0.12 (0.023–0.33)	1.1 (0.30–4.0)	1.6 (0.27–3.8)	0.024 (0.002–0.087)	0.003 (<0.002–0.009)
TDIs[c]	1–4	1.0	20	0.3	0.05	0.27

Note: Numbers in parentheses indicate range values.

[a] pg kg^{-1} body wt. day^{-1}.

[b] µ kg^{-1} body wt. day^{-1}.

[c] Tolerable daily intakes (TDIs) were cited from Oostdam et al. (1999) and Van Leeuwen et al. (2000).

It is argued that DRCs induce various toxic effects such as cancer in animal bodies (Birnbaum, 1994). Furthermore, *p,p′*-DDE and β-HCH, the compounds that are there generally abundant in human breast milk, have been reported as an androgen antagonist and environmental estrogen, respectively (Keice et al., 1995; Willett et al., 1998). These observations imply that abundance of POPs in human breast milk may adversely affect development and reproductive systems of Asian children. However, it is difficult to draw any firm conclusion from Table 18.2 whether adverse effects by POPs have already occurred in Asian infants, because TDIs used here are estimated on the basis of life span exposure. Not only TDIs from life span but also TDIs of POPs estimated from breast-feeding period may be needed (LaKind et al., 2001).

If only the risk of PTS is considered, breast milk containing high levels of such contaminants should not be fed to infants. Feeding with formula milk diet not contaminated by PTS is one of the measures for protecting infants from the risk. In human breast milk, however, not only general nutrients but also essential components for infant's growth and development such as secretory IgA, oligosaccharides, lactoferrin and lysozyme, which can increase their resistance to common infections, are present (Lonnerdal, 2000). In addition, long-chain polyunsaturated fatty acids in human breast milk are indispensable for brain development of infants and it is reported that breast-feeding is associated with significantly higher scores for cognitive development than formula feeding (Uauy and Peirano, 1999). It is suspected that deficiency of breast-feeding negatively affects the growth and development of infants, while multiple and quantitative effects of these components are not completely elucidated. Furthermore, in some Asian developing countries, water used for many formula milk preparations may contain various infectious organisms and environmental contaminants, which may adversely affect infant health (Carpenter et al., 2000). Considering all these factors, breast-feeding is essential for the infants, as recommended elsewhere (LaKind et al., 2001; Longnecker and Rogan, 2001; Abelsohn et al., 2002). But it is necessary to reduce the levels of PTS in human breast milk, especially OC insecticides such as DDTs and HCHs in Asian developing countries and dioxins in Indian dumping site, to save the infants from possible toxic effects. In case of dioxins, however, it is estimated that 86% of dioxins in human breast milk comes through mobilization from adipose tissue and 14% from dietary sources, and so it may be difficult to reduce dioxin concentrations in human breast milk through short-term dietary control (Koppe, 1995). This means that the females have to lessen PTS exposure through dietary source from the early days of their life span. It is necessary to elucidate whether recent input and illegal use of OC insecticides are present and to continuously investigate temporal trends of POP pollution in Asian developing countries to remedy the situation. Furthermore, in the dumping sites of Asian developing countries, especially India, urgent control and regulation of pollution sources of DRCs are required.

Overall, our results suggest that in some Asian developing countries, OC insecticides such as DDTs and HCHs may be still in use and the residents are continuously exposed to these contaminants. Furthermore, we demonstrated that in India the concentrations of dioxins in human breast and bovine milk from the open dumping site were significantly higher than those from the reference sites and other Asian developing countries, indicating that significant pollution sources of dioxins are present in the Indian dumping sites and the residents around these have been exposed to relatively higher levels of these contaminants via bovine milk. Because of no control measure for dioxin emissions in dumping sites in Asian developing countries like India, it can be anticipated that the pollution by dioxins may increase further and, hence, the residue levels in human breast milk may also increase in future, although it is claimed that the residue levels of PTS in human breast milk decreased recently in developed countries like Japan. Further investigations on the pollution sources and human exposure to PTS in Asian developing countries, especially OC insecticides and dioxins in open dumping sites, are needed to elucidate future pollution trends and to assess infant health risk.

18.6. Conclusions and recommendations

Multi-media monitoring studies and surveys have made substantial contributions to the discovery, description and understanding of the environmental problems caused by persistent man-made chemicals. Over the last three decades, comprehensive monitoring surveys using the 80,000 specimens archived in *es-BANK* have been conducted in our laboratory to make clear various issues of PTS contamination including extent of pollution, transport behavior and fate, spatial and temporal trends and toxic impacts on environmental quality, wildlife and human health. With particular emphasis on Asian developing countries, the region that recently received considerable attention due to the potential emission sources of PTS, the following conclusions can be made on the basis of these monitoring studies:

– Despite considerable efforts to curtail and/or mitigate the pollution, PTS are still ubiquitous in both biotic and abiotic spheres, particularly in Asian developing countries, where some of these chemicals are still being used in considerable quantities. In general, the hot spots of PTS pollution were found in the areas where they have been heavily used; elevated HCH residues were found in many samples collected from India and South China, which are the two largest HCH users. DDT pollution was found to be high in China and Vietnam due to the large quantity used in China and very recent application in Vietnam. A recent survey conducted using mussels and skipjack tuna as bioindicators revealed that PBDEs, a new PTS, exhibited higher concentrations in Korea, Hong Kong coasts and nearby areas in East China Sea, suggesting the presence of significant sources of PBDEs in highly industrialized zones.

- As a result of monitoring surveys in different environmental media and biological samples, the transport behavior of PTS can be characterized as "local" and "global". DDTs and PCDD/Fs have less potency for long-range atmospheric transport, and their sources are therefore located in the proximity of areas where they were extensively used. On the other hand, HCHs and, to a lesser extent, PCBs and PBDEs exhibit relatively high ability for transport through atmosphere and their contamination may extend globally in future. From the human health point of view, the toxic impacts of "localized contaminants" such as DDTs and PCDD/Fs are of great concern in Asian developing countries. In addition, from the global point of view, the regulations on the "global contaminants" like PCBs and particularly the modern chemicals, PBDEs, should be implemented in order to mitigate their potential emission to the pristine areas.
- PTS pollution in Asian developing countries and nearby seas and oceans exhibited somewhat unique temporal trends as compared to developed nations. Seas and open oceans serve as final sink for such chemicals, and time trends of OC pesticides showed a slow decline; while those of PCBs seemed in a steady state or very slow decrease. With recent rapid growth of industry and human activities, the East Asian countries such as southern China, including Hong Kong, and Korea may be a hot spot of PBDE contamination due to the extensive manufacture and dumping of computer devices and electronic appliances. As a result, our recent study on temporal trends of PBDEs in this region clearly demonstrated a substantial increase in PBDE residue levels in small cetaceans collected from Hong Kong coastal waters. In any event, temporal trends of PTS in developing countries are among the most important environmental issues that certainly deserve systematic and long-term investigations in future.
- As far as toxic impacts of PTS are concerned, the open dumping sites for municipal wastes in Asian developing countries are potential sources of many chemical contaminants. The quality of environment in

these areas has been gradually degrading with severe disturbance to the ecosystem. More serious are the long-term impacts of PTS on health of humans living in and around these dumping sites. Detection of substantial residues of DRCs in breast milk of Indian residents at particularly elevated concentrations warrants long-term impacts of dioxins in the next generation—the young children.

- With rapid growth of industrial activities in Asia-Pacific region, the use of modern chemicals such as PBDEs as flame retardants is another issue that needs particular attention. In this context, the role of the e-waste dumping sites as substantial sources of toxic chemicals such as brominated flame retardants, including PBDEs, should be elucidated in future. The increasing trends of PBDE accumulation in marine mammals stranded along Hong Kong coasts and nearby areas in East China Sea indicated that southern China with considerable amounts of electronic wastes coming from various sources all over the world continues to be a hot spot of pollution by PBDEs and other related compounds.
- Considering these critical issues of PTS pollution, it is clear that continued and constant efforts should be made to deal with the environmental problems caused by PTS. Over more than five decades when persistent organic chemicals were first used, despite considerable attempts to reduce their emissions, PTS continue to pose challenges for mankind, and scientific community is still in the initial steps to mitigate the ill effects of these toxic chemicals on the environmental quality, biodiversity and humans. Comprehensive and long-term monitoring programs are urgently needed to be implemented with close collaboration and proper capacity building in the local areas where hot spots of pollution are conspicuous. In this context, well designed monitoring of temporal trends of PTS residues in developing countries over extended period of time is crucial for tracing the unrevealed sources and predicting future prospects of their pollution state. In addition, the issue of human exposure to toxic chemicals, particularly people who are currently residing in extremely poor living conditions such as open dumping sites for municipal waste in major urban areas in developing countries, should be the prime target for future research.

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