PERSISTENT ORGANIC POLLUTANTS IN ASIA: FATE AND DISTRIBUTION IN THE OCEAN AND ATMOSPHERE

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For my true Love

Ching Fen

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SUMMARY

In 2001, 122 nations (including Singapore) signed the Stockholm Convention (UNEP) to phase out a suite of 12 persistent organic pollutants (POPs) considered as a potential risk to the environment and human health. Singapore ratified its obligations under the convention in May 2005. The objective of this research was to investigate the occurrence of POPs in Asia's marine environment and to investigate the processes affecting the fate and distribution of these compounds in a tropical region. Particular attention has been focused on the role of the sea-surface microlayer (SML) i.e. the uppermost 40-100 μm layer of the ocean, in controlling the fate and distribution of POPs between the ocean and atmosphere.

A primary study on POPs in Singapore's marine environment was conducted on sediments, including polybrominated diphenyl ethers (PBDEs). The geographical distribution of POPs in sediment samples revealed the ubiquity of these POPs in the coastal waters of Singapore, which can be classified as 'moderately' contaminated with respect to ecotoxicological impacts on marine organisms.

SML samples were collected using a self-designed glass drum sampler during both the wet and dry seasons in Singapore. In general, POPs were enriched in the SML by a factor of between 1.5 and 4, where data represents the first available SML enrichment factors for POPs in Asia. The concentration of POPs in bulk seawater and the SML were higher by a factor of 50 during the wet season compared to the dry season, indicating that wet deposition from the atmosphere is a key source of POPs to coastal waters. Samples collected before and immediately after heavy rainfall events showed an increase of POP concentrations by a factor of 6 in the SML, but remained in the same range for bulk seawater.

The distribution of POPs between the dissolved phase and suspended particulate matter (SPM) in the seawater column of Singapore, including the SML, was investigated. The vertical profiles of POPs in the water column indicate the occurrence of major sediment resuspension processes of POPs to the water column. The SML plays an important role in the fate of dissolved and SPM associated POPs.

Seawater and SML samples were collected from the marine environment of Hong Kong, China. Enrichment factors were comparable to those from Singapore, but elevated concentrations of dichlorodiphenyltrichloroethanes (DDTs) were detected, where inputs of DDT to Hong Kong's marine environment are likely to be ongoing. Concentrations of PBDEs in the SML are reported for the first time, and their enrichment in the SML was found to be in the same range as for the similarly structured polychlorinated biphenyls (PCBs).

Atmospheric samples of POPs were collected in Singapore, as well as during a sailing expedition across the Indian Ocean. Atmospheric samples collected in Singapore were relatively low in contamination for DDTs and PCBs, but moderately contaminated with hexachlorocyclohexane isomers (HCHs). Atmospheric concentrations of POPs were generally lower over the Indian Ocean compared to recent data reported for the Atlantic Ocean. Data comparison over a 30 years period showed that atmospheric concentrations of POPs, i.e. DDTs and HCHs, have declined significantly over the Indian Ocean. The first data on the prevailing concentrations of atmospheric PBDEs over regions of the open Indian Ocean are reported.

The effect of the SML on the air-sea gas exchange of POPs was investigated. It was determined that ignoring the SML as a controlling boundary layer leads to a high level of uncertainty in the POPs flux calculation, particular for more hydrophobic compounds with high a potential for enrichment in the SML. The residence time of POPs within the SML was calculated in the range of 0.2 to 3 minutes, and evidence is presented that hydrodynamic processes adjacent to the ocean surface plays an important role in the air-sea gas exchange of the more hydrophobic POPs.

Overall, this work has provided key data on the fate and distribution of POPs in the ocean-atmospheric environment of Southeast Asia, the region of the Indian Ocean and Hong Kong, China. Investigations have revealed that the SML plays a critical role in the distribution of POPs in the marine environment. It has also been proven that wet deposition from the atmosphere is an important ocean-scavenging process for POPs during the wet season in tropical regions. The data, in particular those derived from the open Indian Ocean, have provided key insights into our knowledge and understanding on the distribution and fate of POPs in the atmosphere and marine environment.

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NOMENCLATURE

Symbols

c	concentration
D	Diffusivity coefficient
d	diameter
F	Gas exchange fluxes across air-sea interface
H	Henry's Law constant
H'	Dimensionless Henry's Law constant
K_d	Distribution Coefficient
K'_d	Apparent Distribution Coefficient
K_{oa}	Octanol-air partition coefficient
K_{ow}	Octanol-water partition coefficient
K_{ol}	Overall mass transfer coefficient
k_a	Mass transfer coefficient across air-layer
k_w	Mass transfer coefficient across water-layer
l	length
M	Molar mass
m/z	Mass to charge ratio
R	Ideal gas law constant
r	Pearson coefficient of linearity
S	Breakthrough correction factor
s	rotation speed
Sc	Schmidt number
T	Temperature
t	time

u_x	Wind speed at height x
V	Volume
η	Kinematic viscosity
μ	Dynamic viscosity
γ	Thickness of sea-surface microlayer
Φ	Density
σ	Variances

Abbreviations

AET	Apparent Effect Threshold
BDE	Brominated Diphenyl Ether
BT	Back Trajectory
CB	Chlorinated Biphenyl
CCME	Canadian Council of Ministers of the Environment
CLRTAP	Convention on Long Range Transport of Air Pollution
DCM	Dichloromethane
DDD	dichlorodiphenyldichloroethane
DDE	dichlorodiphenyldichloroethylene
DDT	dichlorodiphenyltrichloroethane
DOC	Dissolved Organic Carbon
DP	Dissolved Phase
EF	Enrichment Factor
EI	Electron Impact
EPA	Environmental Protection Agency
ER-L	Effects Range-Low

ER-M	Effects Range-Median
GC-MS	Gas Chromatography - Mass Spectrometry
GC-IT-MSMS	Gas Chromatography - Ion Trap - Tandem Mass Spectrometry
GESAMP	Joint Group of Experts on the Scientific Aspects of Marine Pollution
GF	Glass Fiber
GIO	Gross Industrial Output
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
HYSPLIT	HYbrid Single-Particle Lagrangian Integrated Trajectory
ISO	International Organization of Standardization
LF	Load Factor
LOD	Limit of Detection
LRT	Long Range Transportation
MAE	Microwave Assisted Extraction
METEX	Meteorological Data Explorer
MW	Molecular Weight
NEA	National Environment Agency
ND	Not Detected
NIST	National Institute of Standards and Technology
OC	Organochlorine Compound
OCP	Organochlorine Pesticide
PBDE	Polybrominated Diphenyl Ether
PCA	Principal Component Analysis
PCB	Polychlorinated Biphenyl
PCNB	Pentachloronitrobenzene
PEL	Probable Effect Level

POPs	Persistent Organic Pollutants
PRE	Pearl River Estuary
PSU	Practical Salinity Unit
PUF	Polyurethane Foam
RPD	Relative percent difference
SQAL	Sediment Quality Advisory Level
SQG	Sediment Quality Guideline
SIM	Selected Ion Monitoring
SML	Sea-Surface Microlayer
SPM	Suspended Particulate Matter
SRM	Standard Reference Material
TEL	Threshold Effect Level
TMSI	Tropical Marine Science Institute
TOC	Total Organic Carbon
TR	Traces
UNEP	United Nations Environmental Program
UNECE	United Nations Economic Commission for Europe
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

CHAPTER I

Introduction

I-1 Background

Persistent organic pollutants (POPs) are a group of man-made chemicals which are very resistant to natural breakdown processes and therefore extremely stable and long-lived in the environment. They are of significant concern due to their toxicity and have the potential to induce toxicological impacts on both wildlife and humans (Jones and de Voogt, 1999). They are subject to bioaccumulation in the lipid fraction of biological tissues, thus leading to their biomagnification in the marine ecosystem. POPs have also been implicated in causing adverse effects on endocrine systems in a wide range of marine organisms (Tanabe, 2002), and are characterized by low water solubility and high octanol-water partition coefficients (K_{ow}) resulting in accumulation in sediments and suspended particulates in seawater. The transport of particulates to the deep ocean and bottom sediments by gravitational settlement is considered as an important global sink for POPs, particularly for the less volatile and highly hydrophobic compounds. It has been shown that, due to their semi-volatility and resistance to degradation, POPs are transported long distances in the atmosphere leading to a global redistribution of this class of pollutants, even to remote polar regions (Bard, 1999). Major international institutions, such as the United Nations Environmental Program (UNEP) Global Convention on POPs, the United Nations Economic Commission for Europe (UNECE) Convention on Long-range Transboundary Air Pollution, the Oslo-Paris (OSPAR) Convention for the Protection of the North-East Atlantic and the World Health Organization (WHO) have established programs to investigate the behavior of POPs in the global environment. However, there is a paucity of data for regions including Africa, Central and South America, the Indian Ocean and Asia, whereas extensive databases exist for North America and Europe (UNEP, 2003). Asia is considered to be a major source of POPs at the global scale (Iwata et al., 1993 and 1994) and may play a significant role in the transfer of POPs to the remote polar regions. Many of the developing countries, which are still using persistent pesticides, are located in the tropics. The tropical climate, with year-round elevated temperatures and heavy rainfall events during monsoon periods, promotes the rapid dissipation of contaminants through air and water (Tanabe et al. 1994). Bard (1999) pointed out the importance of the tropics as a source of evaporating POPs from soil and water to the atmosphere with subsequent transport towards the poles. At the poles, POPs condense out of the colder air, known as "cold condensation" effect (Wania and Mackay, 1993). However, the occurrence of POPs in the tropics, including Southeast Asia, is poorly documented.

The Stockholm Convention on POPs was adopted in 2001 in response to the urgent need for global action to protect humans and the environment from POPs (UNEP, 2001). 122 nations, including Singapore, have signed the Stockholm Convention. POPs comprise a large group of chemicals, and UNEP has listed 12 organochlorine compounds of particular concern, known as the "red list" – or "dirty dozen". The "red list" of contaminants includes nine organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), dioxins and furans. The nine OCPs are: Aldrin, Dieldrin, Endrin, dichlorodiphenyltrichloroethane (DDT), Chlordane, Heptachlor, hexachlorbenzene (HCB), Toxaphene and Mirex. Hexachlorohexanes (HCHs) are not included in the list, but due to their environmental concern and wide usage as pesticide, HCHs are generally defined together with POPs by UNEP. Countries, who have signed the Stockholm Convention, have pledged to ban the production, import and use of POPs on the red list. Furthermore, signatories agreed within two years of ratification to perform an inventory of the sources and discharge of POPs into the environment, as well to form regulations and promote environmental education and awareness in this field. Many countries in Southeast Asia agreed to the ratification of the convention including Singapore, Thailand, Philippines, Vietnam, and Myanmar. However, several countries have not yet ratified, including Malaysia, Indonesia, and Bangladesh (UNEP, 2001) by August 2005.

Others POPs of potential concern for humans and the environment have been identified in the recent years. Among them, the polybrominated diphenyl ethers (PBDEs) are of great interest to scientists due to their striking similarities in physicochemical properties, environmental and toxicological characteristics relative to PCBs. PBDEs are flame retardants used in a wide range of materials such as textiles, plastic products, and electronic devices. As for PCBs, PBDEs can be found in all environmental compartments, particularly in air, marine sediments, human breast milk and biota, where even polar species demonstrate the widespread PBDE contamination (De Witt, 2002). Although widespread PBDEs contamination of the environment is documented, and can be tracked back to the 1970's in Europe and USA (De Wit, 2002), there is a paucity of data on contamination levels for the region of Southeast Asia. There is much evidence that Asian environment is highly contaminated with PBDEs (Uneo et al., 2004; Martin et al., 2004, Liu et al., 2005), and the shipment of electronic waste to China, India and Pakistan for disposal is a major source of PBDEs to the Asian environment (Martin et al., 2004).

Even though many of the chemicals that can be classified as POPs are now banned in many countries, large amounts of POPs continue to be stored in sediments, soil and the food chain. However, there is much evidence in the literature, that harmful POPs continue to be used in several countries. In Southeast Asia, for example, the usage of

Lindane (γ-HCH) has been reported recently for Malaysia (UNEP, 2002a; Abdullah, 2003), for Vietnam (UNEP, 2002a; Nhan, 2003) and Papua New Guinea (UNEP, 2002a), whereas the use of Chlordane and Heptachlor has been reported for Bangladesh (Matin, 2003). The pesticide Dicofol is also commonly used in these countries, as well as in China (Qiu et al., 2004). Dicofol is manufactured from technical DDT and after the synthesis reaction, DDT and the intermediate product, α-chloro-DDT, remains in the Dicofol product as impurities (Qiu, 2004). Nowadays, formulation of Dicofol contains usually about 0.1% of DDT (Gillespie et al., 1994), but the fraction of DDT in Dicofol produced in China is not restricted, and DDTs originating from Dicofol may be a serious contemporary problem (Qiu et al., 2004). Pesticides, including HCHs and DDTs, are likely to be still in use in India (Raghu et al., 2003; Voldner and Li, 1995) and China (Qiu et al., 2004; Voldner and Li, 1995).

The world's oceans play a key role in the fate of POPs, acting as both a sink and source. The oceans receive inputs from POPs via riverine transport, the resuspension of contaminated sediments, municipal discharge, and wet and dry deposition. In turn, POPs can be removed from the water bodies of the oceans via adsorption on particulates and subsequent gravitational settlement, and evaporation into the atmosphere via the ocean surface. Although the transport of particulates to the deep ocean and bottom sediments is considered as an important global sinks for POPs (Gustafson et al., 1997; Wania and Daly, 2002), it may be the transfer processes governing the transport of POPs between the ocean and atmosphere that determines the global distribution of POPs. The sea-surface microlayer (SML), the interfacial boundary between the atmosphere and the oceans with a typical thickness of 40 to 100 µm, plays a critical role in the air-sea gas exchange. The SML is enriched in naturally occurring surface-active organic compounds, including protein, lipids and surfactants, giving it a distinct chemical composition (Hunter, 1997). Upwelling, diffusion, convection and bubble formation are know to be significant transport vectors of organic matter, including contaminants, to the sea surface (Hardy, 1982). POPs are known to enrich significantly in the SML by factors of up to 100 in coastal areas relative to underlying subsurface waters (Wurl and Obbard, 2004), and therefore the SML may play a significant role in the air-sea gas exchange of POPs. To date, there has been no attempt to study the effects of the SML on the air-sea fluxes of POPs, even though the importance of this research field has been previously emphasized:

"…it is usually assumed that the interface is passive with respect to transfer…Will the evaporating solute appreciably be delayed in its journey from water to air by the storage capacity of the interface?" (Mackay et al., 1991)

"…interfacial effects and sea ice cover could have a profound, yet so far largely ignored, impact on the air-sea exchange of POPs in the oceans…The interfacial effect is quite likely to be increased by the presence of a sea surface microlayer." (Wania et al., 1998)

"It is often not realized that partitioning also occurs at the air-water interface, where an excess concentration may exist." (Mackay, 2001)

The reason that the effects of the SML on sea-air fluxes of POPs have been largely ignored to date is due to the challenges posed in quantifying POPs in the SML, and the lack of a strong understanding of the effects of environmental variables on the properties of this layer of the ocean.

The fact that Southeast Asia is contaminated with POPs and considered to be a major source on a global scale, as well as the continued usage of POPs, justifies the need for a detailed study on the fate and distribution of POPs in Asian regions. Providing data for the first actual measurements of air-sea fluxes of POPs via the SML, and to evaluate the potential importance of the SML as a controlling interface for the air-sea gas exchange, will lead to an improved understanding of the global distribution of POPs.

I-2 Study Objectives

This research focuses on the fate and distribution of POPs in Singapore's and Hong Kong's marine environment, the distribution of atmospheric POPs in Southeast Asia and over the Indian Ocean, and ultimately the role of the SML in the dynamic air-sea gas exchange of POPs. The specific objectives and its scope of the research are as follows:

1. To assess the extent of POP contamination in Singapore's coastal marine sediments. More specifically: (a) to quantify POPs in Singapore's coastal marine sediments and data from Singapore in an Asian and international context; (b) to identify potential sources of POPs to the marine environment of Singapore; and (c) to evaluate ecotoxicological effects of Singapore's marine sediments using sediment quality guidelines. Refer to Study 1 in Chapter IV.

2. To provide the first data of contamination levels of POPs and enrichment factors (EF) in the SML from a tropical region, and to investigate the temporal distribution of POPs in the SML during monsoon and dry season periods. Refer to Study 2 in Chapter V.

3. To measure the concentration and distribution of POPs in the water column and sediments at two sites with different hydrodynamic characteristics in the coastal marine environment of Singapore. More specifically (a) to investigate the distribution of POPs between the dissolved phase and suspended particulate matter in the water column; (b) to assess the enrichment of POPs within the lowest and uppermost boundary layer of the water column, the sediment-bottom water layer and SML; and (c) to identify the role of the sediment-bottom water layer and SML in the fate of POPs. Refer to Study 3 in Chapter VI

4. To investigate the occurrence of POPs and EF in the SML of Hong Kong's marine environment. More specifically: (a) to assess concentration levels of POPs in SML and seawater samples of five marine sites around Hong Kong; (b) to provide the first data on the occurrence of PBDEs in SML samples; (c) to compare data with those obtained from Singapore; and (d) to identify sources and pathways of POPs to Hong Kong's marine waters. Refer to Study 4 in Chapter VII.

5. To assess the concentration and distribution pattern of atmospheric POPs in Southeast Asia and over the Indian Ocean. More specifically: (a) to report the first data on atmospheric levels POPs from Singapore; (b) to provide first data on marine atmospheric POPs collected from a sailing boat so as to minimize contamination originating from ship engines; (c) to compare data with these available from the literature reported within the last three decades in order to determine temporal trends of atmospheric POPs in this region. Refer to Study 5 in Chapter VIII.

6. To investigate the role of the SML in the dynamic air-sea gas exchange of POPs. More specifically: (a) to provide a mathematical model to calculate air-sea gas fluxes of POPs via the SML; (b) to provide first scientific data for air-sea fluxes of PCBs and HCHs isomers via the SML; (c) to investigate the effect of physicochemical properties of POPs, wind speed and EF of POPs in the SML on the air-sea fluxes via the SML. Refer to Study 6 in Chapter IX.

CHAPTER II

Literature Review

II-1 Persistent Organic Pollutants (POPs) and Their Behavior in the Environment

II-1-1 Definition

POPs are lipophilic, persistent, and organic man-made chemicals which are toxic to both wildlife and humans and have the potential to undergo long range global transportation (Vallack et al., 1998). UNEP (2001) has defined a ‘red list’ of POPs to emphasis the importance of a ban and a reduction in use of certain chemicals, including nine first generation pesticides, industrial chemical products and byproducts. The ‘red list’ includes: Aldrin, Dieldrin, Endrin, dichlorodiphenyltrichloroethane (DDT), Chlordane, Heptachlor, Hexachlorobenzene (HCB), Toxaphene, Mirex, polychlorinated biphenyls (PCBs), dioxins and furans. However, in the recent years new chemicals have been detected in the environment with properties which are consistent with the definition of POPs, and are therefore regarded as a “new class” of POPs. Among these chemicals, the groups of polybrominated diphenyl ethers (PBDEs), polychlorinated naphtalenes and chlorinated paraffins have attracted the attention of governmental institutions, environmental protection organizations and the broader scientific community. Hexachlorocyclohexanes (HCHs) are persistent toxic substances and have been widely used as insecticides until recently, particularly in Asia. They are less bioaccumulative than the organochlorine pesticides (OCPs) on the ‘red list’, but due to their environmental concern and great potential to undergo long range transportation, HCHs are generally defined together with POPs by UNEP.

II-1-2 Chemical structures and nomenclature

The chemical structures of some key POPs are presented in Figure II-1. Greek letters are used to identify various isomers of Chlordanes and HCHs, i.e. α- (or cis-) and γ-(or trans-) for Chlordanes; and α-, β-, γ- and δ- for HCHs. The group of PCBs consists of 209 congeners, with a degree of chlorination ranging from 1 to 10 chlorine on the biphenyl structure and sub grouped in the following homolog: mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona- and deca-chlorinated biphenyls. Individual congeners are identified to the nomenclature suggested by Ballschmiter et al. (1992).

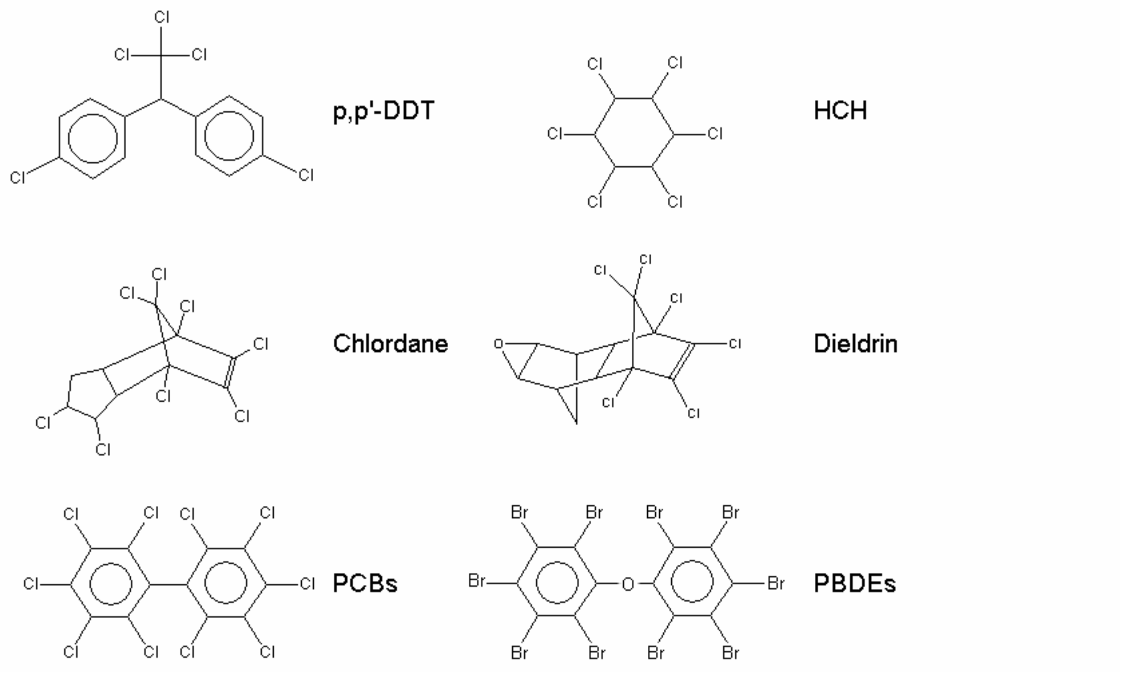


Figure II-1: Chemical structures of some POPs

II-1-3 Physicochemical properties of POPs

Models for the transport and global distribution of POPs require knowledge of the physiochemical properties of these compounds. The properties of most interest are vapor pressure, water solubility, octanol-water partition coefficient (K_{ow}) and the Henry's

Law constant, which represents an air-water partition coefficient (Paasivirta et al., 1999). Physicochemical data of some POPs are given in Table II-1.

Compound	log K_{ow}	Water Solubility [mg/L]	Vapor Pressure [Pa]	Henry Constant [Pa m^3/mol]
Chlordane	6.0	0.05 - 0.1	0.001 - 0.004	2.9 - 9.5
Dieldrin	5.2	0.2	1×10^{-4} - 9×10^{-4}	1.0 - 3.3
DDTs	5.5 - 6.0	0.001- 0.005	2×10^{-4} - 9×10^{-9}	1.2 - 6.0
HCHs	3.8 - 4.4	1.0-30.0	4×10^{-5} - 0.08	0.002 - 0.8
Mono-CBs	4.3 - 4.7	1.2 - 5.5	0.9 - 2.5	58.0 - 74.0
Di-CBs	4.9 - 5.3	0.06 - 2.0	0.0018 - 0.279	17.0 - 92.2
Tri-CBs	5.5 - 5.9	0.015 - 0.4	0.0136 - 0.143	24.3 - 92.2
Tetra-CBs	5.6 - 6.5	0.0043 - 0.1	5.9×10^{-5} - 0.0054	1.7 - 47.6
Penta-CBs	6.2 - 6.5	0.004 - 0.02	3×10^{-4} - 0.009	24.8 - 151.4
Hexa-CBs	6.7 - 7.3	4×10^{-4} - 0.001	2×10^{-5} - 1.6×10^{-3}	11.9 - 81.8
Hepta-CBs	6.7 - 7.0	4.5×10^{-4} - 0.002	2.7×10^{-5}	5.4
Octa-CBs	7.1	2×10^{-4} - 3×10^{-4}	2.7×10^{-5}	38.1
Nona-CBs	7.2 - 8.2	1.8×10^{-5} - 1.1×10^{-4}	6.3×10^{-6}	100.0
Deca-CB	8.3	1.2×10^{-6}	5.0×10^{-8}	20.8
BDE 28	5.9 [a]	0.07 [c]	0.0028 [c]	
BDE 47	6.8 [a]	0.015 [c]	1.9×10^{-4} [c]	
BDE 99	7.3 [a]	0.009 [c]	1.8×10^{-5} [c]	
BDE 100	7.3 [a]	0.04 [c]	3.3×10^{-5} [c]	
BDE 153	7.9 [a]	0.001 [c]	2.1×10^{-6} [c]	
BDE 156				
BDE 183	8.3 [a]	0.002 [c]	4.7×10^{-7} [c]	
BDE 209	8.7 [b]			

Table II-1: log K_{ow} values, water solubility (at 25 ˚C), vapor pressure (at 25 ˚C) and Henry's Law constant of selected OCPs and PCB homolog groups from Mackay et al. (1997). Data for PBDE congeners as specified. [a] Braekvelt et al. (2002), [b] Wania and Dugani (2003), [c] Tittlemier et al. (2002).

POPs are typically 'water-hating' chemicals and characterized by a low water solubility and relatively high K_{ow} value. Thus, they tend to come out of aqueous solution and associate with organic matter of soil, sediments and suspended particulate matter in the aqueous phase (Jones and de Voogt, 1999). In general, the less water soluble POPs, illustrated by higher K_{ow} values, tend to accumulate on organic matter and in biota in a higher fraction. For example HCH isomers have relative high water solubility and a low log $K_{ow} < 4$, and therefore their bioaccumulation is considered to be insignificant (van der Oost et al., 2003). In contrast, DDTs have higher K_{ow} values of 5.6-6.2 and can be expected to have a significant bioaccumulative potential. PCBs congeners are known to be highly variable in physicochemical properties according to their chlorination grade. Water solubility and vapor pressure can vary by up to a magnitude of 10^8, with a decreasing order of these properties with increasing chlorination grade. The vapor pressure and water solubility are the key parameter of POPs to enter the gas phase in the environment and therefore determine the potential to undergo atmospheric long range transport (Bard, 1999).

Overall, HCH isomers, Heptachlor, Chlordane, Toxaphene and lower chlorinated PCBs are likely more subjected to atmospheric long range transport, where DDTs and higher chlorinated PCBs tend to accumulate more regional in soil, sediments and biota. However DDTs were found in the atmosphere over the polar regions and long-range transport should be appreciated for compounds with lower vapor pressure and higher K_{ow} values.

It should be noted that physicochemical properties of POPs are very dependent on prevailing environmental conditions. They are subject to measurement uncertainties (Holmes et al., 1993) and are reported in a wide range, rather than consistent, values (Mackay et al., 1997). This makes it particularly challenging to theoretically model the behaviors of POPs in the environment.

II-1-4 Persistence

A major character of POPs is their resistance to chemical and biological degradation via oxidation, reduction, hydrolysis, photolysis and other environmental reactions leading to high persistence and accumulation in the environment (Klečka et al., 2000). Half-life times, the time in which half of the amount of the chemical is removed from the environment, for selected PCB congeners were reported by Sinkkonen and Paasivirta (2000) and range from 3 to 500 days, 60 days to 27 years and 3 to 38 years for air, water and sediments respectively. Chlordane, DDT, Dieldrin and HCHs isomers have a half-life time in air and surface water of 5 h to 2 days, 1 to 7 days, 4 h to 2 days and 2.3 days, and 238 to 1,386 days, 7 to 350 days, 175 to 1,080 days and 30 to 300 days (γ-HCH) respectively (Mackay et al., 1997).

After five half-life degradation episodes, most of the chemical will be removed from the environment with about 3% remaining. Assuming that typical air speeds are about 1 m/s (86 km/day) a half-life time of at least 2 days will be needed to achieve atmospheric long-range transport, e.g. 1000 km. An atmospheric half-life time greater than 2 days is considered necessary for the ability of a chemical to undergo long-range atmospheric transport in the protocols of the Convention on Long Range Transport of Air Pollution (CLRTAP) (Vallack et al., 1998). However, degradation in the tropics can assumed to be substantially faster than in temperate and polar regions, as suggested by Klečka et al. (2000) and Raghu et al. (2003), but is poorly understood. For example, Lindane degrades much faster in Indian soil than under temperate conditions (Raghu et al., 2003).

II-1-5 Usage of POPs in Asia

Pesticides are intentionally released at their point of application. Many first generation pesticides like DDT, Lindane and Chlordane are officially banned and have been gradually replaced by less persistent and less bioaccumulative pesticides. However, in 1998 it was reported that OCPs (such as DDT, HCH, Chlordane and Heptachlor) were still being used in agriculture and disease control in some developing countries, especially in tropical regions (Vallack et al., 1998). More specifically, the use of these pesticides has been reported for Malaysia (UNEP, 2002a; Abdullah, 2003), Vietnam (UNEP, 2002a; Nhan, D.D., 2003), Papua New Guinea (UNEP, 2002a) and Bangladesh (Matin, 2003). HCHs and DDT are likely to be used in India (Voldner and Li, 1995; Li, 1999; Raghu et al., 2003). The pesticide Dicofol is manufactured in China and contains DDT as impurities with unknown content as reported from Qiu et al. (2004). Dicofol is used in countries of Southeast Asia (Taylor et al., 2003) and is likely to act as a source for DDT contamination, even though DDT is banned in these countries.

PCBs were widely used as dielectric fluids in transformers and large capacitors, as pesticide extender, plasticizer in sealants, heat exchange fluid, hydraulic lubricants, cutting oil and in plastics, paints, adhesives and carbonless copy paper (Vallack et al., 1998). PCB production in most countries was banned in the 1970s and 1980s. However, the United Nations Economic and Social Council, Economic Commission for Europe (UNECE) reported some production of PCBs for certain countries with economies in transition, but which should eliminate the production as soon as possible, and not later than 31 December 2005 as stated in the Protocol to the Convention on Long-range Air Pollution on Persistent organic Pollutants (UNECE, 1998). Leakage from old equipment, building materials, stockpiles and landfill sites continue to be a major source of PCB emissions. A large number of PCB-containing transformers and capacitors still remain in use in China (Fu et al., 2003). The restricted use, production and import of PCBs are reported for the Philippines and Vietnam (UNEP, 2002a).

There is mounting evidence that the marine environment of Asia is significantly contaminated with PBDEs (Uneo et al., 2004; Martin et al., 2004; Liu et al., 2005). De Wit (2002) reported that Asia consumed 42% of world production of DeBDE – a commercial product containing approximately 98% of the congener BDE 209. This product is widely used in many synthetic materials including textiles and printed circuit boards as flame retardants. In addition to imported PBDEs to Asia, the shipment of electronic waste (so-called ‘e-waste’) to China and India for disposal is also a major source of PBDEs to the Asian environment (Martin et al., 2004). For example, it was reported that 145 million electronic devices were scrapped in Guangdong Province, southern China in 2002 alone, and this likely to be a significant source of environmental contamination with PBDEs.

II-2 The Sea-Surface Microlayer (SML) and its Contaminations of POPs

II-2-1 Dimension and properties of the SML

The SML of the oceans represents the boundary layer between the atmosphere and ocean. Hunter (1997) defined the SML as follows:

> *“The sea-surface microlayer is that microscopic portion of the surface ocean which is in contact with the atmosphere and which may have physical, chemical or biological properties that are measurably different from those of adjacent sub-surface waters.”*

This definition avoids a reference to the physical thickness of the SML, which can vary by at least two orders of magnitudes depending on the type of sample technique used (see II-2-2). However, the SML has often been operationally defined as roughly the top of 1 to 1000 µm of the ocean surface. Zhang et al. (1998) described a multiple-layer model in which physicochemical properties of the SML change rapidly. The thickness of the SML in the multiple-layer model was empirically determined as 50 ± 10 µm and further studies by Zhang et al. (2003a) confirmed the thickness of the SML as approximately 60 µm based on measurements using pH-microelectrode. However, the thickness of the SML may change due to changing meteorological conditions and the organic matter composition of the SML (Liu and Dickhut, 1998). Based on the literature (Hardy, 1982; Liss and Duce, 1997) and Zhang's studies it is proposed that a SML of a thickness of 60 µm could be meaningfully used for studying physicochemical properties of the SML, and up to 1000 µm for biological properties, depending on the organism, or ecological features of interest.

There are many gaps in the understanding of the physical, chemical and biological properties of the SML, but its environmental significance is widely appreciated. One of the most significant processes controlled by the SML may be the transfer of material between the ocean and atmosphere (Frew, 1997). The SML can serve as both a sink and a source of anthropogenic compounds, including POPs and heavy metals (Wurl and Obbard, 2004). Contaminations of the SML with POPs are summarized in Table II-2 and have been reviewed by Wurl and Obbard (2004). The SML is also an essential micro-habitat for a vast diversity of microorganisms (neuston), larvae and fish eggs. Exposure of the biota in the SML to residual pollutants has important implications with respect to the ecology of the wider marine environment (Hardy, 1997). The SML also plays a vital role in the transfer of energy between the atmosphere and ocean.

Region	Year	Compound	Concentration (ng/L)	EF	References
Biscayne Bay, Florida Straits	1968	DDT residues	80-12710	80-12710	Seba and Corcoran (1969)
Narragansett Bay, Rhode Island	1972	ΣPCBs	450-4200	9-62	Duce et al. (1972)
North Central Pacific	1972	DDT residues	<0.02-15.4	<15	Williams and Robertson (1973)
		ΣPCBs	5.2-50	0.9-3	
Swedish West Coast	1972	DDT residues	$39x10^{6}$		Larsson et al. (1974)
		ΣPCBs	$33x10^{6}$		
Sargasso Sea	1973	DDT residues	<0.05-0.7	0.8-4	Bidleman and Olney (1974)
		ΣPCBs	<3.8-19.3	2.7-20	
Western Baltic Sea	1974	DDT residues	0.1-3.4		Stadler and Ziebarth (1976)
		ΣPCBs	1.1-5.9		
Western Baltic Sea	1976-1978	DDT	<0.05		Gaul and Ziebarth (1980)
		α-HCH	5.5-19.0	1.4	
		β-HCH	<0.02-1.3	0.6-3	
		Lindane	3.2-15.6	1.9-2.3	
		ΣPCBs	29.9-235.2	12-21	
Mediterranean Sea	1977	DDT	39.9		Mikhaylov (1979)
		DDD	9.2		
		DDE	13.2		
Rijeka Bay, Adriatic Sea, Croatia	1977-1981	p,p'-DDT	<1-12.5	1-39	Picer and Picer (1992)
		p,p'-DDD	0.2-8.1	0.2-93	
		p,p'-DDE	<0.1-4.7	0.5-16	
		ΣPCBs	1-597	2.2-59	

Table II-2: Concentrations and enrichment factors (EF) of POPs in the SML from various regions of the world.

Region	Year	Compound	Concentration (ng/L)	EF	References
Blanca Bay, Argentina	1980-1981	o,p'-DDT	<3.6-100.7	0.1-21.3	Sericano and Pucci (1984)
		p,p'-DDT	<4-316.2	0.2-13.2	
		β-HCH	14.3-219.5	0.5-23.1	
Mediterranean Sea, Monaco	1981-1982	Lindane	3-7.8	4.6-780	Burns et al. (1985)
		ΣPCBs	3.2-35.9	15-49	
Mediterranean Sea, open water	1982	DDD	0.005	2.5	Burns and Villeneuve (1987)
		Lindane	0.05	25	
Baltic Sea and north-east Atlantic	1980-1984	DDT	0.22-17.9	<0.1-44	Mohnke et al. (1986)
		α-HCH	1.1-11.9	<0.1-8	
		β-HCH	0.16-3.46	<0.1-7	
		Lindane	1.40-32.4	<0.1-13	
		δ-HCH	0.06-0.68	<0.1-4	
		ΣPCBs	5.5-46.0	<0.1-59	
Los Angeles, California	1986	ΣDDT	47-179		Cross et al. (1987)
		Lindane	<1		
		ΣPCBs	8141-30708		
Atlantic Ocean and Gulf of Mexico	1989	ΣDDT	< 0.2		Sauer et al. (1989)
		ΣPCBs	<1		
Sea of Japan	1992	α-HCH	0.92-1.75	1.1-1.2	Chernjak et al. (1995)
		β-HCH	0.15-0.44	0.8-1.4	
		Lindane	0.40-1.59	0.9-4.7	

Table II-2: Continued.

Region	Year	Compound	Concentration (ng/L)	EF	References
Barents Sea	1992	p,p'-DDT	<0.0006		Chernjak et al. (1995)
		p,p'-DDE	<0.0006		
		α-HCH	0.33-0.51	0.7-1.1	
		β-HCH	0.11-0.17	0.8-1.8	
		Lindane	0.32-0.45	1.4-1.5	
		ΣPCBs	<0.001		
Alexandria, Egypt	1997	DDT	0.1-14	1.9-3.2	Abd-Allah (1999)
		DDD	0.1-28	1.7-2.7	
		DDE	1.9-45	2.3-3.0	
		Lindane	2.4-27	2.2-3.5	
		ΣPCBs	36.6-412.2	1.9-2.9	
Mediterranean Sea, northern coastline of Spain	2001	ΣPCBs, diss.	3.2-45.3	0.2-30.6	García-Flor et al. (2005)
		ΣPCBs, part.	1.9-10.8	0.1-12.6	

Table II-2: Continued.

Naturally occurring surface-active substances including organic surfactants, proteins, fatty acids and amino acids are enriched in the SML compared with sub-surface waters resulting in distinctive physical and chemical properties of the sea-surface. A major source of surface-active substances to the SML is the production by phytoplankton and degradative processes (Zutic et al., 1981). Condensation of relatively low molecular weight exudates may form complex surface-active macromolecular structures (Zutic et al., 1981). These compounds are concentrated in the SML by a number of physical processes including diffusion, turbulent mixing, scavenging and transport by bubbles and buoyant particles (Hardy, 1982). The distinctive chemical composition of the SML is the key factor for the accumulation of many anthropogenic contaminants in this boundary layer.

II-2-2 SML sampling techniques

In the past 40 years, several techniques for sampling the SML have been deployed and the advantages and disadvantages of 21 different SML sampling techniques were reviewed by Hühnerfuss (1981a, b). The thickness of SML collected was found to be dependent on the technique used. The screen sampler (Garrett, 1965), glass plate sampler (Harvey and Burzell, 1972) teflon plate sampler (Miget et al., 1974) are the most widely used SML sampling techniques, collecting SML with a thickness of approximately 150-400 µm, 50 µm and 30 µm respectively. All of these samplers are operated manually, and allow the collection of samples of a relatively low volume of not more than two liters. A rotating drum sampler for automatic sampling was first described by Harvey (1966) and permits the collection of several liters of sample within 20-60 min, thereby minimizing risks of sample contamination. Carlson et al. (1988) used a rotating glass drum sampler, whereas Hardy et al. (1988) used a teflon-coated drum. Overall, the drum sampler can be considered as the state-of-the-art SML sampling device, but questions remain as to whether water adhering to the drum dilutes the SML sample and whether there are compromises to sample integrity from device fabrication materials.

II-3 Fate and Distribution Mechanisms of POPs in the Marine Environment

The presence of DDTs and PCBs in the Antarctica was first reported in the 1960s and 1970s (George and Fear, 1966; Sladen et al., 1966; Risebrough and Carmigani, 1972), and in the Arctic in the 1970s (Bowes and Jonkel, 1975; Clausen and Berg, 1975; Goldberg, 1975). However, the first findings of POPs in polar region were not accidentally found, as scientists in the 1960s hypothesized that these chemicals, particular DDT, could be transported over long distances. George and Fear (1966) pointed out that if any area of the world were to be free of pesticide contaminations, it would seem probable that the Antarctica would be such place because of its remoteness, low abundance of animals and plants, and lack of known application of pesticides on the continent. Their finding of DDTs in seals and penguins, as well as those of Sladen et al. (1966) can be considered as the first evidence for the global distribution of DDTs. Three decades later, it is now known that concentrations of POPs found in polar regions are surprisingly high, given their remoteness from known sources (Wania and Mackay, 1993). The first hypothesis on the migration and deposition of POPs in polar regions was based on the theory of evaporation in warm climates with subsequent transport to polar regions followed by atmospheric condensation, known as ‘global distillation’ (Goldberg, 1975). Wania and Mackay (1993) emphasized the importance of the physicochemical properties of POPs and prevailing condition of cold environments in the long-term spatial distribution of relative to emission source and transport pathways. The volatility of the compound and the ambient atmospheric temperature both have a strong influence on their spatial distribution. Wania and Mackay also suggested that POPs may migrate to higher latitudes in a series of ‘jumps’ characterized of evaporation and condensation, as aligned by seasonal temperature changes at mid-latitudes. This is known as the ‘grasshopper effect’ (Wania and Mackay, 1996). The wide range of physicochemical properties for a diversity of POPs (see Table II-1) leads to a distinctive evaporation and condensation temperature profile for individual POPs. Therefore, it has been suggested that more volatile POPs migrate faster and further to the poles than less volatile POPs, and individual POPs are thereby fractionated over the globe along a latitudinal gradient, a process known as ‘global fractionation’ (Wania and Mackay, 1993). Global monitoring studies of POPs, e.g. Iwata et al., (1993), Simonich and Hites (1995), support the hypothesis of global distillation and fractionation.

The migration of POPs to polar regions is predominately via the atmosphere, which acts as a mobile phase for POPs. Soil may act more as a stationary phase, whereas the ocean is an intermediate phase of mobility and retention potential. A comparison of soil-air and air-sea gas exchanges fluxes of PCBs from Sweden may illustrate the importance of the air-sea gas exchange for a temperate region. The soil-air gas fluxes of PCBs in southern Sweden were estimated at up to 4500 ng/(m^2 year), but generally below 440 ng/(m^2 year) (Backe et al., 2004). Air-sea gas fluxes of PCBs measured along the Swedish West Coast were substantial higher with values up to 100 ng/(m^2 day), but generally below 20 ng/(m^2 day) (Sundqvist et al., 2004). Air-sea gas exchange plays an important role in the global distribution of POPs, particularly in polluted coastal areas. However, air-sea gas exchange is a process of two directions and atmospheric input of POPs to the ocean can be significant, particularly for the more water soluble chemicals, like HCHs (GESAMP, 1989). It was hypothesized that the SML may influence the air-sea gas exchange process (Mackay et al., 1991; Wania et al., 1998; Mackay, 2001), but the effects are still unknown due to the lack of actual field data. Wania et al. (1998) pointed out that studying the effects of the SML on air-sea gas exchange of POPs is complicated by the great difficulties in quantifying these chemicals in the SML.

Other important pathways affecting the fate of POPs in the environment are wet and dry atmospheric deposition, as well sedimentation to the deep ocean. Deposition processes of POPs were reviewed by Wania et al. (1998), and it should be noted here that wet deposition may be important for the fate of POPs in tropical regions during monsoon periods. The transport of particulates to the deep ocean and bottom sediments is considered to be a global sink for POPs (Gustafson et al., 1997; Wania and Daly, 2002).

II-4 POPs in the Marine Environment of Singapore

II-4-1 Usage of POPs in Singapore

Singapore is located about 120 km north of the equator with Malaysia to the north and Indonesia to the south. The country is fully industrialized with a population of four million people within a confined land area of 700 square kilometers. Singapore is characterized by a tropical climate along with abundant precipitation (average annual rainfall of 2400 mm, NEA, 2004). Singapore is affected by the monsoon seasons receiving water masses from the South China Sea and Gulf of Thailand during October to April, and from the Java Sea and Celebes Sea during May to September (Knox, 1987). Strategically located in the South China Sea and Straits of Malacca, Singapore is a major port hub, with up to 142,000 ship movements per year (2002 data). Such a high level of ship movements are likely to act as a source of pollutions to the marine environment. The country is also home to the third largest petroleum refining industry in the world, with a refining capacity in excess of 1 million barrels per day. Agricultural activities are extensive in the region of Southeast Asia, but almost non-existent in Singapore.

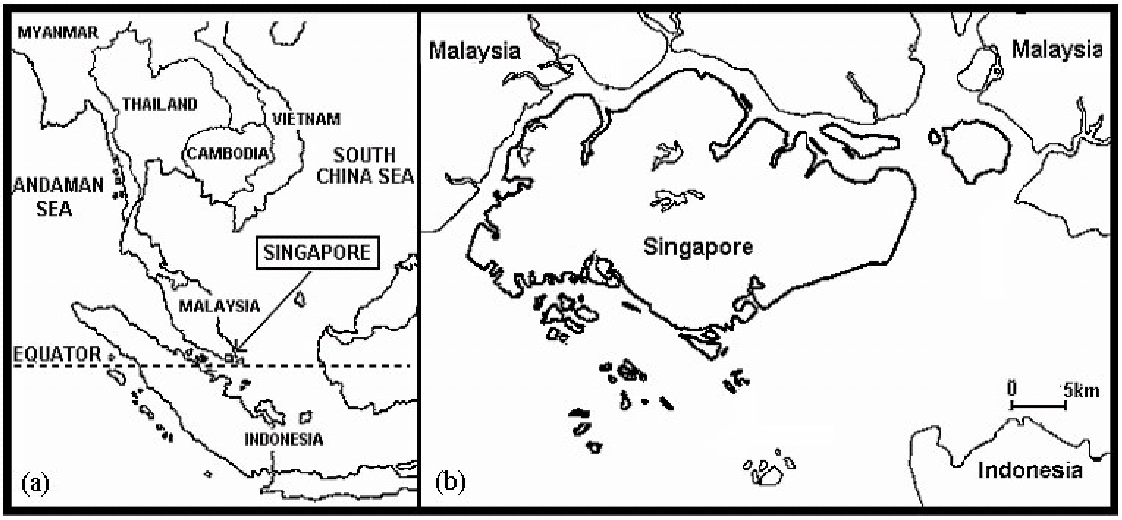


Figure II-2: Geographical location of Singapore (a) and map of Singapore (b).

All of the POPs of concern in this study are officially banned in Singapore, but in some cases quite recently; e.g. Chlordane was banned in 1999 (UNEP, 2002a). All electrical transformers containing PCBs should have been be disposed of by end 2002 (UNEP, 2002a). There are no available data on the usage or possible sources of PBDEs as flame retardants in Singapore.

II-4-2 Concentration levels of POPs in the environment of Singapore

In the 1990's, DDT residues were detected in human blood serum in Singapore and partly attributed to seafood consumption (Luo, et al., 1997). More recently Bayen et al. (2005a) reported concentrations of POPs in seafood consumed in Singapore with a mean concentrations of 0.95, 3.72, 3.76 and 0.17 ng/g for ΣChlordane, ΣDDTs, ΣPCBs and ΣPBDEs respectively (as mean values of various seafood). Concentrations of ΣChlordane, ΣPCB, ΣPBDE in green mussels collected from the marine environment of Singapore were in the same range as reported for seafood (Bayen et al., 2003; Bayen et. al., 2004a), but lower by a factor of 6 for ΣDDT. A mean value of ΣPBDEs in human adipose tissue was reported for Singapore with 3.6 ng/g (Li et al., 2005). OCPs and PCBs were analysed in unfiltered seawater samples collected around Singapore and the prevalence of HCHs (range of 0.02 to 18 ng/L) and ΣPCBs (range of 0.2 to 62 ng/L) were shown, but DDTs appeared to be present in a lower concentration range of 0.02 to 1.4 ng/L (Basheer et al., 2003a). However, no detailed study on the fate and distribution of POPs in the tropical marine environment of Singapore is reported in the scientific literature.

CHAPTER III

Materials and Methods

III-1 Chemicals

All chemicals used for this study were of high purity grade, unless otherwise stated. Solvents of pesticide grade were used throughout the study and purchased from Tedia (Fairfield, OH, USA) and/or Aldrich (St. Louis, MO, USA). Mixed standard solutions for organochlorine pesticides (OCPs) (Z-014C-R) and polychlorinated biphenyls (PCBs) (C-QME-01) were obtained from AccuStandard (New Haven, CT, USA). $^{13}C_{12}$-labeled PCB congeners CB 28, 52, 101, 138, 153 and 180 were used as surrogates and $^{13}C_{12}$-labeled PCB congeners CB 32, 141 and 208 as internal standards (Cambridge Isotope Laboratories, MA, USA). Standard solutions for polybrominated diphenyl ethers (PBDEs) (BDE-CSM, BDE-47S, BDE-99S and BDE-100S) were obtained from AccuStandard. Pentachloronitrobenzene (PCNB), purchased from AccuStandard, was used as surrogate for the first two investigations (Chapter IV and V). Sodium sulfate (pesticide grade) and silica gel (No. R10040B, Silicycle, Canada) were baked at 400 °C for at least 10 h prior to use. High purity nitrogen and helium gas (>99.9995%) were purchased from SOXAL (Singapore).

III-2 Materials

All glassware and sample containers were soaked in detergent solution overnight, and then rinsed several times with hot tap water and DI water, and then dried at 220 ˚C for at least 12 h. Acetone was used to rinse glassware prior to use. Pasteur pipettes and sample vials were cleaned by rinsing with acetone, heated to 400 ˚C for 12 h and kept sealed in a glass bottle prior to use. Pasteur pipettes and sample vials were rinsed with acetone and dried at 220 ˚C prior to use. Glass fiber (GF) filters (Whatman GF/A 1.6 µm, Ø 47 mm; GF/B 1 µm, Ø 125 and 150 mm) were baked for 16 hours at 450 °C wrapped in precleaned aluminum foil (baked at 450 °C for 16 hrs) and stored in an air and moisture tight container. Polyurethane foam (PUF) plugs (Ziemer Chromatographie, Mannheim, Germany; length 60mm, diameter 50mm, density 0.03 g cm^{-3}) were used to collect atmospheric POPs from the gaseous phase and pre-cleaned as described in Chapter XIII.

III-3 Sampling Techniques

III-3-1 Design, development and operation of a sea-surface microlayer sampler

Several liters of sample are needed for the quantification of POPs in the SML. Therefore, a rotating drum sampler was designed for SML collection, as shown in Figure III-1. A glass drum was used since the thickness of SML collected by the glass plate method, or glass drum sampler, is consistent with the most recently reported thickness of the SML as 50 ± 10 µm (Zhang et al. 1998; Zhang et al., 2003a). The mechanical construction was fabricated by Prosimus PTE (Singapore) and the electrical system was developed in-house. The sampler device was designed for trace organic pollutants analysis, where only stainless steel, anodized aluminum, glass and Teflon materials were used for construction (Hillebrand and Nolting, 1987). The SML sampler was attached to the small research vessel '*Hammerhead'* (a 38' aluminum landing craft workboat) by a 5m long aluminum beam located starboard to avoid contamination from the engine. The sampler device was attached to the beam through suspension springs. The tension of suspension is adjustable through the length of attachment to stabilize sampler during operation of rougher sea conditions. The SML is collected under capillary force by the glass drum (cylinder), partly immersed in the water and oriented parallel to the direction of travel direction to avoid build-up of surface components ahead of the sampler. The physical principle of the phenomena capillarity, upon which this sampling technique is based, is described by Probstein (2003).

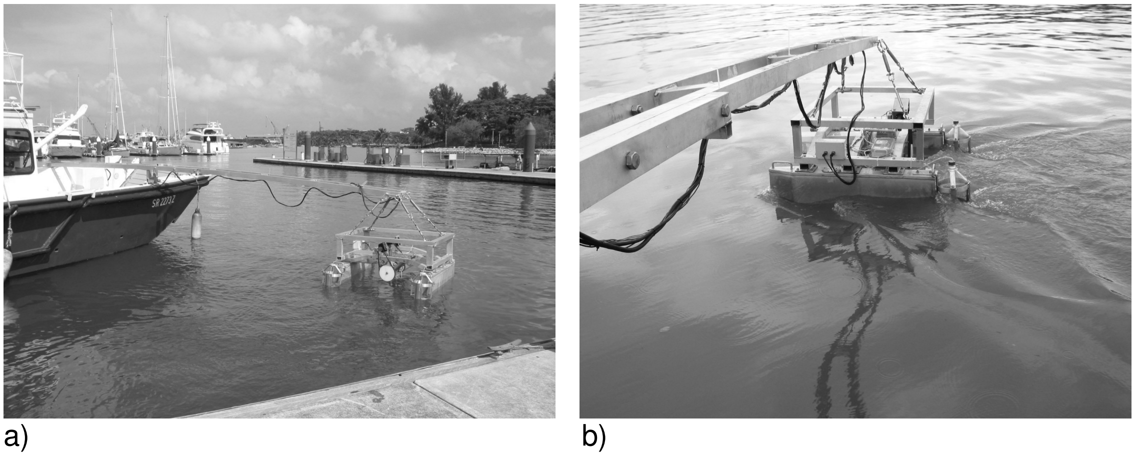

a) b)

Figure III-1: Rotating drum sampler for the collection of SML samples. a) attached to the research vessel, b) during sampling collection.

The SML sample is drawn on to the ascending side of the rotating glass drum and then scraped off by an inclined wiper located on the downward side. The downstream wiper overhangs, and leads into, an elbow glass port which is connected to one of two 12V DC Teflon diaphragm pumps (Greylor, FL, USA). The thickness of the SML has been calculated using following formula (Liu and Dickhut, 1998):

$$\gamma = \frac{V_{sample}}{\pi * d * l * t * s} * 10^{-6} \qquad (1)$$

where γ is the thickness of the SML (μm); V_{sample} is the volume of collected SML sample (ml); d is the diameter of glass drum (cm); l is the length of the glass drum; t is the time period of sample collection (min); s is the rotation speed of the glass drum (RPM).

Seawater was collected from a depth of 1 m simultaneously with the second pump. Teflon tubes were used to transfer the SML and seawater samples to the boat for on-line filtration over a precleaned GF/B filter (Whatman, 1 µm, Ø 125 mm or Ø 150 mm), except for samples collected for the second study (Chapter V), which were collected directly into 10 liter glass containers attached to the sampler device. GF filters showed the lowest retention of certain POP compounds of <10% (House and Ou, 1992) and widely used in the filtration of seawater subjected to POP analysis (Grasshof et al., 1999; IOC, 1993). The rotation speed was set to approximately 12-14 rpm resulting in an SML collection thickness of 60-80 µm, depending on prevailing environmental conditions. Meteorological data and water temperature were standard parameters measured during SML sampling. Sampling was conducted under calm to moderate sea conditions at wind speeds below 4 m/s so as to ensure the occurrence of the SML. In calmer sea conditions, SML samples were collected over an area of about 200 m^2 at lowest boat speed of approximately 2 km h^{-1}. During rougher sea conditions, the boat was anchored for the duration of the sampling event so as to minimize disturbance to the surface layer from the sampler itself. About 10 liters of SML sample could be collected within a 90 min period. Filters were wrapped in pre-cleaned aluminum foil and kept frozen until further treatment in the laboratory. The filters were not dried in order to avoid potential contaminations. Concentrations of POPs are given in terms of water volume, but not in terms of SPM mass.

III-3-2 Air sampling

Particles were collected on a glass fiber filter of 47 mm diameter (Whatman GF/A, 1.6 µm). Compounds in the gas phase were adsorbed on two PUFs plugs in series (50 mm diameter, 60 mm length, density of 0.03 g cm^{-3}). GF/A filters and PUFs were placed in dual cartridge stainless steel vacuum flasks. A high-volume air pump (H8400B, F&J

Specialty Products, Inc., USA), equipped with a flow gauge, was used to collect between 50-70 m^3 of air in Singapore and 70 to 200 m^3 over the Indian Ocean. For local air sampling in Singapore, GF/A filters and PUFs were loaded into the cartridges under a purified nitrogen atmosphere so as to avoid contamination from ambient air, and then stored in an air- and moisture-tight plastic containers. The GF/A filters and PUFs were kept frozen after sampling inside the cartridge, and transferred directly into extraction vessels for microwave-assisted extraction (see Chapter III-4) under a nitrogen atmosphere. PUFs used for air sampling over the Indian Ocean were wrapped in pre-cleaned aluminum foil and stored in tin containers. The tin container itself was stored in an air- and moisture-tight plastic container. Air samples were stored in a freezer at -18 °C and kept cool in an ice-box during transport to Singapore.

III-3-3 Sediment sampling

Surface sediment samples were collected using a stainless steel grab sampler with a sampling area of about 0.5 m^2. All sediment samples were kept in pre-cleaned and solvent-rinsed glass jars and kept frozen until further treatment.

III-4 Sample Treatment and Extraction Methods

III-4-1 Liquid-liquid extraction of aqueous samples

All aqueous samples were extracted within a few hours after collection and spiked with surrogate standard. Samples were extracted directly in the sample container with 3 x 200 mL of hexane. The samples were shaken for 10 mins, and then transferred in a 10 liter separation funnel. Phases were allowed to separate for 30 mins before transferring the aqueous phase back to the sample container and the organic phase into a 1000 mL round bottom flask. In case of the collection of unfiltered samples, shaking was performed for 20 mins. The extracts were kept at -20 ˚C before reducing the volume of cold extracts to approximately 2 mL using a rotary evaporator at a water bath temperature of 18 ˚C.

III-4-2 Microwave-assisted extraction

Microwave-assisted extraction (MAE) was performed in a Mars X microwave oven (CEM, Matthews, NS, USA). MAE is widely used as an alternative extraction technique to Soxhlet extraction for environmental samples, such as soil, sediments and biota (Lopez-Avila et al., 1995; Bayen et al., 2004a and 2004b). MAE was used for the extraction of glass fiber filters containing suspended particulate matter, sediments and PUF plugs. Further details on the solvent mixture used and temperature oven program are given in the subsequent chapters. Supernatants were transferred to a 250 mL round bottom flask after cooling to room temperature, and reduced to approximately 2 mL using a rotary evaporator at 18 ˚C.

III-4-3 Soxhlet extraction

Soxhlet extraction was used to compare analyte extraction efficiency in the development of a novel extraction method for PUFs using MAE. Soxhlet extraction has been widely used for the extraction of PUFs (Iwata et al., 1993; Kallenborn et al., 1998; Harrad and Mao, 2004). Soxhlet apparatus was rinsed prior to extraction for 2 h with 200 mL of acetone:hexane (3:2, v:v). Extracts were reduced to about 2 mL using a rotary evaporator at 18 ˚C.

III-5 Sample Extract Cleanup for POPs Analysis

A silica gel cleanup column, containing 4 g (aqueous and atmospheric samples) or 6 g (SPM and sediment samples) of silica gel topped with 2 cm of anhydrous sodium sulfate, was washed with 2 x 15 mL hexane. Each weighted batch of silica gel was deactivated to 5 % with DI water. The sample extracts were then transferred onto the column and eluted with 130 mL hexane and 15 mL dichloromethane (USEPA Method 3630C, 1996). Elutes were collected in a single fraction. Extracts were concentrated to approximately 2 mL using a rotary evaporator at 18 ˚C, and then further to 200 µL using a gentle purified nitrogen gas stream. The extracts were then kept in sealed vials at -20 ˚C prior to analysis. The weights of all standards and sample extracts were recorded before and after analysis to control evaporation loss during storage.

III-6 Gas Chromatography-Mass Spectrometry Analysis

The analysis and quantification of POPs in the sample extracts were performed using either a Shimadzu QP-5050 (Shimadzu Asia-Pacific, Singapore) gas chromatograph coupled with a mass spectrometer (GC-MS) or a Varian 4000 gas chromatograph ion trap tandem mass spectrometer (GC-IT-MSMS) (Varian Inc., Australia). The configuration of the GC-MS and GC-IT-MSMS are given in sections III-6-1 and III-6-2, respectively. Except when specified otherwise, DDTs (or ΣDDT) refer to the sum of p,p'-DDT and its metabolites p,p'-DDD and p,p'-DDE, Chlordanes (or ΣChlordane) to the sum of cis- and trans-Chlordane, HCHs (or ΣHCH) to the sum of α-, β-, γ- and δ-HCH; and PCBs (or ΣPCBs) to the sum of congeners 17/31, 18, 28, 33, 44, 49, 52, 70, 74, 82, 87, 95, 99, 101, 110, 118, 128, 132, 138, 149, 151, 153, 156, 169, 170, 171, 177, 180, 183, 187, 191, 194, 195, 199, 205, 206 and 209. PBDEs (or ΣPBDE) refer to the sum of congeners 28, 47, 99, 100, 153, 156, 183 and 209, except when specified otherwise.

III-6-1 Configuration of GC-MS (Shimadzu QP-5050)

The QP5050 GC-MS was equipped with a Shimadzu AOC-20i auto sampler and a DB-5 fused silica capillary column (30 m x 0.32 mm I.D., film thickness 0.25 µm). Purified helium was used as the carrier gas with a flow rate of 1.5 ml/min. Four µL of sample was injected into the GC-MS in splitless mode with an injection time of 1 min. Injection and interface temperatures were set to 280 ℃ and 300 ℃, respectively. The oven temperature for analysis of OCPs and PCBs was programmed from 70 ℃ to 140 ℃ at a rate of 25 ℃ min^{-1}, 140 ℃ to 179 ℃ at a rate of 2 ℃ min^{-1}, 179 ℃ to 210 ℃ at a rate of 1 ℃ min^{-1}, 210 ℃ to 300 ℃ at 5℃ min^{-1}, and held for 10 minutes. For analysis of PBDEs, the oven temperature was programmed as follows: oven temperature of 120 ℃ held for 1 min, from 120 ℃ to 215 ℃ at 10 ℃ min^{-1}, from 215 ℃ to 270 ℃ at 3 ℃ min^{-1} and from 270 ℃ to 300 ℃ at 10 ℃ min^{-1}, held for 10 minutes. The analysis was conducted in selective ion monitoring mode (SIM). Selected mass ions and retention times for each contaminant are presented in Appendix A.

III-6-2 Configuration of GC-IT-MSMS (Varian 4000)

The Varian 4000 GC-IT-MSMS was equipped with a CP 8400 auto sampler and DB 5 fused silica capillary column (60 m x 0.32 mm I.D., film thickness 0.25 µm) for the analysis of OCPs and PCBs. A CP-Sil8 fused silica capillary column (10 m x 0.53 mm I.D., film thickness 0.25 µm) was used for the analysis of PBDEs. Purified helium was used as the carrier gas with a flow rate of 1.5 ml/min. Three µL of sample was injected into the GC-IT-MSMS in splitless mode with an injection time of 2 mins. Manifold, injection, ion trap and transfer line temperatures were set to 60 ℃, 260 ℃, 220 ℃ and

280 °C respectively. The oven temperature for analysis of OCPs and PCBs was programmed as described in section III-6-1. For the analysis of PBDEs, the oven temperature was programmed as follows: 80 °C (held for 1.5 min) to 250 °C at a rate of 12 °C min^{-1}, 250 °C to 300 °C at a rate of 25 °C min^{-1}, and held for 10 minutes. The ion trap was operated in internal EI-MS/MS mode. The multiplier off set was +300 V. The filament emission current was 80 μA for the internal EI mode. A resonant wave form (collision induced dissociation, CID) was selected for all compounds. Selected mass ions and retention times for each contaminant are presented in Appendix.

III-7 Quality Assurance for POPs Analysis

III-7-1 Spiking of surrogate standard

Surrogate standards were spiked into samples before extraction to determine any loss of analytes during the whole analytical procedure. $^{13}C_{12}$-labeled PCBs are routinely used as recovery standards for POPs analysis (e.g. Kallenborn et al., 1998; Jaward et al., 2004a; Jaward et al., 2004b; Harrad and Mao, 2004). $^{13}C_{12}$-labeled PCB congeners 28, 52, 101, 138, 153 and 180 were used in this study as surrogate standards, unless the use of Pentachloronitrobenzene (PCNB) as surrogate is specified.

III-7-2 Analysis of standard reference materials (SRM) and spiked samples

SRMs are widely used to check the precision and accuracy of analytical methods. Sediment –SRM 1441c- was analyzed to validate the analytical methods for the analysis of PCBs and OCPs in sediments and suspended particulate matter (SPM). However, there are no available SRMs for organics in aqueous samples, due to inherent instability. Therefore, the extraction efficiency for PCBs, OCPs and PBDEs in aqueous samples was checked by the extraction of spiked artificial seawater of a salinity of 30 psu, and the analysis of a pair of spiked and unspiked seawater samples. Spike sample recoveries were also performed for sediment samples to evaluate matrix interferences originating from the different composition of samples. Spiking with standard solution was also conducted to check extraction efficiency of PCBs, OCPs and PBDEs from PUF plugs.

III-7-3 Field and procedural blanks

The analysis of field blanks was performed for GF filters and PUF plugs. Both materials were kept and stored in exactly the same way as those used for sampling so as to evaluate potential contamination during transport and storage. Field blanks were processed in the same way as samples. A procedural blank was prepared by evaporating 600 mL of hexane to 2 mL, with subsequent handling as sample extracts. The limit of detection (LOD) was calculated as the average of five procedural blank peak areas plus three times the standard deviation (SD) (Brügmann and Kremling, 1999). Only concentrations above LOD were reported.

III-7-4 Replicates

Samples were collected and analysed in duplicates, unless otherwise specified. The concentrations of the duplicate samples were compared by their relative percent difference, RPD = (A-B)/(average of A and B), according to the procedure of the International Organization of Standardization (ISO/IEC 17025, 2005).

III-7-5 Quality assurance for GC-MS and GC-IT-MSMS analysis

External calibration was undertaken for POPs quantification during the first two studies described in Chapters IV and V. $^{13}C_{12}$-labeled PCB congeners 32, 141 and 208 were used as internal standards for the other studies and added to samples prior to analysis.

For GC-MS analysis, analytes with a difference in retention time of more than 0.1 min relative to standards were not quantified. For each analyte, a minimum of two ions were monitored and peaks with a primary to secondary ion ratio of more than a 20% variation from the standards were not quantified. Given the low expected analyte concentrations in seawater samples, this was considered to be acceptable for positive identification, as suggested by Erickson (1997).

For GC-IT-MSMS analysis, three quality control criteria were applied to ensure correct analyte identification: (a) a signal to noise ratio greater than three; (b) GC retention times matched (±0.1 min) those of standard compounds; and (c) the threshold match, calculated by GC-IT-MSMS software using library and sample spectrum, was greater than 600. The value of 600 was derived from a comparison of the threshold match of both standard solution and samples.

III-8 Safety and Good Laboratory Practices

III-8-1 Chemical handling

As discussed in Chapter II, POPs are toxic to human health and potentially carcinogenic. All standards containing POPs and sample extracts were kept in sealed containers in a freezer dedicated for chemical and sample storage. POPs standards, sample extracts, solvents and any other harmful chemicals were handled under a fume hood with good ventilation. Personal protection, including lab coat, nitrile gloves and safety goggles were worn in the laboratory. Respiratory masks were available and worn when necessary. Solvent and solid contaminated wastes (e.g. used silica gel) were collected for sending to a chemical recycling company.

III-8-2 Equipment safety

High pressure inside the extraction vessel of the MAE system may occur in rare circumstances. To avoid any hazard, the vessels are equipped with membranes which disrupt at 200 psi to release pressure, where escaping fumes would be diverted under a fume hood.

GC-MS equipment does not represent any major hazard. To avoid emission of any contaminants in ambient air, an active carbon filter was installed on the rotary pump and good ventilation in the laboratory was ensured.

III-8-3 Operations on research vessel

During operations on the research vessel, the general safety instruction from the Tropical Marine Science Institute, National University of Singapore was followed. No sampling was conducted near shipping lanes, or at locations which could cause any harm to the crew or researchers onboard. The instructions of the captain and crew members were followed strictly and promptly.

CHAPTER IV

Occurrence of Persistent Organic Pollutants (POPs) in Singapore's Coastal Marine Sediments and Ecotoxicological Assessment

IV-1 Introduction

Sediments, particularly estuarine sediments, are one of the major sinks for persistent organic pollutants (POPs) in the marine environment. Most have a relatively short residence time in the water column, due to their hydrophobic character (low water solubility) which leads to bioaccumulation and strong sorption onto suspended particulate matter (SPM). They are carried to bottom waters and are finally trapped in marine sediments, even in sediments of the deep ocean (Gustafsson et al., 1997). The key concern associated with contaminants adsorbed to sediments is that many commercial marine species and food-chain organisms spend a major portion of their life-cycle living in or on marine sediments. Dave and Nilsson (1999) reported that sediments collected from the open ocean, far from any industrial and agricultural activity, were contaminated with POPs and showed toxicity to marine species. Bottom-dwelling organisms collected in the Canadian Arctic showed elevated concentrations of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) (Bright et al., 1995), thereby indicating widespread dispersion of these contaminants in sediments. POPs are not necessarily fixed permanently in sediments, but may be remobilized via sediment disturbances and changes in both redox potential and pH as reviewed by Eggleton and Thomas (2004).

Past and on-going reclamation, dredging, construction and shipping activities impact Singapore's marine environment, as pointed out by Najar et al. (2003). Voie et al. (2002) suggested that dredging may resuspend fine, contaminated particles that eventually re-settle on the seabed forming a thin, contaminated sediment layer. These particles may originate from relative sediment layers that originally settled on the seabed several decades ago, at a time when POPs were highly prevalent. Zhang et al. (2004) predicted that high shear velocities within the bottom boundary layer of Singapore's water column produces high levels of shear stress and turbulence, with the potential for sediment resuspension and transport. On the other hand, commercial marine organisms including filter feeding species are cultured in Singapore's waters (Chou and Lee, 1997).

The objective of this study was to collect marine sediments from Singapore's coastal environment and evaluate prevailing levels of OCPs, PCBs and polybrominated diphenyl ethers (PBDEs) within the context of reported values from elsewhere, and with reference to available sediment quality and exotoxicological standards.

IV-2 Materials and Methods

IV-2-1 Sample collection

Thirteen surface sediments were collected in June 2003 using a grab sampler. Sampling stations were located in northeastern (sample series NE) and southwestern (sample series SW) coastal regions of Singapore (Figure IV-1). Stations in the southwestern region were located adjacent to petroleum refining industries and adjacent to major shipping lanes. Stations in the northwestern region are affected by shipping lanes, land reclamation and catchment run-off.

After collection, samples were stored at –20 ºC. Prior to further sample extraction, samples were defrosted, dried at 35 ºC for 12 h in an oven and homogenized.

IV-2-2 Sample treatment and analysis

Five grams of sediment were extracted using a microwave assisted extraction (MAE) procedure, as described in Chapter III-4. Sediment samples were weighed in a teflon-lined extraction vessel. Sediment samples were extracted in duplicate, whereas 10 µL, 10 µl and 5 µL of OCP (1000 µg/L), PBDE (1000 µg/L), and PCB (500-2000 µg/L) standard solution were added respectively to one of the duplicates to test for recovery of the analytes. To every sample and blank 10 µL of Pentachloronitrobenzene (PCNB, 1000 µg/L) standard were added as surrogate standards. The samples were extracted with 50 mL of acetone-hexane (3:2) in a microwave oven CEM Mars X (CEM, Matthews, NC, USA) for 18 min at 115 °C. After extraction, the vessels were allowed to cool to room temperature. The supernatant was filtered through glass wool and combined with 2-3 mL acetone-hexane (3:2) to rinse the extraction vessel. The extracts were concentrated to approximately 2 mL in a rotary vacuum evaporator at 25 °C. A cleanup column, containing 6 g of silica gel topped with 2 cm of sodium sulfate was used for cleanup of the extracts (see Chapter III-5). The extracts were then concentrated to approximately 5 mL in a rotary evaporator at 25 ºC, and then further to 1 mL under a gentle gas stream of purified nitrogen. The extracts were kept in sealed vials at –20 ºC prior to analysis. Sample analysis was conducted using a Shimadzu QP5050 GC-MS, as described in Chapter III-6-1. All results for sediment analysis are reported on a dry-weight basis.

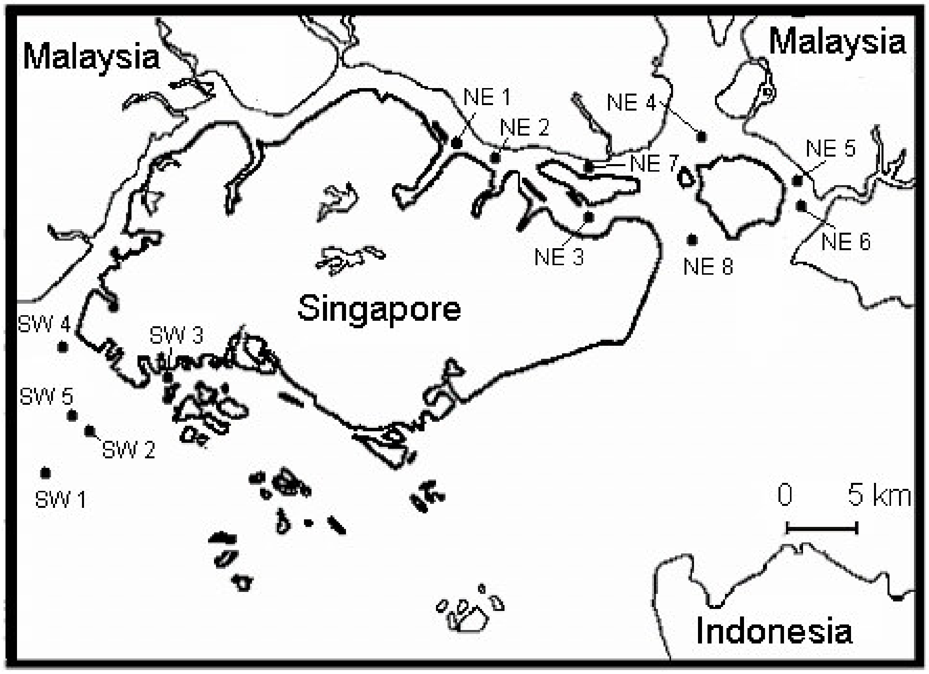


Figure IV-1: Location of sample stations

IV-3 Results and Discussion

IV-3-1 Quality assurance

The complete analytical procedure was validated by analyzing the sediment standard reference material 1941b (NIST). Results for the reference material were within the range of certified values specified for the target compounds – except for the result for CB 128 which was out of range by 3%. Spiked sample recoveries of PCBs, PBDEs, DDTs, HCHs, Chlordane´s, Heptachlor, Heptachlor epoxide, Dieldrin, Aldrin, Endrin´s, Endosulfan I/II, Endosulfan sulfate, Mirex, Methoxychlor were in the range of 79-104%, 82-95%, 75-126%, 68-125%, 67%-122%, 71-99%, 75-120%, 70-108%, 73-122%, 83-109%, 75-123%, 76-107%, 72-95% and 69-86%, respectively. Recovery of surrogate standard was in a range of 88 to 97% for all samples. The relative percent differences (RPD) of duplicate samples were in a range between 2 and 12%. Procedural blanks were included with each batch of eight sediment samples. Control standards were included every six samples during analysis to check instrument performance.

IV-3-2 Polychlorinated biphenyls (PCBs)

Concentrations of PCB congeners and ΣPCBs are summarized in Table IV-1. Total PCB concentrations ranged widely from 1.4 to 329.6 ng/g. High concentrations were found in samples close to highly industrialized areas dominated by petrochemical plants. A notable decline in the concentration of ∑PCBs could be observed seawards from stations SW 3 over SW 2 to SW 1 (62.2–14.1 ng/g), and confirms a dispersion of PCBs moving seaward. A concentration of 138.5 ng/g was found in the Straits of Johor, at northern part of Singapore (NE 2). Shipyards and industrial areas are likely sources for PCBs in this area. Lower concentrations of ΣPCBs between 1.4 and 55.4 ng/g were found in the northeastern part of Singapore, which is affected by agricultural and fish farming activities. Relative high concentrations of higher chlorinated PCBs (62–69% chlorination grade) were found in the sediment samples, which are less volatile and therefore more persistent. Dominant higher chlorinated congeners were PCB 206 and 208. Aroclor 1260, 1262, 1264 and 1270 contain these higher chlorinated PCBs, and therefore may be the origin of PCBs found in the marine sediments of Singapore.

Principal Component Analysis (PCA) was applied to the relative composition of samples, normalized to the concentration of ∑PCBs and specific Aroclor congener composition profiles (Figure IV-2). All samples are similar in composition to Aroclor 1221, 1232 and 1242 but not absolutely equivalent (Group II), except for those samples collected from stations SW 1 and SW 4, which are more similar to Aroclor 1254 (Group I).

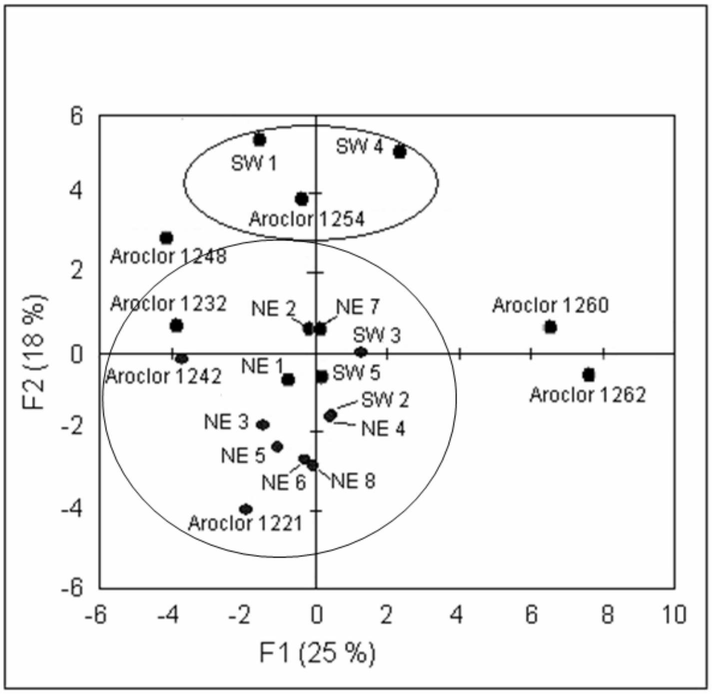


Figure IV-2: PCA score plot of the composition of PCB congeners and Arochlor mixtures in marine sediments. Congener specific concentrations were normalized to total sediment concentrations at each location.

Stations SW 1 and SW 4 are located furthest from the industry area of Jurong Island. Sediment PCB composition at stations SW 3 and NE 1 had the most similar profile to Aroclor 1242, where SW 3 is located closed to Jurong Island and NE 1 is close to shipyards. Sediments collected at stations NE 5, NE 6 and NE 8 located south of the island Pulau Tekong showed a PCB composition most similar to Aroclor 1221. However, samples collected further inside the Straits of Johor, at sample locations NE 3, NE 4 and NE 7 have a more variable PCB composition.

Station	SW1	SW2	SW3	SW4	SW5	NE1	NE2	NE3	NE4	NE5	NE6	NE7	NE8
PCB 28	< 0.6	< 0.6	< 0.6	31.9	7.9	4.5	7.7	7.5	< 0.6	< 0.6	5.7	< 0.6	< 0.6
PCB 31	0.3	< 0.03	8.0	8.9	< 0.03	0.4	7.4	< 0.03	7.2	< 0.03	< 0.03	1.0	0.2
PCB 33	< 0.3	< 0.3	14.3	11.4	< 0.3	< 0.3	12.7	1.7	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
PCB 44	0.8	< 0.2	< 0.2	13.3	1.3	1.7	5.6	2.2	1.0	0.8	< 0.2	3.4	< 0.2
PCB 49	< 0.3	< 0.3	3.9	10.7	0.4	2.0	7.5	1.4	1.6	0.7	< 0.3	< 0.3	< 0.3
PCB 53	0.6	< 0.1	2.7	11.2	1.5	1.2	5.8	1.0	< 0.12	< 0.1	< 0.1	2.7	< 0.1
PCB 70	0.7	< 0.2	3.2	13.3	1.2	1.5	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
PCB 74	1.0	< 0.3	< 0.3	13.9	1.4	1.5	7.0	2.2	< 0.3	< 0.3	< 0.3	3.0	< 0.3
PCB 87	2.2	0.9	< 0.3	13.3	< 0.3	2.1	2.4	2.5	< 0.3	1.2	< 0.3	2.9	< 0.3
PCB 118	1.5	< 0.2	< 0.2	13.6	< 0.2	< 0.2	4.0	< 0.2	< 0.2	< 0.2	< 0.2	3.4	1.2
PCB 128	< 0.2	< 0.2	1.3	13.1	1.2	< 0.2	4.5	1.4	< 0.2	< 0.2	< 0.2	1.8	< 0.2
PCB 138	1.2	1.2	0.7	13.9	1.1	1.5	4.5	1.2	1.3	0.7	< 0.4	1.8	< 0.4
PCB 153	< 0.2	13.3	19.4	0.6	0.9	21.9	13.6	1.7	2.2	< 0.2	13.0	< 0.2	< 0.2
PCB 206+208	< 0.4	10.0	< 0.4	< 0.4	41.0	16.7	21.3	36.1	15.0	35.8	15.5	27.7	< 0.4
ΣPCB	14.1	29.1	62.2	329.6	72.5	60.6	138.5	79.8	34.6	44.7	38.3	55.4	1.4
BDE-47	3.4	4.0	11.1	4.5	4.7	3.7	13.8	5.1	4	3.8	5.5	4.3	12.7

Table IV-1: Sediment mean concentrations of major PCB congeners, ΣPCB and BDE 47 in ng/g dry weight .

PCA analysis could not confirm the presence of Aroclor mixtures containing higher chlorinated PCB congeners. This may be due to the presence of only two major congeners PCBs 206 and 208, compared to the wider presence of tri-, tetra-, penta- and hexa-chlorinated homologs. Therefore, it is suggested that a variety of Aroclor mixes of lower (21–42%) and higher (>60%) chlorination grade were introduced to Singapore's marine environment in the past. The PCB composition profile found in tissues of the filter feeding green mussel (*Perna viridis*) collected from Singapore's coastal waters was found to be similar to that of Aroclor 1254 (Bayen et al., 2003). Green mussels feed mainly on particulates in seawater, and the PCB composition may be different to that found in bottom sediments. However, highly chlorinated PCBs with a high K_{ow} are more likely to be adsorbed to suspended particulate matter (SPM) than low chlorinated PCBs (Hong et al., 2003). Settlement of suspended particulate matter onto the seabed may therefore lead to relatively elevated concentrations of higher chlorinated PCBs in the sediments. Hartmann et al. (2004) reported a relatively enriched fraction of higher chlorinated PCB congeners in surface sediments from the Narragansett Bay, USA. Import of PCBs was banned in Singapore in 1980, Malaysia in 1995 and in Indonesia in 1994, but continued use of PCBs is reported for the Philippines and Vietnam (UNEP, 2002a).

IV-3-3 Organochlorine pesticides (OCPs)

Concentrations of OCPs are summarized in Table IV-2. Concentrations of ΣHCHs (sum of α-, β-, γ- and δ-HCH) ranged from 3.3 ng/g at Station SW 4 to 46.2 ng/g at station NE 2. 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. These levels are comparable to those reported in Hong Kong (0.1–16.7 ng/g) by Richardson and Zheng (1999), but higher than those reported for Daya Bay, China (0.3–4.2 ng/g) by Zhou et al. (2001) (Table IV-3). The mean percentage composition of α-, β-, γ- and δ-HCH to ΣHCHs for sediments analysed in this 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 to lead to an accumulation of β-HCH in sediments, and a 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. Evidence of ongoing usage of HCH in Southeast Asia is presented in Chapter VIII. Indonesia banned Lindane (γ-HCH) in 1991 and Thailand in 2002 (UNEP, 2002a). However, Lindane may still be used on palm oil and coconut plantations in Malaysia (UNEP, 2002a).

Concentrations of ΣDDT ranged from 2.2 to 11.9 ng/g 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, 0.1–20.3 and 2.5–11.9 ng/g, respectively (Table IV-3). The concentrations of DDT and its metabolite DDD and DDE are higher at sample stations around Jurong Island (SW 1 to SW 5) by a factor of around 2 compared to sediments from the Straits of Johor (NE 1 to NE 8), in particular concentrations of DDT. The highest concentrations for ΣDDT were found at stations SW 4 and SW 5 at 11.9 and 10.5 ng/g, respectively and the lowest at both stations NE 2 and NE 4 at 2.2 ng/g. However, the ratio of DDT to the sum of DDE and DDD is smaller than 1 (range of 0.20–0.77) at all stations, implying that there has been no recent introduction of DDT to the marine environment of Singapore. Bayen et al. (2004a) made the same conclusion, based on levels of DDTs in the tissues of green mussels (*P. viridis*). As DDT has been banned for a longer period than HCHs in many countries of Southeast Asia, DDT is present at a lower concentration.

Station	SW1	SW2	SW3	SW4	SW5	NE1	NE2	NE3	NE4	NE5	NE6	NE7	NE8
α-HCH	4.4	4.9	7.2	0.9	2.0	2.6	8.4	5.8	6.4	4.6	9.3	2.9	2.4
β-HCH	3.2	5.3	4.6	0.7	2.6	4.3	11.1	5.2	6.0	4.1	4.2	4.3	2.7
γ-HCH	3.1	1.1	< 0.7	0.8	3.5	2.7	13.4	8.8	5.7	7.7	< 0.7	5.1	2.6
δ-HCH	3.1	1.4	7.2	0.9	3.3	5.3	13.3	2.9	5.2	4.0	8.0	3.8	2.3
ΣHCH	13.8	12.7	19.0	3.3	11.4	14.9	46.2	22.7	23.3	20.4	21.5	16.1	10
DDT	3.5	3.6	2.5	3.2	4.2	2.3	< 0.5	2.1	< 0.5	< 0.5	0.6	1.9	2.2
DDD	2.8	1.5	3.5	4.0	3.7	1.8	1.3	2.4	1.5	1.5	2.1	3.2	3.8
DDE	2.5	0.6	2.7	4.7	2.6	1.1	0.9	1.6	0.7	1.2	1.6	4.1	3.7
ΣDDT	8.8	5.7	8.7	11.9	10.5	5.2	2.2	6.1	2.2	2.7	4.3	9.2	9.7
cis Chlordane	0.8	1.0	<0.3	9.0	0.6	1.1	1.1	1.1	1.3	1.3	1.4	8.5	2.5
trans-Chlordane	1.5	2.9	1.4	9.7	1.2	1.7	1.5	1.3	1.4	1.9	1.3	10.0	4.0
Heptachlor	2.7	1.2	< 0.9	0.9	2.0	4.2	< 0.9	9.0	< 0.9	2.3	< 0.9	2.9	4.6
Heptachlor epoxide	6.8	2.9	< 0.7	0.8	6.7	6.1	< 0.7	5.9	< 0.7	3.2	5.5	4.3	5.1
Aldrin	< 0.3	< 0.3	< 0.3	< 0.3	1.2	< 0.3	< 0.3	< 0.3	0.6	1.4	1.1	1.0	0.5
Dieldrin	4.4	1.7	3.7	< 1.2	1.9	3.4	3.8	4.0	2.2	3.8	2.3	3.9	1.6
Endrin	3.4	2.0	< 1.3	< 1.3	3.4	2.2	< 1.3	< 1.3	4.0	2.9	< 1.3	< 1.3	< 1.3
Endrin aldehyde	2.9	3.0	< 2.0	< 2.0	2.5	3.4	2.1	< 2.0	4.2	4.1	< 2.0	< 2.0	< 2.0
Endosulfan I	< 0.9	< 0.9	< 0.9	< 0.9	2.2	1.0	< 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	1.6	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
Endosulfan sulfate	0.8	< 0.7	< 0.7	1.3	1.0	< 0.7	< 0.7	1.3	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7
Mirex	0.6	0.7	< 0.1	0.6	< 0.1	0.6	1.0	0.9	0.7	0.6	0.8	0.6	< 0.1
Methoxychlor	1.2	< 0.4	0.6	0.5	< 0.4	0.6	0.5	1.2	< 0.4	0.8	0.7	< 0.4	< 0.4

Table IV-2: Sediment mean concentrations of OCPs in ng/g dry weight.

Among the chlordane-related compounds (*cis*-Chlordane, *trans*-Chlordane, Heptachlor and Heptachlor epoxide), the concentration of ΣChlordane (*cis*- and *trans*-Chlordane) in sediments is high at Station SW 4 and NE 7 at 18.7 and 18.5 ng/g, respectively, and higher by a factor of two compared to reported data from Hong Kong (Table IV-3). At the other stations, the concentration of ΣChlordane ranged between 1.4 and 6.5 ng/g, whereas the concentration of *cis*-Chlordane is either equal or higher by a factor of 2 than the concentration of *trans*-Chlordane. Chlordane was banned in Singapore only in 1999, later than in some other Southeast Asian countries (UNEP, 2002a). Heptachlor was detected at up to 9.0 ng/g and Heptachlor epoxide, a degradation product of Heptachlor, at a peak concentration of 6.8 ng/g. The concentrations of Heptachlor epoxide are higher by factors of 1.1 to 3.4 than Heptachlor, except for sediments from stations SW 4 and NE 3, 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, 2002a).

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). Concentrations of Dieldrin were higher, ranging from below the limit of detection i.e., <1.2–4.4 ng/g. Endrin was detected in a range from below the limit of detection i.e., <1.3–4.0 ng/g. Endrin aldehyde, a metabolite of Endrin, was found in a range of below the limit of detection i.e., <2.0–4.2 ng/g. 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, 2002a).

Location	Year	ΣPCBs	ΣDDTs[g]	ΣHCH	Σchlordane[j]	ΣPBDEs[k]	Reference
Osaka Bay, Japan	1990	63-240[a]	2.3-11.9	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					0.01-2.4	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

[a] PCB mixture basis (Aroclors)

[b] 2 * ΣPCB_{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 x ΣPCB_{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

Table IV-3: Comparison of OCPs, PCBs and PBDEs concentrations in sediments from regions in Asia (ng/g dry weight, n.d.=not detectable).

Endosulfan I, Endosulfan II and Endosulfan sulfate were only detected in sediments from a few stations at low concentrations between 0.8 and 2.2 ng/g. Mirex and Methoxychlor were found frequently among stations at low sediment concentrations ranging from 0.6 to 1 ng/g and 0.5 to 1.2 ng/g, respectively.

IV-3-4 Polybrominated diphenyl ethers (PBDEs)

Among the PBDE congeners measured i.e. BDE 47, BDE 99 and BDE 100 (detection limit of 0.98, 0.92 and 0.87 ng/g, respectively), only BDE 47 could be detected in sediments, at a concentration range of 3.4–13.8 ng/g (Table IV-2). The concentration of BDE 47 was lower and less variable among sample locations relative to PCBs congeners, indicating a more dispersed input of this compound into the marine environment around Singapore. The highest concentrations were found at stations SW 3, NE 2 and NE 8. The main sources of PBDEs at these stations are likely to be harbor and industrial activities, shipyards and intense shipping traffic. Among the other stations, the concentrations of BDE 47 in sediments varied between 3.4 and 5.5 ng/g. Results are higher by a factor of 6 compared to levels reported for Osaka Bay, Japan (Table IV-3). Congeners found in green mussel tissue collected around Singapore were BDE 47 and BDE 99 (Bayen et al., 2003).

IV-3-5 Ecotoxicological assessment

The sediment quality guidelines (SQG) specified by the USEPA (1997) and by the Canadian Council of Ministers of the Environment (CCME, 2002) were used to assess the potential ecotoxicological impacts of organic contaminants measured in the surface sediments of Singapore. Effects range-low (ER-L) and effects range-median (ER-M) values are used to predict potential impacts of contaminants in sediments, whereas ER-L values correspond to the lower 10 percentile and ER-M values to median values, when the chemical concentration of a contaminant in marine sediments are sorted according to the degree of their effects levels. ER-L represents the value at which toxicity may begin to be observed in sensitive marine species, whereas ER-M represents the concentration below which adverse effects are expected to occur only rarely. Beside the threshold effect level (TEL), the probable effect level (PEL) is used as the criterion for the prediction of toxicity, and corresponds to a level above which adverse effects are frequently expected.

Sediment quality criteria and concentration ranges of major POP contaminants are summarized in Table IV-4. The ΣPCB concentration is below the ER-M value (180 ng/g) except at Station SW 4, where a concentration level of 329.6 ng/g exceeds the PEL value of 189 ng/g. Based on these criteria, the toxicity of PCBs in sediments can be ranked as intermediate. For ΣDDT, the levels at all sample locations exceeds the ER-L value, but are significantly lower than the ER-M values, leading to an intermediate ranking of sediment toxicity. The apparent effects threshold (AET) of 9 ng/g for benthic organisms for ΣDDT exposure is exceeded in sediments from stations SW 4, SW 5, NE 7 and NE 8. The PEL value for Lindane (γ-HCH) is exceeded by a factor of up to 11, except for the stations SW 3, SW 4 and NE 6, and ecotoxicological impacts to marine organisms are therefore considered to be likely. The ER-M and PEL values for ΣChlordane are exceeded at Stations SW 4, NE 7 and NE 8 and may be expected to induce ecotoxicological impacts. A PEL value for Heptachlor of 2.7 ng/g is exceeded in sediments collected at stations NE 1, NE 3, NE 7 and NE 8 by factor of up to 3 times. Concentrations of Dieldrin at all sample locations exceed the ER-L of 0.02 ng/g, except at Station SW 4, but are substantially lower than the ER-M of 8 ng/g.

Compound	c_{min}	c_{max}	c_{avg}	ER-L[a]	% above ER-L[b]	ER-M[c]	% above ER-M[b]	TEL[d]	% above TEL[b]	PEL[e]	% above PEL[b]
ΣPCBs	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
ΣDDT	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
ΣChloranes[f]	< 1.67	18.7	5.4	0.5	100	6	23.1	2.26	84.6	4.79	23.1

[a] Effects range-low value.

[b] Percentage of samples above level.

[c] Effects range-median value.

[d] Threshold effect level.

[e] Probable effect level.

[f] Sum of cis- and trans-Chlordane.

Table IV-4: Minimum, maximum and average concentrations of major POP contaminants in ng/g, and corresponding sediment quality criteria.

Only the sediment collected from station SW 1 slightly exceeded the PEL of 4.3 ng/g for Dieldrin, but at 77% of all stations the concentrations exceed the AET of 1.9 ng/g for echinoderm larvae. A PEL of 62.4 ng/g for Endrin was not exceeded in any of the sediments analysed. For Endosulfan I, Endosulfan II and Methoxychlor only the sediment quality advisory levels (SQAL) of 0.29, 1.4 and 1.9 ng/g, respectively are available. These levels are only exceeded in sediments for Endosulfan isomers, but not for Methoxychlor. No threshold levels are available for Mirex. PBDEs are not included in sediment quality guidelines and ER-L, ER-M, TEL and PEL values could not be found in the literature. The concentration levels of PBDE in Singapore's sediments may be classified as high when compared with concentrations reported for sediment from Osaka Bay, Japan (Choi et al., 2003) (Table IV-3).

IV-4 Conclusions

This study has provided data on the levels of selected OCPs, PCBs and PBDEs in surface sediments of Singapore's coastal water, an area with intensive ship traffic and industrial activity. Due to a diversity of inputs including industry, ship traffic, wastewater and sewage discharges, and agricultural runoff from the north, high levels of PCBs as well as the organochlorine pesticides HCH, Chlordane and chlordane-related compounds were found in sediments. However, levels of DDT and its metabolite DDE, and Dieldrin are present at similar or lower concentrations when compared to data reported for Hong Kong, Japan and China. The threshold effects level (TEL) and probable effects level (PEL) are exceeded by one order of magnitude for Lindane (γ-HCH), but not for DDT and its metabolite. The distribution of DDT and its metabolites, suggest no recent input of DDT into Singapore's marine sediments. This is not the case for HCHs isomers, where the profile does suggest recent inputs. PCBs were found at low to high chlorination grades, indicating a diverse input of Arochlor mixtures to the local marine environment. Ship traffic and oil-related industry are likely the sources of PCBs in Singapore’s sediments. Based on the sediment quality guidelines (SQGs) stipulated by USEPA (1997) and those of the Canadian Council of Ministers of the Environment (2002), and via comparison with concentration levels of OCPs, PCBs and PBDEs reported for other countries in Asia, marine sediments in Singapore can be classified as moderately contaminated, with probable ecotoxicological impacts to the marine environment. It is therefore recommended that a more intensive sediment sampling programme be implemented in Singapore, so as to fully evaluate potential ecotoxicological risks arising from contaminated sediment exposure.

CHAPTER V

Occurrence of Persistent Organic Pollutants (POPs) in the Sea-Surface Microlayer (SML) and Seawater during the Northeast Monsoon in Singapore

V-1 Introduction

The tropical climatic zone is characterized by high ambient temperatures and heavy rainfall, which are likely to influence the fate and distribution of POPs in the environment. As pointed out in Chapter II, it is likely that POPs such as organochlorine pesticides (OCPs) are still used in developing Asian countries in both agriculture and public health control. Data for hexachlorocyclohexane (HCH) isomers in air, water, soil and sediments reported by Ramesh et al. (1989, 1990 and 1991) for India were compared by Tanabe (1991) with data from Japan to identify specific behavior patterns of HCH isomers under tropical and temperate climates. HCH isomers were dissipated in air and water faster in the tropical climate of India than the temperate climate of Japan, where this chemical was more associated on soil and sediment particulates. As a general conclusion, the transfer of chemicals, such as HCH isomers into the atmosphere is much greater in tropical than temperate zones. However, Wania et al. (1998) pointed out that wet deposition is an important process, scavenging POPs from the atmosphere to the ocean. The magnitude of this process is related to the intensity of precipitation and its seasonal variations.

Southeast Asia is influenced by the strong northeast monsoon and southwest monsoon, which are characterized by rainfall amounts of about 1200 mm and 700 mm respectively.

The onset of the northeast monsoon occurs in mid-November with a peak the following January, whereas the southwest monsoon prevails between June and September (Lim and Azizan, 2004).

To date, there have been no field studies on how much contamination the SML receives during rainfall events. Therefore, this study was conducted to determine the concentrations of POPs in the SML and seawater samples in a tropical region during the wet season. The first data on concentration and enrichment of POPs in the SML of a tropical climate was acquired, and possible sources identified.

V-2 Materials and Methods

V-2-1 Sample collection

Three sampling surveys were conducted between November 2003 and March 2004 at the coastal sampling stations shown in Figure V-1 and sampling details are given in Table V-1. Stations 1 (Pulau Seletar) and 2 (Pulau Tekong) are affected by shipping traffic and river discharges. Stations 3 (St. John Island) and 7 (Raffles Lighthouse) are located 4 km and 15 km seawards from the main island of Singapore, respectively. Station 3 is likely to be affected by surrounding shipping anchorage. Station 4 (RSYC) is located within a marina and is potentially affected by boat fuelling activities, as well as nearby shipyards and ferry traffic. Stations 5 (Povan Reservoir) and 6 (Kranji) are located nearby mangrove areas, and areas of fish farming and agricultural activities.

The sampling procedure for the collection of SML and seawater samples is provided in detail in Chapter III-3-1. The revolution rate of the glass drum was set to 7-8 rpm, resulting in a thickness of collected SML of between 20 and 60 μm (average 48 ± 8 μm). For this study, all SML and seawater samples were collected unfiltered directly into 10 liter glass container attached to the SML sampler, as described in Chapter III-3-1.

Only two rainwater samples of sufficient volume could be collected in March 2004. The samples were collected four km north of Station 4 at the Tropical Marine Science Institute/National University of Singapore. Approximately, one liter rainwater samples were collected in glass container using a stainless steel funnel (0.4 m in diameter).

Meteorological data and temperature of the surface water (0.5 and 40 cm depth) were recorded at each sample location and are summarized in Table V-1.

V-2-2 Sample treatment and analysis

All seawater, SML and rainwater samples were spiked with Pentachloronitrobenzene (PCNB) surrogate standard and extracted within a few hours of collection, as described in Chapter III-4-1. Rainwater samples were extracted by following the procedure for the extraction of seawater (Chapter III-4-1), but the volume of hexane used was 3x50 ml. All extracts were cleaned-up using a silica gel column, using the procedure described in Chapter III-5. Analysis of sample extracts was performed on a Shimadzu QP5050 GC-MS, according to the procedure described in Chapter III-6-1.

Location	Date	γ [µm][a]	Current	Tide	Wind Speed [m/s]	Temperature [°C]			Humidity [%]	Slick {%}[d]
						Air	Surface Water[b]	Water[c]		
Survey 1										
1	07.11.03	40	calm	low	0.7	32.4	31.7	30.3	60	50
2	18.12.03	52	moderate	high	1.7	28.7	29.2	28.6	71	0
3	11.12.03	41	moderate	high	2.2	28.2	28.9	28.2	60	0
4	05.11.04	47	calm	low	1.1	26.9	28.5	28.0	79	30
5	19.11.03	50	low	low	2.1	30.7	30.7	29.7	71	5
6	17.12.03	51	low	low	2.3	28.7	29.5	28.2	62	15
Survey 2										
1	14.01.04	41	calm	low	2.4	29.5	29.3	27.7	70	20
2	05.02.04	53	calm	high	2.1	29.6	28.4	28.3	69	0
3	09.02.04	43	moderate	low	2.2	29.2	30.0	28.3	63	0
4	21.01.04	40	calm	high	1.3	27.6	23.8	23.6	64	20
5	15.01.04	45	low	low	1.7	29.3	29.3	28.1	68	10
6	04.02.03	44	moderate	high	3.8	28.8	29.3	28.1	71	15
Survey 3										
1	03.03.04	60	calm	low	2.6	30.6	31.2	30.3	60	20
2	17.03.04	20	strong	high	2.9	29.6	28.9	28.5	60	0
3	18.03.04	22	strong	high	2.5	32.2	28.7	28.0	72	0
4	11.03.04	42	low	low	1.9	28.5	28.4	28.1	77	25
5	04.03.04	46	low	low	1.5	27.4	27.5	26.8	71	10
6	10.03.04	47	low	low	3.2	29.3	27.5	27.0	68	20
7	24.03.04	48	low	low	1.2	30.2	29.2	28.7	63	0

[a] Thickness of collected SML

[b] at depth 0.5 to 1 cm

[c] at depth 40 cm

[d] visual observation according to IOC (1985)

Table V-1: Description and environmental characteristics (seawater and atmosphere) of sample stations.

V-3 Results and Discussion

V-3-1 Quality assurance

In this study, Pentachloronitrobenzene (PCNB) was used as a surrogate standard and analyte recoveries were between 78 and 92%. Seawater samples (n=7) were collected at Station 4 prior to the first sampling event and used to check recoveries of spiked seawater samples. Samples were split into two sub-samples and then analysed unspiked and spiked with OCP and polychlorinated biphenyls (PCB) standard solution. Spiked sample recoveries of PCBs, dichlorodiphenyltrichloroethane (DDTs), HCHs, Chlordane's, Heptachlor, Heptachlor epoxide, Dieldrin, Aldrin, Endrin ketone and aldehyde, Endosulfan I/II, Endosulfan sulfate and Methoxychlor were in the range of 79-104%, 82-95%, 75-126%, 68-125%, 67-122%, 71-99%, 75-120%, 70-108%, 73-122%, 83-109%, 75-123%, 76-107%, 72-95% and 69-122%, respectively. The efficiency of the extraction method for unfiltered seawater samples was checked by analyzing the extracts from consecutive extraction steps (as described in Chapter III-4-1), and recoveries were considered to be satisfactory after three extraction steps.

Since the SML sampler was used for the first time during this study, sample collection time was limited. Consequently, only samples from Station 4 were collected in triplicate and as single samples at other sample stations. Analysis of triplicate samples yielded a reproducibility of the overall method better than 25% for OCPs and 22% for individual PCB congeners. Method blank analysis was conducted for every six samples. Analysis of a control standard was carried out for every four samples analysed, so as to check the overall performance of the analytical system during analysis.

V-3-2 Concentration levels of POPs in the SML and seawater samples

Among the nineteen OCPs analysed, HCHs isomers (α-HCH, β-HCH, γ-HCH and δ-HCH) and DDT residues (p,p'-DDT, p,p'-DDD and p,p'-DDE) were most abundant in subsurface and SML samples. The concentration range for ΣHCH and ΣDDT in subsurface water varied from 0.4 to 27.2 ng/L and 10 to 630 pg/L, respectively and in SML samples from 0.6 to 64.6 ng/L and 6 to 650 pg/L, respectively (Figure V-1 and V-2). Data for OCP concentrations for subsurface water in this study are comparable with previous studies on bulk seawater conducted elsewhere in Southeast Asia (Table V-2). However, the concentrations of OCPs reported for the SML in this study are lower than those available data from the 1980's reported for SML samples taken from coastal areas in temperate regions of the world, by a factor of 20 up to 700 for DDT and its metabolites, and up to 3 for HCH isomers (see Table II-2) (Wurl and Obbard, 2004). The enrichment factors (EF) of OCPs in the SML relative to subsurface water for ΣHCH and ΣDDT were 0.8 to 6.9 and 0.2 to 7.6 respectively, but generally ranged between 1.2 and 4.0. EF values are lower for Singapore SML samples compared to those collected in coastal areas from temperate climatic zones. EF values reported for an estuary in Argentina ranged between 0.1 and 23.1(Sericano and Pucci, 1984) and 0.2 to 93 in coastal offshore waters of Croatia (Picer and Picer, 1992). Comparable EF values of 1.7 to 3.5 were reported for SML samples collected in the subtropical zone of Alexandria, Egypt (Abd-Allah, 1999).

Concentration of other OCPs in seawater samples (SML and subsurface) were mainly below the limit of detection, ranging between 0.01 and 0.2 ng/L among all sample stations. At sample location no. 6 (Kranji), Endosulfan I, Endosulfan II, Aldrin, and cis- and trans-Chlordane were present at above limits of detection for the first and third survey in November/December 2003 and March 2004 respectively. The wider range of OCPs detected at this location may be due to discharges from agricultural catchments to the north of Singapore.

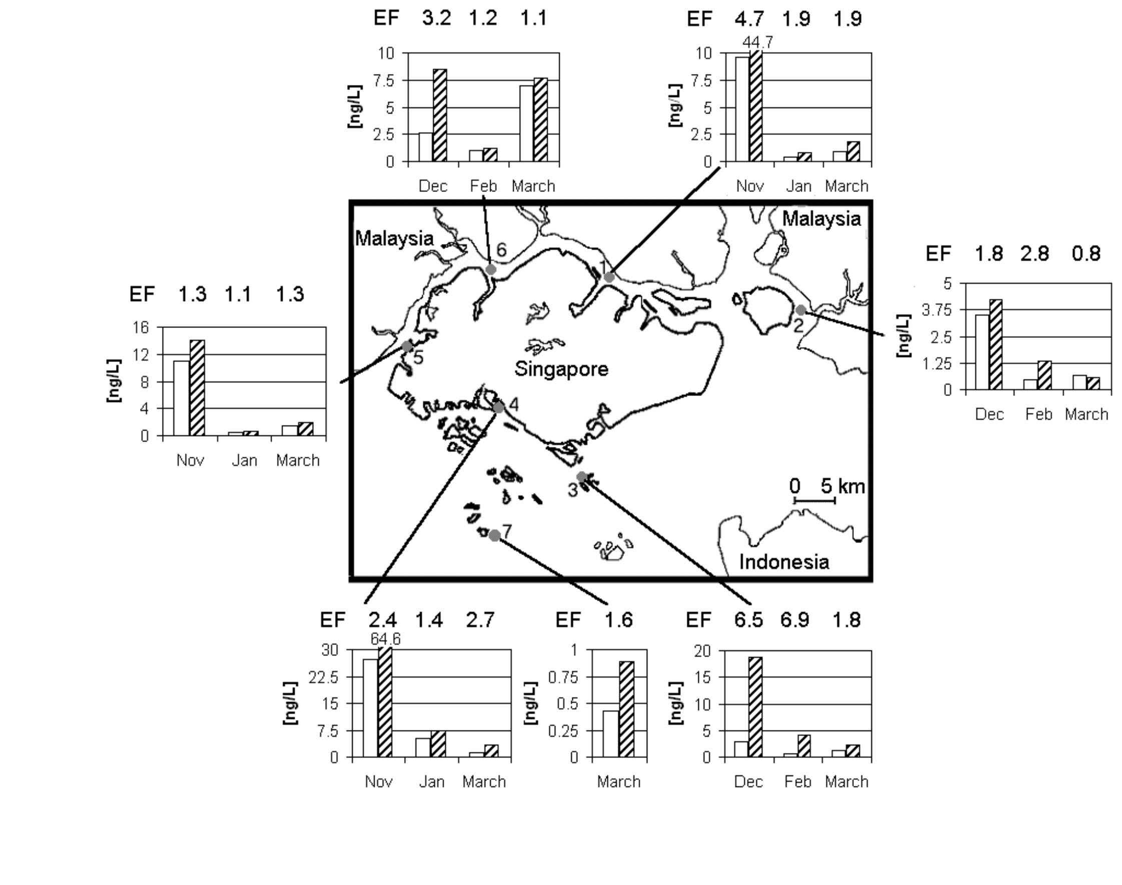


Figure V-1: Concentration and enrichment factors (EF) of ΣHCH in seawater (□) and SML (▨).

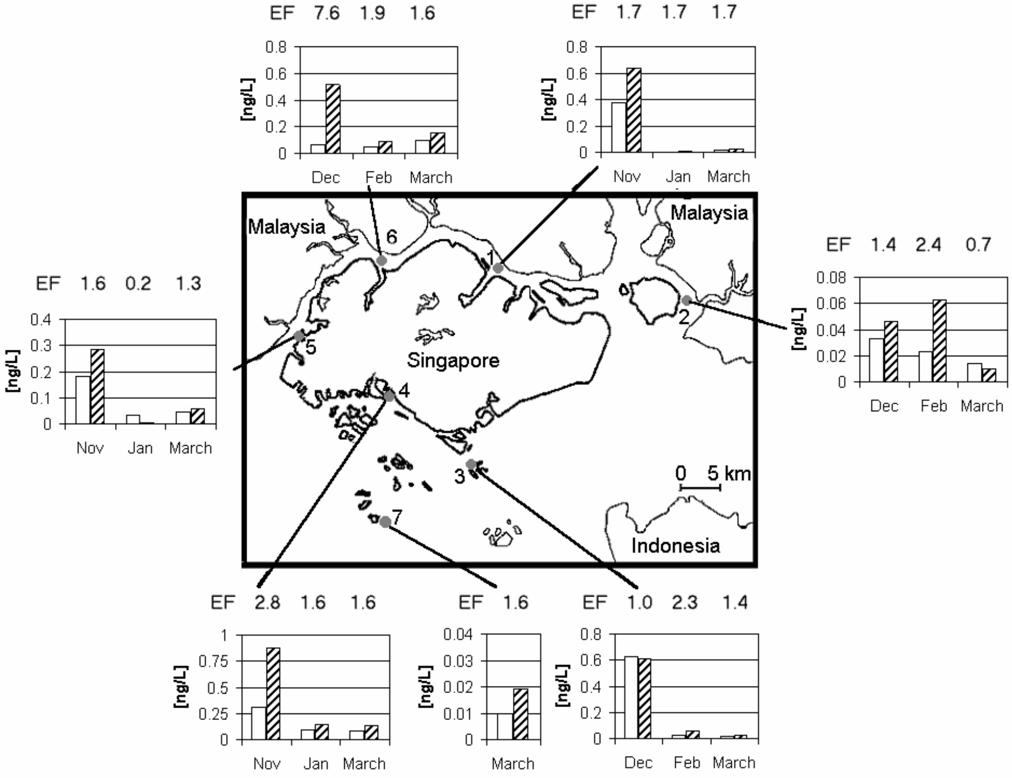


Figure V-2: Concentration and enrichment factors (EF) of ΣDDT in seawater (☐) and SML (▨).

Location	Year	ΣPCBs	ΣDDTs	ΣHCHs	Reference
South China Sea[a]	1989/1990	0.01 - 0.033[c]	0.004 - 0.012[e]	0.007 - 0.91[i]	Iwata et al., 1993
Strait of Malacca, Malaysia[a]	1989/1990	0.02[c]	0.007[e]	0.48[i]	Iwata et al., 1993
Java Sea, Indonesia[a]	1989/1990	0.022[c]	0.006[e]	0.058[i]	Iwata et al., 1993
Indonesia[b]	1999			42.2[f]	UNEP, 2002
Phillipines[b]	1999			11.1[f]	UNEP, 2002
	2000		7.4[f]	10.1[f]	UNEP, 2002
Thailand[b]	1999		3.72[f]	15.3[f]	UNEP, 2002
	2000			14.25[f]	UNEP, 2002
Viet Nam[b]	1999		49.27[f]	13.3[j]	UNEP, 2002
Singapore[b]	2002	0.04 - 61.76[d]	0.03 - 2.58[g]	1.93 - 18.44[k]	Basheer et al., 2003a
Singapore[b]	2004	0.045 - 1.80[c]	0.01 - 0.63[h]	0.43 - 27.16[l]	this study

[a] open ocean

[b] coastal water

[c] sum of 40 PCBs congeners

[d] sum of 8 PCB congeners

[e] sum of p,p'-DDE, o,p'-DDT and p,p'-DDT

[f] sum not specified

[g] sum p,p'-DDD and p,p'-DDT

[h] sum p,p'-DDE, p,p'-DDD and p,p'-DDT

[i] sum of α-HCH and γ-HCH

[j] only γ-HCH

[k] sum of α-HCH, β-HCH and γ-HCH

[l] sum of α-HCH, β-HCH, δ-HCH and γ-HCH

Table V-2: Reported concentrations (ng/L) of OCPs and PCBs in bulk seawater in the region of Southeast Asia.

Concentrations of ΣPCBs ranged between 0.05 and 1.8 ng/L and 0.07 and 12.4 ng/L in seawater and SML samples, respectively and EF values ranged between 0.7 and 39.6, as shown in Figure V-3. In general, EF values were between 1.1 and 4.0. Concentrations of ΣPCBs in SML samples in this study are lower than for available data reported for SML samples since the early 1980's taken from coastal areas in temperate regions of the world, by a factor of up to 50 (Wurl and Obbard, 2004). The data presented in this study are more comparable with the recently reported concentrations of ΣPCB in the SML collected offshore from Barcelona (García-Flor et. al., 2005) than for data reported in the 1980's for the Rijeka Bay (Adriatic Sea), with concentrations of up to 597 ng/L (Picer and Picer, 1992) and for the harbor of Los Angeles with concentrations ranging between 8,141 to 30,708 ng/L (Cross et al., 1987) (see Table II-2). In comparison, the data of Picer and Picer (1992) and Cross et al. (1987), shows that the area of the harbor of Los Angeles is highly contaminated. The data reported from Abd-Allah (1999) and García-Flor (2005) originated from samples collected within a four-year period in the Mediterranean Sea in the coastal area of Alexandria, Egypt and Barcelona, Spain. In comparison the concentrations of ΣPCB reported in both studies differ by a factor of up to 10, and such a marked decline of PCB contamination in the marine environment of the Mediterranean Sea within this short time period is not probable. It is therefore more likely that concentrations of contaminants in the SML occur in a wide concentration range, most likely due to the heterogonous nature of the SML, as affected by prevailing environmental conditions and industrial activities. However, as seen in Table V-2 the reported PCB concentrations for bulk seawater from this study are substantial lower than reported for Singapore by Basheer et al. (2003a). The extraction method used by Basheer et al. (2003a) is a novel analytical development than one in common practice, and also the availability of various PCB calibration solutions containing commercial mixture or different congener patterns make a comparison of PCB concentrations in environmental samples difficult (Martin et al., 2003).

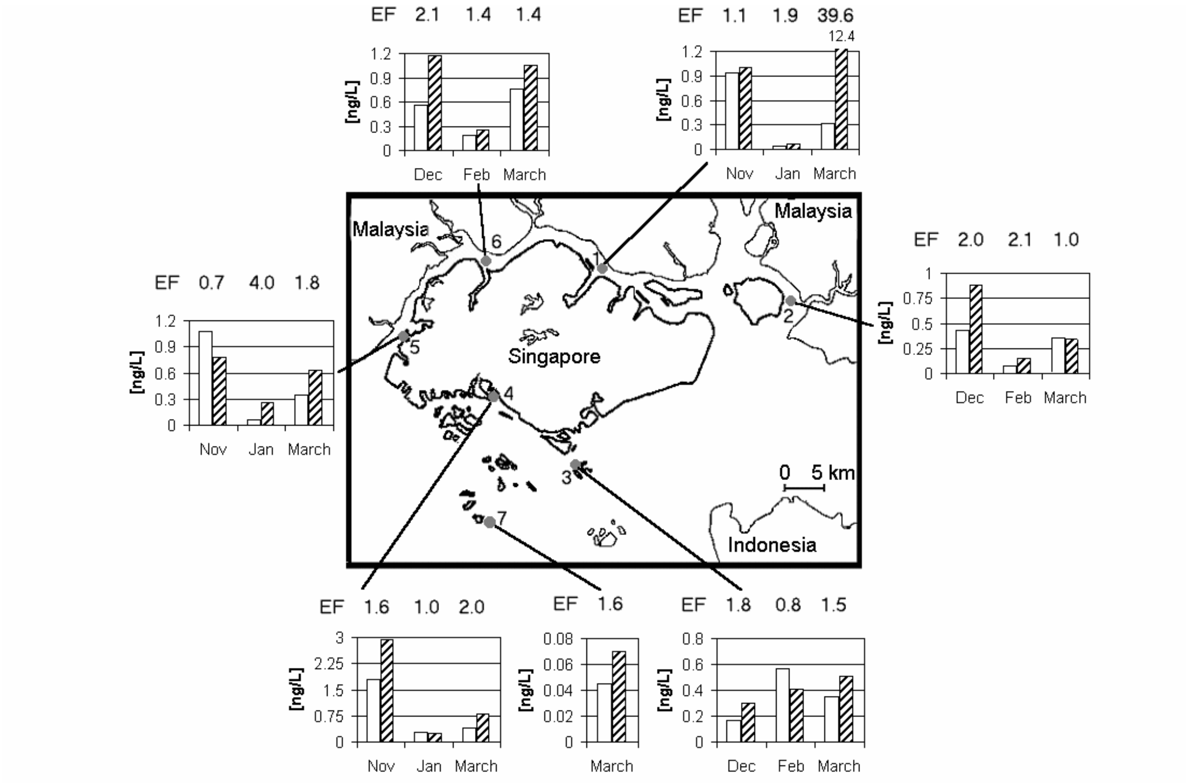


Figure V-3: Concentration and enrichment factors (EF) of ΣPCB in seawater (☐) and SML (▨).

However, it should be noted that a higher surface temperature of the ocean in tropical areas may be expected to lead to a lower concentration level of semi-volatile OCPs and PCBs in the SML compared to temperate climate zones.

V-3-3 Spatial distribution of POPs in SML and seawater samples

The spatial distributions of HCHs, DDTs and PCBs measured in SML and seawater samples are significant. The highest concentrations of ΣHCH, ΣDDT and ΣPCB were found at Station 4, located within a marina. A petrol station and leisure boat activities within the marina led to frequently observed petroleum hydrocarbon slicks on the water surface during sample episodes. Positive correlation between the presence of petroleum hydrocarbon and enrichment of OCPs in the SML was reported by Mikhaylov (1979); Mohnke et al. (1986) suggested that petroleum hydrocarbons may act as an ‘extracting agent’ for OCPs from subsurface waters to the SML. However, in this study, sample collection within visible slicks was avoided, and EF values were comparable to these found at other sample locations. Beside leisure boat activities within the marina, Station 4 may also be affected by nearby shipyards that could act as source of PCB contamination via the dismantling of defunct ship equipment (Hess et al., 2001). Sources of OCPs are likely to include releases from sediment resuspension processes to the water column, as well as wet and dry atmospheric deposition. The lowest concentrations of POPs in the SML and seawater sampler were found 15 km offshore at Station 7. Greater hydrodynamic dispersion and distances from potential contamination sources are known to result in a declining gradient of contaminant levels in both subsurface and SML waters (Sericano and Pucci, 1984; Cross et al., 1987; Picer and Picer, 1992). At Station 3, 4 km offshore, the concentrations of ΣHCH and ΣPCB were higher by factor of up to 10 compared to Station 7, and likely more affected by shipping activity and nearby anchorage. Station 1 is located inside the Straits of Johor with low hydrodynamic influences, whereas Station 2 is characterized by stronger currents and river run-off. Generally the concentrations are lower at Station 1 compared to Station 2.

V-3-4 Temporal distribution of POPs in the SML and seawater samples

An evaluation of the temporal distribution of contaminants shows a significant decline of concentrations during the second survey (January-February 2004) compared to the first (November-December 2003) by a factor of up to 50 (see Figure V-1 to 3). Precipitation patterns for Singapore in 2003 and 2004 show that most rain fell between November and mid-January 2003 during the northeast monsoon (approximately 250 mm per month) and in March 2004 (approximately 400 mm). The lowest precipitation events, at 25 mm rainfall, were reported in February 2004 (NEA, 2004). No temporal trend of the EF values of POPs in the SML has been observed.

V-3-5 Effects of precipitation on concentrations of POPs in SML and seawater samples

Figure V-4 and V-5 illustrate the appearance of unfiltered SML and subsurface water samples collected before and after a rainfall on the 4th March 2004 at Station 5 respectively. The blackish appearance of the SML samples collected after the rainfall event may originate from soot particles, as observed visually on the water surface. The appearance of the subsurface sample collected after the rainfall event was visually identical to the subsurface sample collected before the rainfall event, suggesting that the particulates were derived from wet atmospheric deposition.

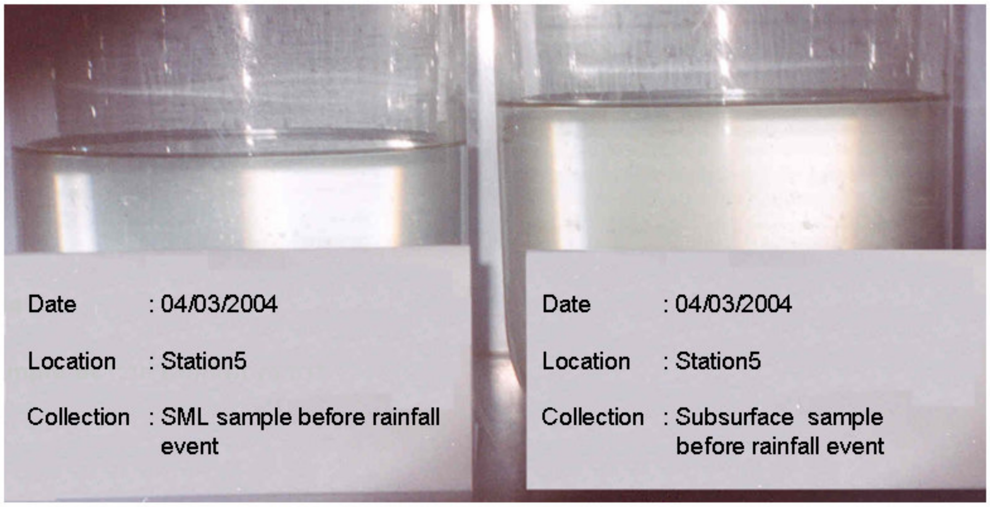


Figure V-4: SML and subsurface samples collected before a rainfall event

Figure V-5: SML and subsurface samples collected after a rainfall event.

It can be concluded that wet deposition was a major source of particulates to the SML, but not for the subsurface layer - at least initially. It is plausible that the subsurface water is affected by the wet deposition via gravitation sinking of particulates, but the extent and significance of this phenomenon could not be ascertained from this study.

During the first (5th November 2003) and third (4th March 2004) survey, SML and subsurface samples were collected prior to and after a heavy rainfall event at Station 4 and 5 respectively. The load factor (LF) (Table V-3), or the enrichment of contaminants before and after a rainfall, is insignificant for subsurface water, but between 2 and 6 greater for the SML. This indicates that wet deposition is a significant source of HCH isomers, DDTs and PCB congeners to the SML, but not for subsurface water. Consequently, the EF value increased significantly after a rainfall event, by up to 20 times.

	Concentration in (ng/L)				Load factor (LF) [a]	
	Before precipitation		After precipitation			
	Sub	SML	Sub	SML	Sub	SML
Station 4 (5th Nov 2003)						
ΣHCH	27.2	64.6	26.1	352	1.0	5.4
ΣDDT	0.3	0.9	0.2	2.2	0.7	2.4
ΣPCB	1.8	2.9	0.8	17.3	0.4	6.0
Station 5 (4th March 2004)						
ΣHCH	1.5	2.0	1.5	3.9	1.0	2.0
ΣDDT	0.04	0.06	0.06	0.3	1.5	5.0
ΣPCB	0.4	0.6	0.3	1.9	0.8	3.2

[a] LF= $c_{Sub, SML}$ (after) / $c_{Sub, SML}$ (before)

Table V-3: Concentrations of ΣHCH, ΣDDT and ΣPCB in SML and subsurface water before and after precipitation events.

In general, the physical effects of rainfall on the structure of the SML are not well understood, but it has been suggested that the small rain droplets below ~1 mm in diameter could form a thin film of lower density water on top of the SML which is then slowly mixed with the saline water below (Hasse, 1997). The impact of bigger raindrops creates a turbulent motion and a disturbance of the SML. However, it has been estimated that the renewal and reorientation of organic surface films can occur within 0.2 seconds following a disturbance event (Dragcevic and Pravdic, 1981), but the mechanism is not well understood. Only two rainwater samples of sufficient volume could be collected in March 2004. The samples were collected four km north of Station 4, and results are summarized in Table V-4. HCH isomers were predominant in the rainwater samples with concentrations of 200.7 and 219.3 ng/L i.e. approximately two orders of magnitude higher than for DDTs and PCB congeners. HCH isomers tend to partition to water and air due to their higher vapor pressure and water solubility than DDTs and PCBs.

Compounds	Rainwater sample 1 (08.04.2004)	Rainwater sample 2 (21.04.2004)
ΣHCH	201	219
ΣDDT	2.0	2.2
ΣPCB	1.3	3.0

Table V-4: Concentration in ng/L of ΣHCH, ΣDDT and ΣPCB in rainwater samples.

V-3-6 Potential contamination sources of Hexachlorocyclohexanes (HCHs)

HCH isomers predominated among the measured OCPs in the coastal waters of Singapore. It has been reported that Lindane (γ-HCH) and technical HCH may be still used in Southeast Asia (UNEP, 2002a; Li, 1999; Taylor et al., 2003).

The α-HCH / γ-HCH ratio can be used to identify the source of HCHs in seawater (Chernyak et al., 1995; Maldonado and Bayona, 2002; Zhang et al., 2003b). The α-HCH / γ-HCH ratio in areas where Lindane has been used typically ranges between 0.2 and 1, due to photochemical transformation of γ-HCH to α-HCH, compared to a range of 4 to 15 for technical mixtures of HCH (McConnell et al., 1993). In this study the α-HCH / γ-HCH ratio in subsurface seawater ranged between 1.1 and 12.9 and in the SML between 0.4 and 29.4. However, in 72% of all subsurface and SML samples the α-HCH / γ-HCH was below 4 implicating Lindane as the main HCH source. Higher ratios may be explained by usage of technical HCH mixtures in the past and/or due to photochemical transformation of γ-HCH to α-HCH in the atmosphere with subsequent deposition to the SML. However, the photochemical transformation of HCH isomers in the atmosphere is not experimentally confirmed, but only speculated to occur (Willet et al., 1998). The key environmental sources to Singapore's marine environment may be the regional usage of HCH isomer pesticides and resuspension of HCH isomers from local sediments. Residual concentrations of HCH isomers in Singapore's coastal sediments have the potential to act as a local source of HCHs to coastal marine waters (see Chapter IV and Chapter VI).

V-3-7 Potential contamination sources of DDT and its metabolites

DDT has been banned in many countries of Southeast Asia for several decades, but was still used at least up until 1994 in Vietnam and Thailand, and usage is restricted in the Philippines (UNEP, 2002a). Despite a ban on DDT in 1983, usage in China is still likely (Chen et al., 2002).

The ratios of DDE/ΣDDT and DDD/ΣDDTs can be used to assess how recently DDT inputs occurred to the environment (Maldonado and Bayona, 2002). In this study, the DDE/ΣDDT and DDD/ΣDDTs ratios in seawater ranged between 0.08 to 0.46 (mean 0.24) and 0.07 to 1 (mean 0.46) respectively, and in SML samples between 0.08 to 0.43 (mean 0.27) and 0.07 to 0.77 (mean 0.41). Since the DDE/ΣDDT and DDD/ΣDDTs ratios are below unity in both subsurface water and SML samples, and it appears that inputs of DDT are still ongoing in Singapore’s coastal waters. DDT inputs may be derived from central Southeast Asia mainly by atmospheric transport from other parts of Asia. DDT residues in Singapore’s coastal sediments may act as a local source of DDTs to marine waters via sediment resuspension processes (see Chapter IV and VI).

V-3-8 Mass distribution of polychlorinated biphenyls (PCBs)

Import of PCBs has been banned in many countries of Southeast Asia, but continued restricted use, manufacture and import of PCBs are reported for the Philippines and Vietnam (UNEP, 2002a). Waste disposal of electrical transformers, oil spillage and sewage from ships may lead to the widespread distribution of PCBs in the marine environment of Southeast Asia. The major PCBs congeners measured in subsurface water and SML samples were PCB 18, 28, 44, 49, 52, 70, 74, 118, 128, 132, 138, 153, 156 and 187. In general tri-, tetra-, and penta-chlorobiphenyls are more abundant in subsurface water, whereas the distribution of PCBs in the SML is characterized by an increasing mass fraction of higher chlorinated PCBs congeners. This can be explained by the higher K_{ow} values of high-chlorinated PCB congeners, and therefore a higher tendency to accumulate in the SML; and the higher association of these congeners to particulate matter, which can be enriched in the SML, particularly after precipitation events as shown in Chapter V-3-5. The mass distribution pattern is similar among sample stations in the north and in the south of Singapore. The mass distribution of PCBs congeners in subsurface water and SML samples for Station 1 and 3 are shown in Figure V-6. The mass distributions in rainwater samples were characterized by tri- and tetra-chlorobiphenyls, which have a relative high vapor pressure relative to the higher chlorinated biphenyls.

V-3-9 Mechanisms of enrichment of POPs in the SML

The chemical composition of the SML is not well understood, but in conclusion from the literature, the SML is enriched in naturally occurring organic compounds, particular protein and organic surfactants (Hunter, 1997). Lipids may contribute a relatively small fraction of the organic matter in the SML (Garabetian et al., 1993). Proteins, lipids and organic surfactants form a hydrophobic film, which is the major driving force for the enrichment of hydrophobic compounds in the SML, as pointed out by Valsaraj (1994). The extent of the hydrophobic character of the SML may vary strongly according to prevailing biological activities at the different sample locations. For example, SML samples collected within a mangrove ecosystems in Singapore were enriched with organochlorine compounds (OCs) with a mean EF ranging between 2.1 and 17 (Bayen et al., 2005b), whereas the mean EF from the offshore location Station 7 in this study was not higher than 1.6.

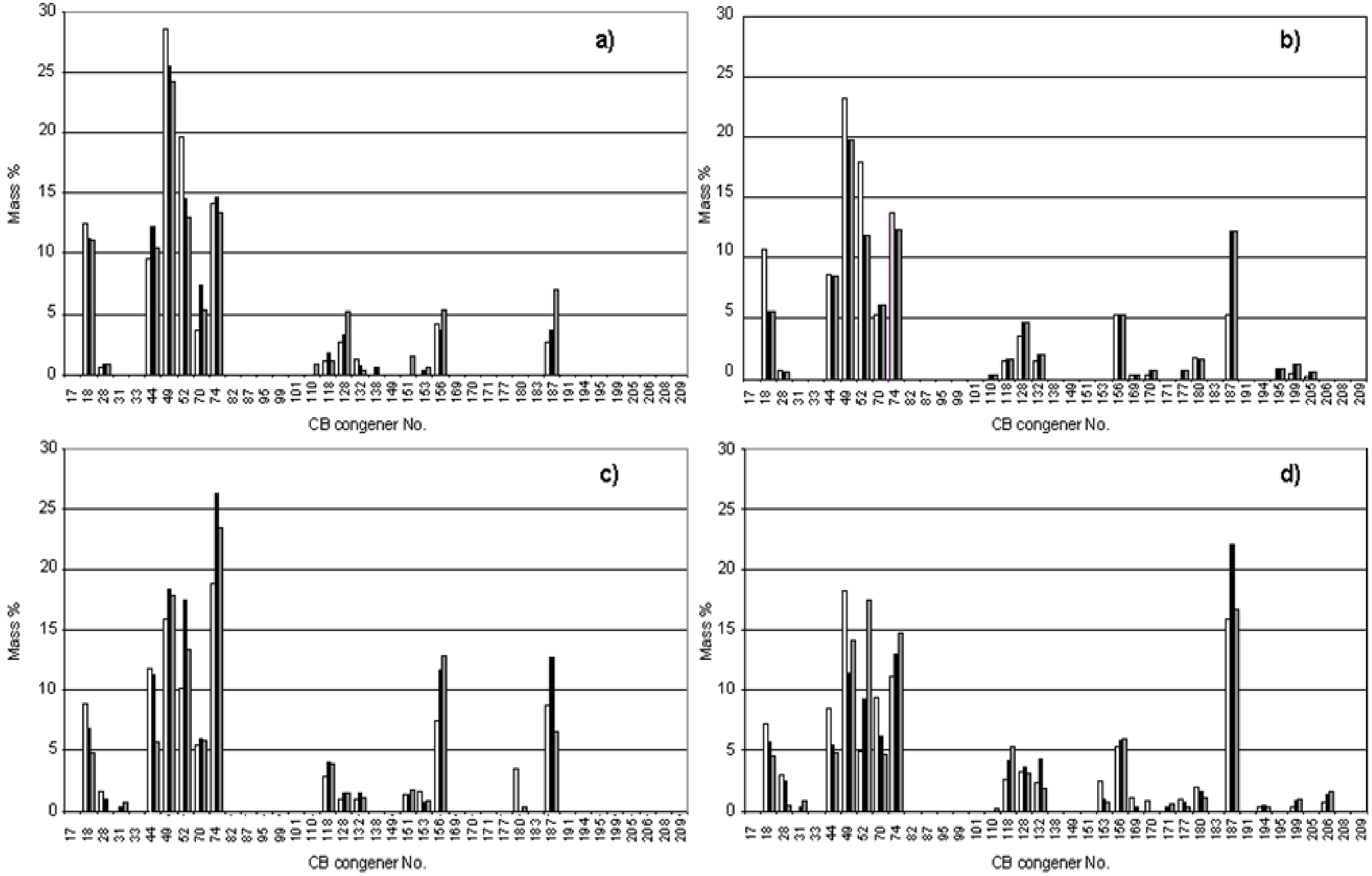
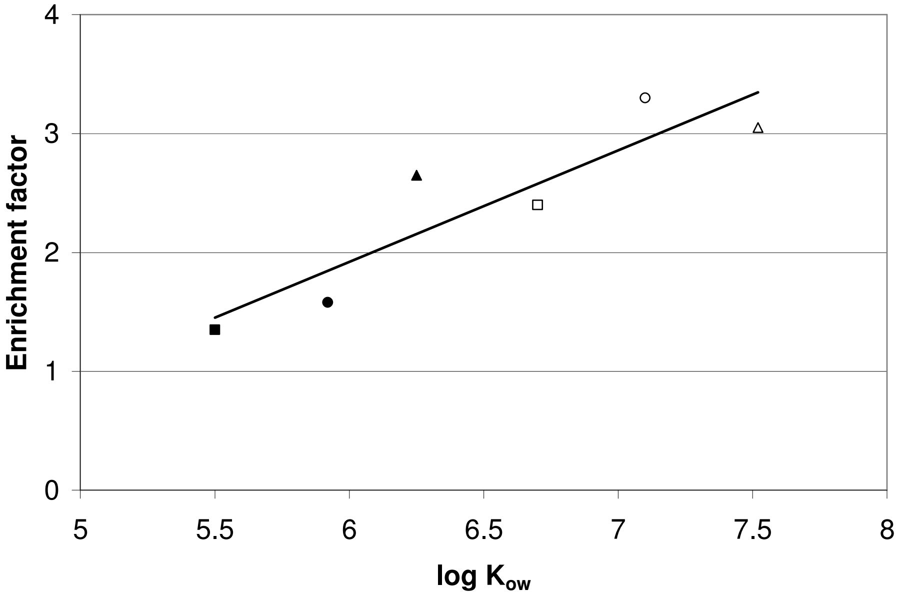


Figure V-6: Mass distribution of PCB congeners at sample location 1 (a) subsurface waters, (b) SML, and at sample location 3 (c) subsurface waters, (d) SML (☐ survey 1, ■ survey 2, ■ survey 3).

The physicochemical properties of a contaminant are important factors in controlling its enrichment in the SML. For example, the average K_{ow} values (Makino, 1998) of tri-, tetra-, penta-, hexa-, hepta- and octa-chlorobiphenyls, and the corresponding average EF value, show a good linear correlation for the representative northern Station 1 (r^2=0.88) and the southern Station 3 (r^2=0.71) (Figure V-8). The lower correlation at Station 3 may be a result of rougher sea conditions and a less pronounced formation of the SML and/or bubble formation at the air-sea interface at the time of sampling.

Hunter (1980) suggested that organic particulates with active compounds adsorbed onto their surface are stabilized at the air-sea interface and act as potential enablers of enrichment. It was shown in a further study that the SML plays an important role in the fate of DDTs and PCBs associated with particulates (see Chapter VI). The SML can receive organic matter from bottom sediments and the water column by upwelling, convection, diffusion and bubble formation. The formation of micro bubbles collected at the air-sea interface is known to be significant transport pathway of organic matter to the sea-surface, particularly for the removal of small particles from the water column (Hardy, 1982). The increasing enrichment of OCs after heavy rainfall events, as shown in this study, lends evidence to the observation that the SML receives a significant amount of organic contaminants from the atmosphere via wet deposition.

a)



b)

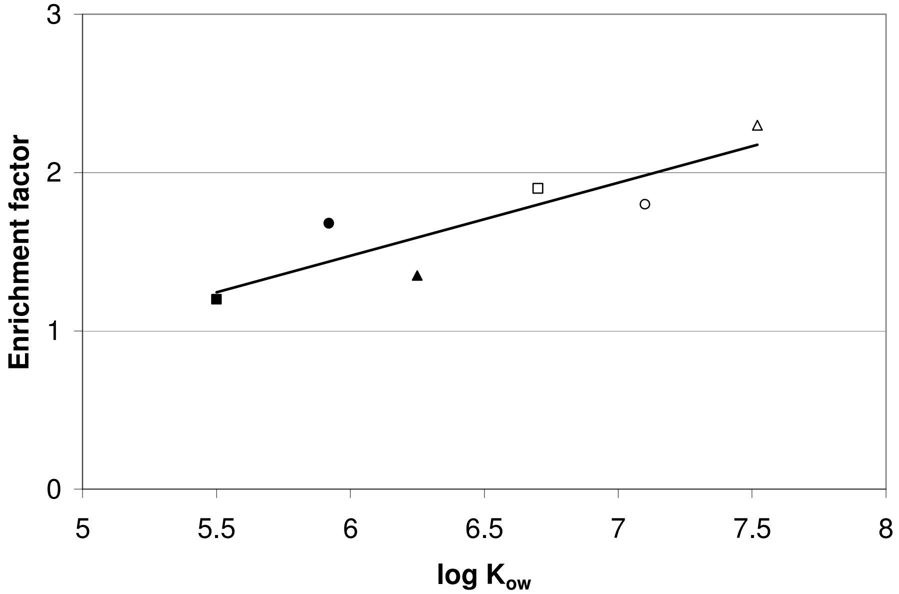


Figure V-7: Correlation between average K_{ow} value of tri- (■), tetra- (●), penta- (▲), hexa- (□), hepta- (○) and octa-chlorobiphenyls (Δ) and corresponding average enrichment factors (EF) at sample location 1 (a) and 3 (b).

V-4 Conclusion

This study has provided data for the first time on the levels of organic pollutants the sea-surface microlayer (SML) for coastal marine waters in Asia. HCH isomers, DDTs and PCB congeners are the most abundant POPs occurring in Singapore’s coastal waters. These compounds are enriched in the SML, but enrichment is lower compared to that reported for temperate climate zones. Semi-volatile POPs may evaporate more rapidly from the SML due to higher water surface temperatures in tropical regions. Measured seasonal changes in the levels of ΣHCH, ΣDDT and ΣPCBs were found to be significant. During times of frequent and intensive precipitation, the levels of POPs in the SML and subsurface water are significantly higher by factors of up to 50. Wet deposition is likely to be a major source of contaminants to the SML. However more experimental data are needed to yield a more profound understanding of the role of the SML in determining the fate and transport of organic contaminants across the SML-atmospheric interface.

CHAPTER VI

Distribution of Persistent Organic Pollutants (POPs) in the Sea-Surface Microlayer (SML), Water Column and Sediment of Singapore's Marine Coastal Environment

VI-1 Introduction

In order to understand the role of the Southeast Asia region as a possible emission source for the global distribution of POPs, it is necessary to elucidate the distribution, behavior and fate of these compounds in various marine environmental compartments. Concentrations of POPs in unfiltered seawater from two depths collected in Singapore's sea were reported by Basheer et al. (2003a), and in sediments from Basheer et al. (2003b), and Wurl and Obbard (see Chapter IV). The partitioning of POPs between the dissolved phase (DP) and suspended particulate matter (SPM) are important for two reasons; (a) POPs in the dissolved phase may play a more important role in terms of bioavailability and eco-toxicity (Zhou et al., 1996) and (b) partitioning between the DP and SPM determines the fate of POPs in the marine environment, e.g. Dachs et al. (1996) suggested that POPs associated with the SPM sink and act as contaminant source to sediments, but resuspension of coastal sediments may act as a source of POPs to the overlying water column. The water column includes two interfaces for exchange processes, the bottom-sediment near water layer and the sea-surface microlayer (SML). Eggleton and Thomas (2004) reviewed factors affecting the release of contaminants during sediment resuspension processes, a known major source of organic pollutants to the water column. Wania et al. (1998) suggested that the partitioning of POPs between the DP and SPM within the water column can significantly affect the extent of volatilization of POPs from seawater. Wania et al. (1998) also pointed to the importance of the SML in the process of air-sea gas exchange of POPs.

The objective of this study was to study the concentration and distribution of polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethanes (DDTs) and hexachlorocyclohexanes (HCHs) in the water column and sediments at two sites with contrasting hydrodynamic characteristics in the coastal marine environment of Singapore. In contrast to previous studies on the distribution of POPs in the water column, the enrichment and distribution of POPs in the lower sediment-bottom water layer and the upper SML as boundary layer of the water column were quantified.

VI-2 Materials and Methods

VI-2-1 Sample collection

The locations of the sample stations are shown in Figure VI-1. Station 1 is located nearby a mangrove area inside the Straits of Johor with restricted water exchange with oceanic water. Station 2 is located in the east of Singapore close to shipping lanes and is likely affected by riverine runoff, but also by water exchange with the open ocean. Seawater samples from subsurface, mid and bottom near water were collected using a teflon diaphragm pump at depths of 1, 4.8 and 6.5 m at Station 1 (max. depth 6.8 m) and at 1, 7, and 10.5 m at Station 2 (max. depth 11m), respectively. The sampling procedure for collection of SML samples is provided in detail in Chapter III-3-1. The revolution rate of the glass drum was set to 13-14 rpm, resulting in a thickness of collected SML of between 76 to 91 μm (average 82 ± 5 μm). The higher revolution rate compared to the previous study was needed in order to supply sufficient power for the rotation of a bigger and heavier glass drum that was used to improve sampling efficiency. All seawater samples were filtered online, as described in Chapter III-3-1. Sediment samples were collected using a grab sampler as described in Chapter III-3-3. The upper sediment layer (about 1-3 cm) was removed with a stainless steel spoon and stored in pre-cleaned glass bottles.

Sub-samples for the determination of the mass of SPM, dissolved organic carbon (DOC) and total organic carbon (TOC) were filtered over pre-cleaned GF/A filters (Whatman, 1.6 µm, 47 mm). Sub samples for DOC analysis were kept in glass test tubes with teflon-lined caps and stored at -20 °C. The GF/A filters for SPM and TOC analysis were stored in glass petri dishes and stored at -20 °C in airtight plastic containers.

Meteorological data, salinity and temperature of surface water (0.5 and 40 cm depth) were recorded during each sampling event and are summarized in Table VI-1.

VI-2-2 Sample treatment and analysis

All samples were spiked with a $^{13}C_{12}$-labeled PCB surrogate standard prior extraction. All seawater and SML were extracted as described in Chapter III-4-1. SPM and sediments samples were extracted with 50 mL acetone-hexane (3:2) in a microwave oven CEM Mars X (CEM, Matthews, NC, USA) for 18 min at 115 °C. After extraction, the vessels were allowed to cool to room temperature. The supernatant was filtered through glass wool and combined with a 2-3 mL acetone-hexane (3:2) rinse of the sample residue. All extracts were cleaned-up using a silica gel column, where the procedure is described in Chapter III-5. Analysis of sample extracts was performed on a Shimadzu QP5050 GC-MS according to Chapter III-6-1.

Station	Profile	Date	d [µm] [a]	Current	Tide	Wind Speed	Temperature [C]			Salinity [psu] [c]
						[m/s]	Air	Surface Water [b]	Water [c]	
1	1a	16th June	83	calm	high to low	2.9	32.3	31.1	30.7	6.8
	1b	30th June	76	calm	high to low	3.7	30.4	31.0	30.4	6.7
	1c	14th July	84	calm	high to low	3.6	31.5	29.2	29.0	6.5
2	2a	23rd June	82	moderate	low to high	2.8	28.5	30.3	29.7	22.1
	2b	07th July	91	moderate	low to high	1.2	31.1	30.0	29.6	21.9
	2c	21st July	79	calm	low to high	2.9	26.5	29.1	28.9	22.2

[a] Thickness of collected SML

[b] at depth of 0.5 to 1 cm

[c] at depth of 40 cm

Table VI-1: Description and environmental characteristic (seawater and atmosphere) of sample stations.

VI-2-3 Determination of TOC, DOC and SPM

The analysis of TOC was conducted using a Shimadzu TOC5000A and a solid combustion unit SSM5000. A continuous flow analyser (AutoAnalyzer 3, Bran-Luebbe, Germany) was used for the analysis of DOC. The mass of SPM was determined gravimetrically on an analytical balance (0.0001 g) by weighing a dried filter before and after sampling.

VI-3 Results and Discussion

VI-3-1 Quality assurance

All analysis was subject to strict quality assurance and control procedures. All samples were collected and analysed in duplicate. Values of relative percent difference of duplicate samples yielded between 14 and 64% in the dissolved phase and 11 and 45% in the SPM. Given the low concentrations, this was considered to be satisfactory. Blank GF filters constituted 20% of the total number of SPM samples in order to evaluate contamination during transport and storage. The SRM 1441c was used to validate analysis of sediments and SPM samples and results fell within the range of certified values. Mean recoveries of the $^{13}C_{12}$-labeled PCB surrogate standard were between 72 and 117 %. Control calibration standards were analysed for every four samples to check instrument performance during analysis.

VI-3-2 The physical environment

The maximum depth of sample Station 1 (Kranji) and 2 (Pulau Tekong) were 6.8 and 11 m respectively (Figure VI-1). The salinity of 6.5 and 22 psu at Station 1 and 2 respectively indicates a freshwater influence via rainfall and a restricted hydrodynamic exchange of coastal waters in the Straits of Johor at Station 1. Gin et al. (2000) reported that marine waters in the Straits of Johor are well mixed, and the salinity profile was constant with depth for all samples collected in this study.

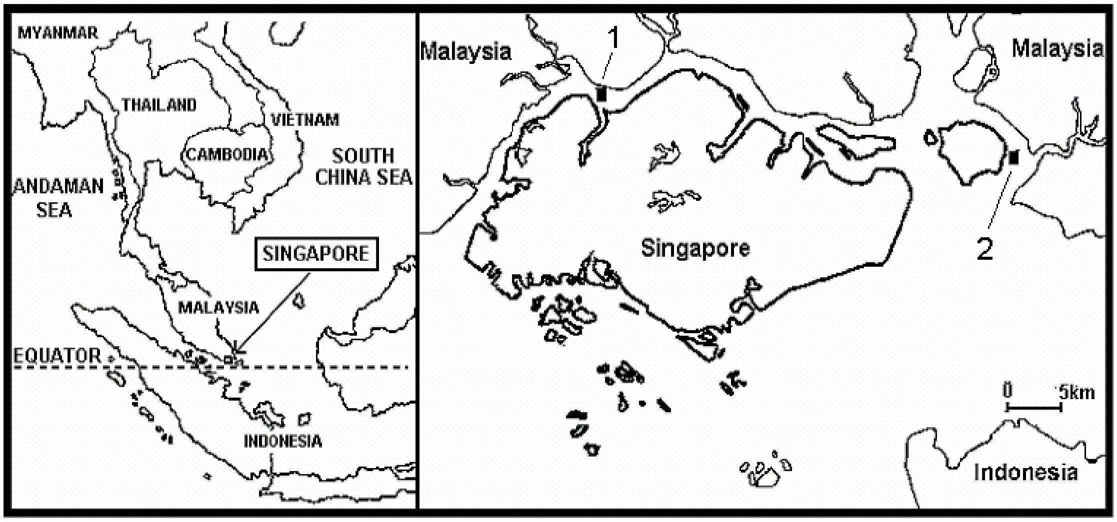


Figure VI-1: Location of sample Station 1 and 2.

The depth profiles of DOC, TOC and SPM were different between the stations, but were similar at each single station (Figure VI-2) between sample events. The profiles at Station 1 showed an enrichment of DOC, TOC and SPM by factors of approximately 2.5, 1.4 and 1.2 in the SML compared to the subsurface. Decreasing levels of DOC with depth suggests a higher level of microbiological activity in the surface at Station 1. At Station 2, concentrations of SPM were enriched in the SML by factors of between 2 and 5, but profiles of DOC and TOC showed little variation with depth.

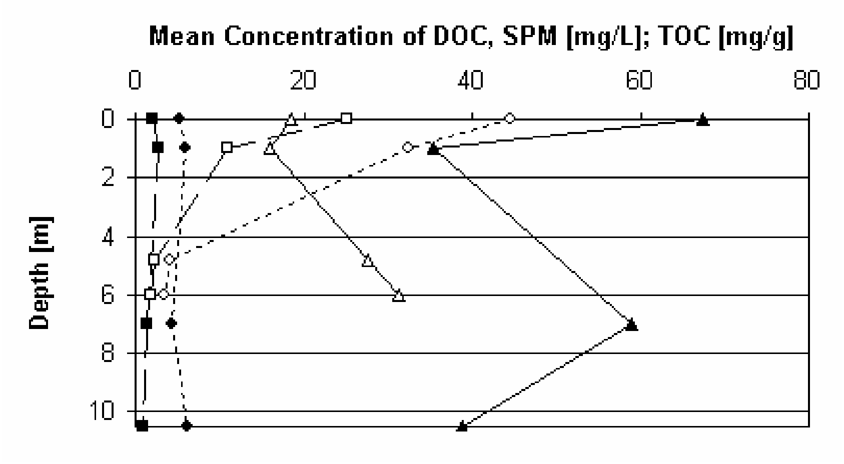


Figure VI-2: Vertical profiles of DOC (□), TOC (○) and SPM (△) at Station 1, and of DOC (■), TOC (●) and SPM (▲) at Station 2.

VI-3-3 Concentrations of POPs in the water column and sediments

VI-3-3-1 Polychlorinated biphenyls (PCBs)

The lower chlorinated PCBs congeners CB 18, 28, 33, 44, 49, 70, 74, 101 and 110 were dominant in the DP and SPM, whereas in the higher chlorinated congeners CB 118, 132, 149, 151 and 153 were mainly found in the SPM and sediments. At Station 1 and 2 the concentrations of ΣPCBs in the DP varied between 130 and 2924 pg/L (mean 991 ± 1115 pg/L) and between 60 and 6979 pg/L (mean 2231 ± 2534 pg/L), respectively (see Table VI-2). The concentrations of ΣPCBs in the SPM ranged from 166 to 1380 pg/L (mean 586 ± 434 pg/L) and 38 to 3793 pg/L (mean 844 ± 1169 pg/L) at Station 1 and 2, respectively. Generally the highest concentrations were found in the lowest and uppermost boundary layer of the water column, the sediment-bottom water layer and SML.

In comparison to reported concentration levels of ΣPCBs from China, the levels found in Singapore were lower by a factor of up to 800 for the DP compared to data from Daya

Bay (Zhou et al., 2001) and the Minjiang River Estuary (Zhang et al., 2003b), but comparable to levels found in the Xiamen Harbour (Zhou et al., 2000) and the Yangtse River (Jiang et al., 2000) (Table VI-3). For the SPM, the concentrations of ΣPCBs were in the same range as that reported for the Yangtse River (Jiang et al., 2000), but substantial higher than levels for the Danube Estuary, Romania (Maldonado and Bayona, 2002) and Ebro River Mouth, Spain (Dachs et al., 1996) of the Mediterranean Sea.

The range of concentration levels of ΣPCBs in surface sediments was 634 to 1356 pg/g (mean 1086 ± 296 pg/g) and from 339 to 943 (mean 630 ± 247 pg/g) at Station 1 and 2, respectively (Table VI-2). Table VI-3 shows that reported levels from Daya Bay, China (Zhou et al., 2001) and the Minjiang River Estuary, China (Zhang et al., 2003b) were higher by factors of 30 to 60 compared to levels found in this study. In comparison to the levels from Singapore, similar concentration ranges for ΣPCBs were reported for Xiamen Harbour, China (Zhou et al., 2000). In previous studies from Singapore from Basheer et al. (2003b), and Wurl and Obbard (Chapter IV) concentrations of ΣPCBs in Singapore's coastal sediments were reported to be higher, but were collected from different sampling sites compared to this study.

	α-HCH	β-HCH	γ-HCH	δ-HCH	ΣHCHs	p,p'-DDE	p,p'-DDD	p,p'-DDT	ΣDDTS	ΣPCBs
Station 1										
DP	3.4-815 (274±295)	29.5-1713 (1422±1130)	15.5-515 (1422±86)	13.1-1660 (474±565)	101-6110 (2275±1819)	<3-29 (12±9)	<4-38 (18±12)	<5-148) (45±53)	15-183 (83±55)	130-2924 (991±1115)
SPM	13-1135 (135±317)	15-680 (119±192)	2-242 (56±86)	3-379 (90±134)	43-2395 (402±679)	<3-94 (11±26)	<4	<5-25 (12±8.7)	<5-124 (19±34)	166-1380 (586±434)
Sediments	58-96 (75±20)	400-1160 (737±387)	379-452 (427±41)	74-150 (103±44)	994-1758 (1464±336)	36-60 (49±12)	11-28 (18±8)	50-80 (62±15)	60-94 (82±16)	674-1356 (1086±296)
Station 2										
DP	64-910 (281±315)	119-2965 (651±920)	4-590 (154±229)	6-2455 (578±890)	210-6415 (1665±2309)	<3-110 (18±32)	<4-185 (28±53)	<5-110 (23±33)	<5-405 (69±115)	60-6979 (2231±2534)
SPM	9-68 (30±19)	7-30 (34±29)	2-20 (10±4)	<2-80 (12±22)	26-184 (85±51)	<3	<4-6 (0.5±1.7)	<5-45 (5±13)	<5-55 (19±20)	38-3793 (844±1169)
Sediments	44-62 (54±9)	146-320 (235±87)	108-176 (188±34)	104-416 (258±154)	521-842 (724±144)	20-50 (32±16)	6-11 (9±3)	63-260 (133±110)	11-39 (28±12)	339-943 (630±247)

Table VI-2: Concentration ranges of HCHs, DDTs and ΣPCBs in dissolved phase (DP, pg/L), suspended particulate matter (SPM, pg/L) and sediments (pg/g dry weight). In bracket mean±sd, n=6.

Location	Year	ΣPCBs			ΣDDTs			ΣHCHs			Reference
		DP	SPM	Sediment	DP	SPM	Sediment	DP	SPM	Sediment	
East Java, Indonesia	1984	0.24-3.5	4[a]		0.006-0.9[b]	n.d.		0.02-1.3[c]	n.d.		1
Ebro River, Spain	1994	0.06	0.01[d]		0.004[e]	0.001[d,e]					2
Danube Estuary, Romania	1995	0.07-0.1	0.004-0.06[d]		0.02-0.04[b]	0.002-0.02[b,d]		0.13[c]	0.004[c,d]		3
Xiamen Harbour, China	1998	0.1-1.7		0.01-0.32	1.1-29.1[b]		<0.01-0.04[b]	3.5-27.8[f]		<0.01-0.25[f]	4
Yangtse River, China	1998	2	0.5-1.3[d]		1.9[g]	0.8-1.4[d,g]		9.9[h]	0.6-1.6[d,h]		5
Minjiang River, China	1999	204-2473		15.2-57.9	40.6-234[b]		1.6-13.1[b]	52.1-515[f]		3.0-16.2[f]	6
Daya Bay, China	1999	91.1-1355		0.85-27.4	30-975[b]		0.14-20.3[b]	35.5-1228[f]		0.32-4.2[f]	7
Pearl River Delta, China	2001				0.07-2.8[g]	0.13-27.6[d,g]		5.7-59.1[f]	0.49-8.0[d,f]		8
Singapore	2004	0.29-2.9	0.33-1.4[d]	0.6-1.1	0.03-0.14[b]	0.005-0.05[b,d]	0.03-0.08[b]	0.80-3.2[f]	0.05-1.1[d,f]	0.7-1.5[f]	10

[a] in ng/g

[b] Sum of p,p'-DDE, p,p'-DDD and p,p'-DDT

[c] Sum of α-HCH and γ-HCH

[d] in ng/L

[e] Sum of p,p'-DDE and p,p'-DDT

[f] Sum of α-HCH, β-HCH, γ-HCH and δ-HCH

[g] Sum of o,p'-DDE, o,p'-DDD, o,p'-DDT, p,p'-DDE, p,p'-DDD and p,p'-DDT

[h] Sum of α-HCH, β-HCH and γ-HCH

Table VI-3: Comparison of PCB and OCP concentrations in the dissolved phase (DP, ng/L), suspended particulate matter (SPM, ng/g or ng/L) and sediments (ng/g dry wt.) from various rivers and estuaries (n.d.= not detectable). References: (1) Hillebrand et al., 1989; (2) Dachs et al., 1997; (3) Maldonado and Bayona (2002); (4) Zhou et al., 2000; (5) Jiang et al., 2000; (6) Zhang et al., (2003b); (7) Zhou et al., (2001); (8) Luo et al., 2004; (9) this study

VI-3-3-2 Organochlorine pesticides (OCPs)

The major OCPs detected during this study were HCH isomers (α-HCH, β-HCH, γ-HCH and δ-HCH) and DDT compounds (DDT, DDD and DDE). The concentrations of Aldrin, Dieldrin, Endosulfan I and II were below the limit of detection (LOD). Cis- and trans-Chlordane were detectable only at low concentrations in the DP ranging between 1 and 6 pg/L. ΣHCHs was present in the DP and SPM in concentration ranges of 101 to 6110 pg/L (mean 2275 ± 1819 pg/L) and 43 to 2395 pg/L (mean 402 ± 679 pg/L) respectively at Station 1, 210 to 6415 pg/L (mean 1665 ± 2309 pg/L) and 26 to 184 pg/L (mean 85 ± 51 pg/L) respectively at Station 2. As shown in Table VI-2 the concentrations of ΣHCHs were substantial higher at Station 1 compared to Station 2, likely due to the restricted water exchange in the narrow Straits of Johor, and the agricultural activities in this area associated with contaminated catchment runoff. Mean concentrations in sediments collected at Station 1 and 2 were 1464 and 724 pg/g respectively. It has been reported that technical HCH mixture and Lindane (γ-HCH) have been banned in many countries of Southeast Asia in recent years, but there is evidence that these chemicals are still used in few countries as insecticides, including Thailand and Malaysia (UNEP, 2002a). However, the concentrations of ΣHCHs in the DP and SPM in estuarine and river water in China are substantially higher compared to the concentrations reported in this study (see Table VI-3).

DDT and its metabolites DDD and DDE were present in Singapore's water column at substantially lower concentrations compared to HCH isomers. The concentrations of ΣDDTs at Station 1 were in a range of 15 to 183 pg/L (mean 83 ± 55 pg/L) in the DP and from <5 to 124 pg/L (mean 19 ± 34 pg/L) in the SPM. The concentrations at Station 2 ranged from <5 to 405 pg/L (mean 69 ± 115 pg/L) in the DP and from <5 to 55 pg/L (mean 19 ± 20 pg/L) in the SPM. Sediment mean concentrations of ΣDDTs were 82 and

95 pg/g at Station 1 and 2 respectively. Monorith et al. (2003) reported that the continued usage of DDT in China and Vietnam is likely. However, DDT has been banned in many countries of Southeast Asia. The relatively high concentrations of DDT reported for rivers and estuaries in China are greater by up to three orders of magnitude compared to Singapore and likely to origin from the ongoing usage of DDT in China.(see Chapter VII).

VI-3-4 Vertical distribution of POPs in the water column

VI-3-4-1 Polychlorinated biphenyls (PCBs)

The vertical concentration profiles of ΣPCBs in the water column of Singapore's marine environment are similar at both stations (Figure VI-3). In general, the concentrations of ΣPCBs in the DP are elevated towards the surface water layer, but at Station 2 a substantial enrichment of ΣPCBs in the DP of the bottom water was observed. The SML was enriched with PCBs in the DP in a range of 1.3 to 7.2 relative to subsurface waters, and contaminants likely originated from atmospheric wet deposition as well as transport processes from subsurface waters.

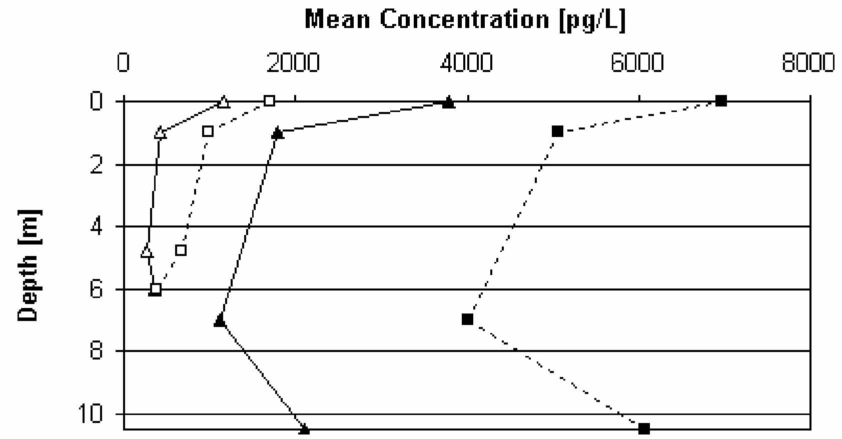


Figure VI-3: Vertical profiles of ΣPCBs in DP (□) and SPM (△) at Station 1, and in DP (■) and SPM (▲) at Station 2.

Higher concentrations of ΣPCBs in the SPM were found to be higher, but with a decreasing concentration trend to mid-depth water, most likely due to sediment resuspension processes. The concentrations of ΣPCBs in the SPM increased towards the surface water layer and were enriched in the SML by a factor of 1.2 to 7.2 relative to the subsurface water layer. It is suggested that this enrichment derived from small size and/or flocculated particles floating on the water surface. Even so an enrichment of ΣPCBs associated to the SPM in the bottom water were found to be of 2 to 3 at both stations compared to the overlying mid-depth waters, no enrichment of SPM was found in this layer at Station 2. A similar observation was reported recently for the Black Sea (Maldonado and Bayona, 2002). It is suggested that different types and size distributions of suspended particulates between water layers may lead to an enrichment of contaminants associated with the SPM, even though the SPM itself is not enriched. Resuspension processes of contaminated sediments may be a source of the enrichment in near bottom waters at both stations. However, the enrichment of PCBs in the SML indicates that dry and wet deposition is a second major source of contaminants to the water column. As shown in Chapter V, the concentrations of organic contaminants increased in the SML by factors of up to 5 following heavy rainfall events.

VI-3-4-2 Organochlorine pesticides (OCPs)

Typical vertical profiles of ΣHCHs are shown in Figure VI-4 and are characterized by lower concentrations of ΣHCHs in the DP for the bottom near waters compared to overlying waters. The concentrations of dissolved HCHs declined from the mid-depth to the subsurface waters and increased by a factor of up to 2 in the SML. Exceptionally, a linear increase of the concentration of dissolved HCHs from the near bottom water to the SML was observed at Station 1 (profile 1c, see Table VI-1).

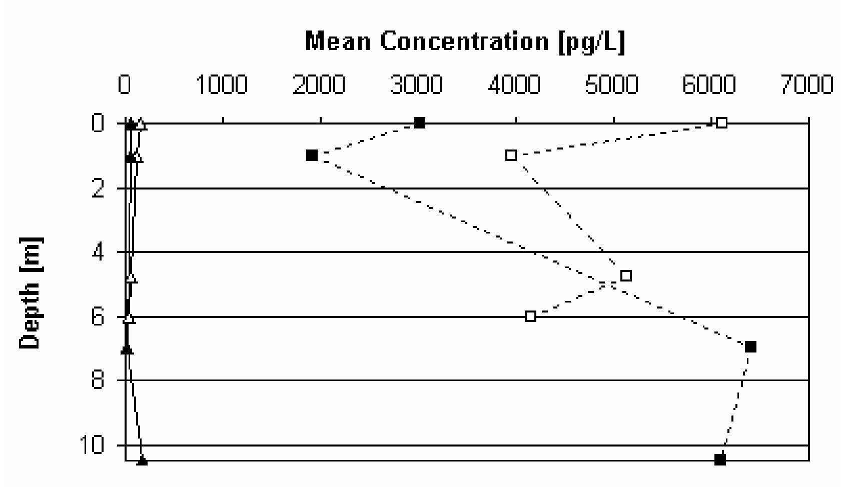


Figure VI-4: Vertical profiles of ΣHCHs in DP (□) and SPM (△) at Station 1, and in DP (■) and SPM (▲) at Station 2.

The profiles of concentration of ΣHCHs associated with SPM differ substantially from the DP, but were similar at both stations. The concentrations of suspended ΣHCHs varied little with depths, except for the profiles 1b, 1c and 2b when a high enrichment in the SML was found (EF = 2.5-7.1) compared to the others profiles (EF = 1.1-1.4). The bottom layers at both stations were not enriched with ΣHCHs associated to the SPM, although an enrichment of SPM in this layer was present. This provides evidence that resuspension processes of sediments may not act as a major source of HCHs into the water column. However, it is suggested that freshwater inputs, such as riverine discharge, as well as dry and wet deposition on the surface, are the major inputs of HCHs into the water column, as indicated by the enrichment in the SML and a decreasing concentrations with depth.

Vertical distribution profiles of DDTs differ substantially from these for HCHs (Figure VI-5).

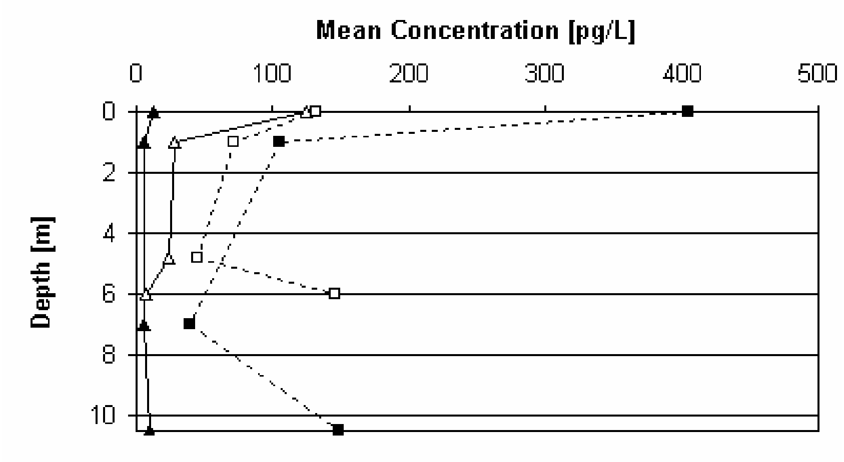


Figure VI-5: Vertical profiles of ΣDDTs in DP (□) and SPM (△) at Station 1, and in DP (■) and SPM (▲) at Station 2.

An enrichment in the SML and near bottom waters of ΣDDTs in the DP could be found by factors of up to 4 and 3 respectively, except for the profiles 2b and 2c. Lowest concentrations of dissolved ΣDDTs were found in the mid-depth waters. ΣDDTs associated to the SPM varied little in concentrations from the subsurface to the bottom near water layers, but were enriched in the SML (EF = 3.3-4.4). Deposition of atmospheric particulates on water surfaces represents a source of particulate organic contaminants and may results in an enrichment of particulate DDTs in the SML. Sediment concentrations of DDT were low compared to levels of PCBs and HCHs indicating that sediment resuspension processes may not play an important role as a source of DDT into the water column. Runoff and precipitation may account for the observed enrichment in the SML and subsurface layer.

VI-3-5 Distribution of POPs between particulate and dissolved phases

VI-3-5-1 Polychlorinated biphenyls (PCBs)

The fractions of PCB congeners bound to the SPM were 24-80% and 8-70% of total PCBs (SPM+DP) at Station 1 and 2 respectively. The lower fraction of PCBs at Station 2 can be explained by the higher water dynamics and exchange with the open ocean at this station, whereas lower hydrodynamic mixing, slack water currents and restricted water exchange in the Straits of Johor may lead to the higher fraction found at Station 1. Particularly in the bottom water at Station 1, a relatively higher fraction of PCB congeners associated with the SPM, ranging between 48 to 80%, was found and is consistent with higher SPM concentrations found in the bottom near water at this station.

To investigate the distribution of PCBs congeners between DP and SPM a distribution coefficient K_d for PCB congeners presented in both phases can be defined as an isothermic linear absorption process under equilibrium condition. K_d is the ratio of an compound in the SPM (mass units per unit mass particulates) and its concentration in solution (mass unit per water volume). As in the study of Schulz-Bull et al. (1998), the concentrations of POPs in the SPM are presented as a mass per unit volume, where the apparent distribution coefficient K'_d can be used as a useful substitute. K'_d is calculated as the ratio of the concentration in the SPM (mass per unit water volume) relative to the concentration in solution (mass per unit water volume). In the case of an equilibrium condition of the water column, a positive linear relationship between log K'_d and log K_{ow} is expected (Hamelink et al., 1971), which has been observed in the northern North Atlantic (Schulz-Bull et al., 1998). However, during periods of high biological activities, strong deviations from linearity have been observed for oceanic regions, indicating non-equilibrium conditions (Schulz-Bull et al., 1995). At Station 1, negative relationships between log K'_d and log K_{ow} were found at all depths. This indication of non-equilibrium condition may derive from the hydrodynamic characteristics of Station 1 and high biological activity in a nearby mangrove area. At Station 2 a positive relationship between log K'_d and log K_{ow} was observed for the SML, subsurface and mid-depth waters, but not for the near bottom waters. Lower biological activities and partial mixing with oceanic waters at Station 2 may lead to this observation. However, the positive relationships observed in this study are still weaker than observed for the northern North Atlantic (Schulz-Bull et al., 1998). It is assumed that an equilibrium conditions in coastal and estuarine waters is unlikely due to intensive sediment resuspension, high biological activities and wastewater discharge. It is known, however, that processes involved in leading to equilibrium conditions of aqueous systems are complex, where key controlling factors include reaction kinetics (Wu and Geschwend, 1986), SPM particle size (Maruya et al., 1996) and the content and type of organic matter in the SPM (Grathwohl, 1990).

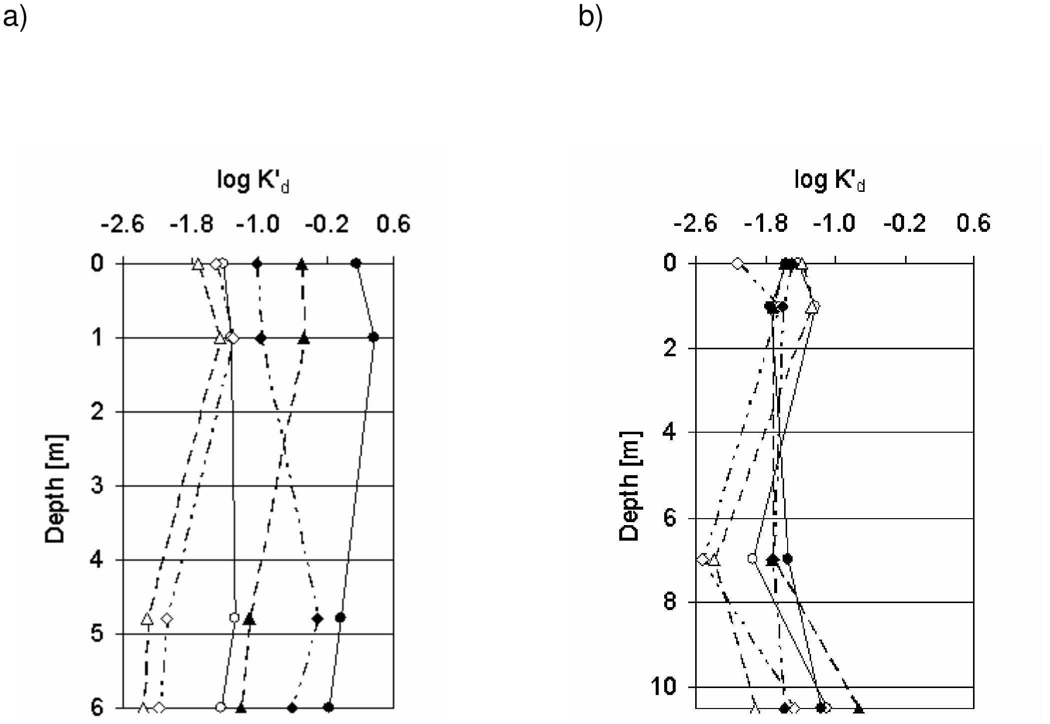
VI-3-5-2 Organochlorine pesticides (OCPs)

As from the physicochemical properties of HCHs, like relative high water solubility and low K_{ow} (see Chapter II-1), the dissolved fraction of HCHs were dominant with 60-99% of the total concentration of HCHs (SPM + DP). This distribution pattern of HCH isomers between DP and SPM was also observed in previous studies for the Pearl River Delta, China (Luo et al., 2004) and for the Black Sea (Maldonado and Bayona, 2002). The concentration of suspended HCHs was only dominant in the SML, relative to the DP, in profile 1c. Although the concentration of SPM at 50 mg/L was high in this sample, the highest SPM concentration of 145 mg/L was detected in the near bottom water layer in the same profile, but corresponded to a ΣHCH concentration of 60 pg/L - lower by a factor of 40 compared to the SML. It can be concluded that a high SPM concentration may not be associated with high levels of contamination of POPs, as observed for the

Black Sea (Maldonado and Bayona, 2002). In general, high vapor pressure and water solubility of HCH isomers are the key properties leading to high mobility and redistribution in the environment, where they are not strongly scavenged by particulates (Hargrave et al., 1988). β-HCH, a known degradation product of γ-HCH and α-HCH in sediments (Wu et al., 1997), was present at a high fraction in the DP (45-90%) and in the SPM (28-78%) among all HCH isomers. It is likely that β-HCH is released into the water column by sediment resuspension. α-HCH was present at fractional proportions of 8-33% in the DP and 16-53% in the SPM. Since α-HCH is often the major HCH isomer occurring in the atmosphere (Willet et al., 1998), it is suggested that wet deposition may be the major pathway of α-HCH into the water column. The lower fraction of γ-HCH (DP: 2-25%; SPM: 3-22%) can be explained by its degradation to other isomers.

In contrast to HCH isomers, lower water solubility and higher affinity to sediments and SPM should lead to a dominant fraction of DDTs associated to the SPM - as observed for the Pearl River Delta, China (Luo et al., 2004) (SPM associated: 90%). However, a lower fraction was reported for the Yangtse River, China (Jiang et al., 2000), Danube Estuary and open water of the Black Sea (Maldonado and Bayona, 2002), Mediterranean Sea and estuaries of the Ebro and Rhone River (Dachs et al., 1996), and coastal areas of Java, Indonesia (Hillebrand et al., 1989) (Table VI-3). As in the previous studies, DDTs in the DP were dominant in this study with a fraction ranging from 44 to 90%, where this distribution pattern is not consistent with the high K_{ow} values for DDTs (Chapter II-1). This can be explained by the following: (a) a relatively low carbon content was found in the SPM in this study (Figure VI-2), thereby reducing the adsorption of POPs, (b) dissolved fractions contain small particles and colloids (< 1 μm) which pass through the filter and contribute to the concentrations of the DP, and (c) the relative high water temperature in the tropical area of Singapore leads to a higher water solubility of POPs and a shift in the distribution pattern towards the dissolved fractions.

The change of the distribution coefficient K'_d with depth is illustrated in Figure VI-6 for Station 1 and 2. The variation of K'_d values with depth at both Stations can be of two reasons; (a) water bodies are not well mixed or more likely (b) the distribution of SPM is heterogeneous.


a)

b)

Figure VI-6: 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).

Profiles at Station 1 are similar for all OCPs, and is characterized by an increase from the SML to subsurface water and a decline to mid-depth waters. A further increase towards near bottom waters at Station 2 may be caused by sediment resuspension processes. The SML may be enriched with small or voluminous floating particulates, whereas subsurface waters will typically be dominated by denser sinking particulates leading to the distinctive pattern observed at Station 1. The profile at Station 2 show that more HCHs and DDTs in the SPM appear proportionally in the SML and subsurface waters than in mid-depth layer relative to the DP. Generally, the profiles in Figure VI-6 show that the SML is an important compartment for the fate of OCPs. Particularly, the pathways of wet deposition and evaporation from the subsurface waters via the SML to the atmosphere may play an important role in the fate and distribution of POPs. These two pathways may be particularly prominent for the tropics as a consequence of heavy rainfalls during monsoon periods (see Chapter V), as well as elevated air and water temperatures. In Chapter IX the role of the SML in the air-sea exchange of POPs was investigated in detail.

VI-4 Conclusions

In summary, this study shows that the distribution of POPs between the DP and SPM is dominated by the resuspension and release of POPs from sediments which is a major source of PCBs and dissolved DDTs to the water column. The EF values of POPs in the SML indicate that the SML has an important role in the fate of dissolved HCHs, and dissolved and suspended DDTs and PCBs. The SML may act as a source of atmospheric POPs via evaporation and, conversely, receives inputs of POPs via dry and wet deposition from the atmosphere. However, the level of POP contamination in the water column and sediments of Singapore’s marine environment can be considered as ‘low’ compared to levels reported from China.

CHAPTER VII

Occurrence and Distribution of Persistent Organic Pollutants (POPs) in the Sea-Surface Microlayer (SML) and Seawater in Hong Kong, China

VII-1 Introduction

Hong Kong is located on the southern coast of China adjacent to the Pearl River Estuary (PRE). The western areas of Hong Kong's marine environment are heavily affected by the PRE, which has an area of 442 440 km^2 and an annual discharge of 308 billion m^3/year (Morton and Wu, 1975). The eastern part is influenced by oceanic waters from the South China Sea during the summer and from the Pacific and East China Sea during the winter (Blackmore, 1998). The waters of Hong Kong's have been divided into an estuarine zone in the west, an oceanic zone in the east and a transition zone between. This transition zone includes Victoria Harbour and adjacent waters, as well Tolo Harbour, a semi-estuarine embayment with high water residence time (Morton, 1989).

The PRE in South China has experienced enormous industrial development with a gross industrial output (GIO) of US$ 145 billion in 2001, accounting for 13% of the total GIO of China. The electronic and telecommunication industries have transformed this region into one of the fastest-growing industrial zones worldwide. The rapid development in urbanization and population growth has led to much concern over environmental damage, including pollution of the PRE (Chen et al., 2004). For example, in addition to imported polybrominated diphenyl ethers (PBDEs) for the use as flame retardants in textiles and electronic devices – Asia consumed 42 % of the world production of the commercial product DeBDE (De Wit, 2002) – the shipment of electronic waste to China for disposal is also a major source of PBDEs to the Asian environment. Martin et al. (2004) reported that in the Guangdong Province alone, located adjacent to the PRE, 145 million electronic devices were scrapped in 2002. The extent of contamination of the PRE with POPs was recently reviewed by Chau (2005).

Local sources of pollution including POPs are present in Hong Kong and several factors contribute to their discharge: (1) the dense population of 6.2 million, (2) heavy industrialization, including one of the busiest container ports in the world, (3) a former lack of regulation to control the release of agricultural and industrial effluents.

Reports on POPs in the environment of Hong Kong includes data on sediments (Richardson and Zheng, 1999; Liu et al., 2005), mussels (Liu et al., 2005), small cetaceans (Ramu et al., 2005), air (Louie and Sin, 2003) and in atmospheric deposition samples (Wong et al., 2004). Reported concentrations of POPs in Hong Kong's coastal waters have been reviewed Phillips (1989). In 1983, concentrations of up to 2600 ng/g of DDT in mussel tissue were reported. Overall, the environment of Hong Kong is moderately contaminated with POPs.

The aim of this investigation was to determine concentrations of polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethanes (DDTs), hexachlorocyclohexanes (HCHs) and PBDEs in seawater and SML samples from Hong Kong, their distribution between the dissolved phase (DP) and suspended particulate matter (SPM) phase, and to identify potential sources. Data reported represents the first measurements of POPs in SML samples from Chinese coastal waters. The data on PBDEs in the SML are the first reported in the literature.

VII-2 Materials and Methods

VII-2-1 Sample collection

The locations of the sample stations are shown in Figure VII-1. In total, five sample stations were sampled in March 2005. Stations 1 (Victoria Harbour), 2 (Tolo Harbour) and 5 (Aberdeen Typhoon Shelter) are considered to be more contaminated due to intensive shipping traffic, nearby industrial areas and a more restricted water exchange with oceanic waters. Station 3 (Deep Bay) located on the western coast, may be influenced by the Pearl River Estuary, whereas Station 4 (Clear Bay) is of more oceanic character.

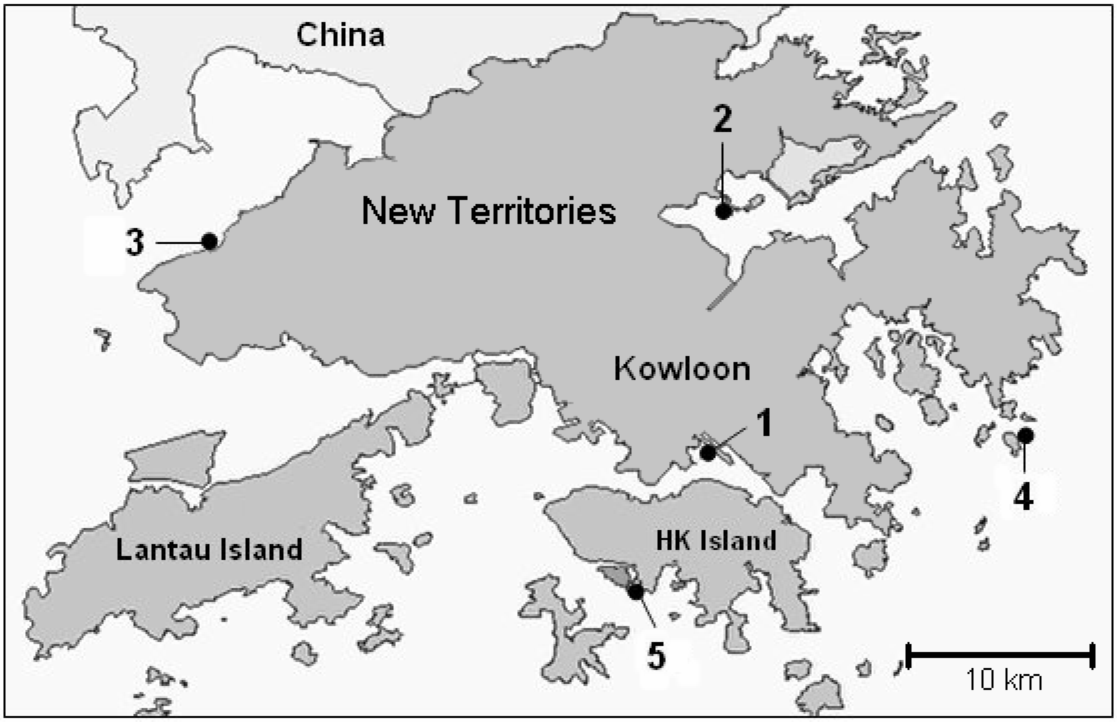


Figure VII-1: Location of sample stations.

The sampling procedure for collection of SML samples is provided in detail in Chapter III-3-1. The revolution rate of the glass drum was set to 13-14 rpm, resulting in a thickness of collected SML of between 65 to 79 μm (average 71 ± 5 μm). Seawater (subsurface) samples were collected at a depth of 1 m. All SML and subsurface samples were filtered online, as described in Chapter III-3-1.

Meteorological data and temperature of surface water (0.5 and 40 cm depth) were recorded during each sampling event and are summarized in Table VII-1.

VII-2-2 Sample treatment and analysis

All samples were spiked with a $^{13}C_{12}$-labeled PCB surrogate standard prior to extraction. All subsurface and SML samples were extracted as described in Chapter III-4-1. SPM were extracted with 50 mL acetone-hexane (3:2) in a microwave oven CEM Mars X (CEM, Matthews, NC, USA) for 18 min at 115 °C. After extraction, the vessels were allowed to cool to room temperature. The supernatant was filtered through glass wool and combined with a 2-3 mL acetone-hexane (3:2) rinse of the sample residue. All extracts were cleaned-up using a silica gel column, where the procedure was described in Chapter III-5. Analysis of sample extracts was performed on a Varian 4000 GC-IT-MSMS, according to the procedure described in Chapter III-6-2.

Station	Date	μ [um][a]	Current	Temperature [°C]			Wind speed [m/s]	Wind direction	Humidity [%]	Slick [%][d]
				Air	Surface Water[b]	Water[c]				
1 (Victoria Harbour)	01.03.2005	72	moderate	14.4	15.5	15.4	4.3	SE to E	77.7	30
2 (Tolo Harbour)	04.03.2005	68	moderate	14.1	14.5	14.4	3.9	NE	43.3	20
3 (Deep Bay)	06.03.2005	79	calm	18.4	15.4	15.3	2.9	E	53.2	10
4 (Clear Water Bay)	11.03.2005	65	calm	20.1	16.5	16.3	0.7	E	64.3	0
5 (Aberdeen Typhoon Shelter)	15.03.2005	73	calm	19.7	15.1	15	2.1	S	63.4	0

[a] thickness of collected SML

[b] at depth 0.5 to 1 cm

[c] at depth of 40 cm

[d] visual observation

Table VII-1: Description and environmental characteristics (seawater and atmosphere) of sample stations in Hong Kong

VII-3 Results and Discussion

VII-3-1 Quality assurance

All analysis was subject to strict quality assurance and control procedures. All samples were collected and analysed in duplicate. The values of relative percent difference of duplicate samples were between 10 and 42% in the dissolved phase and 4 and 29% in the SPM. Given the low concentrations, this was considered to be satisfactory. Blank GF filters constituted 20% of the total number of SPM samples in order to evaluate contamination during transport and storage. Mean recoveries of the $^{13}C_{12}$-labeled PCB surrogate standard were between 76 and 92 % for the DP, and between 76 and 86% for the SPM. Control calibration standards were analysed for every four samples to check instrument performance during analysis. Only single SPM samples from the SML and subsurface were available for analysis from Station 5 due to loss of the duplicates because of leaking extraction vessels.

VII-3-2 Concentrations of POPs in the subsurface waters

VII-3-2-1 Polychlorinated biphenyls (PCBs)

ΣPCB concentrations in the DP and SPM were between 266 and 434 pg/L, and between 86 and 273 pg/L respectively. Average concentrations at each station are given in Table VII-2. Subsurface samples collected at Station 1 (Victoria Harbour) and 2 (Tolo Harbour) were highest in PCB contamination, likely due to restricted water exchange with oceanic waters. Lower concentrations of PCBs, particularly associated to SPM, were detected at Stations 3-5, where the samples were of more oceanic character. CB 49, 149, 170 and

171 were most abundant and represented more than 26% of the total concentration of congeners present in both phases.

The concentrations of ΣPCBs in seawater collected from other coastal regions of China were reported to be in a significant higher concentration range (see Table VII-3). Reported concentrations of ΣPCBs from the Daya Bay (Zhou et al., 2001) and Minjiang River (Zhang et al., 2003b) were higher by a factor of 6000 compared to levels determined from this study. However, data from the Xiamen Harbour (Zhou et al., 2000) and the Yangtse River (Jiang et al., 2000) were more comparable to concentrations obtained during this study. It is known, that Hong Kong's marine environment is influenced by discharge from China via the Pearl River Estuary (PRE) and concentrations of ΣPCBs (sum of DP and SPM) were in a range of 2470 to 6750 pg/L for the PRE (Nie et al., 2005), and therefore approximately 12 times higher than concentrations measured for the nearest station (Station 3) to the PRE. Concentrations of Singapore's coastal waters were higher by a factor of 7 compared to Hong Kong (Chapter VI).

VII-3-2-2 Polybrominated diphenyl ethers (PBDEs)

Concentration of BDE congeners and ΣPBDE in subsurface waters are given in Table VII-4. A concentration range from 11.3 to 62.3 pg/L in the DP and from 26.2 to 32.5 pg/L in the SPM was found for ΣPBDEs among the stations. As for PCB contamination, the highest concentrations of ΣPBDEs were detected at Station 1 (Victoria Harbour) and 2 (Tolo Harbour). Beside these two stations, BDE congeners associated to the SPM were below LODs in subsurface samples. No BDE congeners could be detected in the oceanic waters of Stations 3 and 4. The most abundant BDE congeners were 28, 47, 99 and 100, whereas BDE 153, 156 and 209 were below LOD in all subsurface samples.

Station	1		2		3		4		5	
SML	c_{DP}	c_{SPM}	c_{DP}	c_{SPM}	c_{DP}	c_{SPM}	c_{DP}	c_{SPM}	c_{DP}	c_{SPM}
CB 44	28.0	27.9	17.1	15.9	18.3	16.8	18.3	15.9	17.5	17.1
CB 49	112.0	103.9	67.9	66.6	67.5	71.1	71.8	nd	70.3	68.5
CB 52	nd	17.2	nd	8.7	nd	nd	9.9	nd	9.2	nd
CB 70	20.1	21.9	10.9	12.0	13.0	nd	13.1	12.0	12.3	11.9
CB 74	nd	10.8	6.1	5.8	6.7	nd	nd	nd	6.7	5.9
CB 87	29.2	30.3	17.8	17.1	18.6	nd	18.8	19.6	17.9	17.9
CB 95	18.8	11.9	7.6	5.5	10.6	nd	9.8	6.4	8.3	6.6
CB 99	nd	29.6	17.2	17.6	17.6	16.9	19.6	18.5	18.3	nd
CB 101	30.4	29.3	10.7	18.3	18.8	18.4	18.5	17.8	18.5	15.5
CB 149	52.0	57.5	30.4	30.6	30.9	11.1	32.2	32.0	31.0	32.0
CB 151	23.8	24.9	14.7	13.9	14.5	14.2	15.9	15.7	14.8	15.2
CB 170	nd	56.5	40.0	31.3	33.3	nd	42.8	nd	35.1	nd
CB 171	95.2	71.9	50.8	nd	48.7	35.7	38.6	nd	46.5	nd
CB 177	39.9	27.5	20.8	nd	15.1	10.3	11.2	nd	11.5	nd
ΣPCBs	593.4	543.6	586.7	368.9	595.2	222.9	610.6	137.9	564.2	234.0
Subsurface	c_{DP}	c_{SPM}	c_{DP}	c_{SPM}	c_{DP}	c_{SPM}	c_{DP}	c_{SPM}	c_{DP}	c_{SPM}
CB 44	18.3	13.8	13.8	nd	14.4	13.2	15.1	13.4	14.1	nd
CB 49	59.7	45.0	55.7	nd	58.4	55.2	60.2	nd	58.0	nd
CB 52	nd	nd	nd	nd	nd	nd	7.7	nd	10.6	nd
CB 70	11.8	10.6	10.1	nd	11.0	nd	nd	9.4	10.1	nd
CB 74	7.2	4.8	nd	5.1	5.1	nd	nd	nd	nd	nd
CB 87	16.3	16.3	15.0	13.9	15.5	nd	14.8	15.1	15.4	nd
CB 95	17.8	9.7	7.7	4.7	7.2	nd	4.8	nd	6.1	5.6
CB 99	nd	15.9	14.7	14.9	15.2	nd	nd	nd	15.1	nd
CB 101	20.7	22.2	15.2	nd	13.8	14.2	13.7	14.4	14.6	15.3
CB 149	28.2	33.0	26.3	23.1	25.5	26.5	25.9	23.9	25.7	26.6
CB 151	13.2	13.6	12.1	11.5	12.3	12.4	12.2	12.3	12.3	12.5
CB 170	nd	nd	nd	25.3	30.8	nd	nd	nd	27.9	nd
CB 171	46.5	27.7	30.5	30.8	39.0	33.7	48.8	nd	42.7	nd
CB 177	6.5	nd	5.9	11.4	19.0	16.1	12.3	nd	11.0	nd
ΣPCBs	411.3	273.0	433.5	229.3	342.7	184.2	266.0	88.5	327.1	85.6

Table VII-2: Mean concentrations of major PCBs in the SML and subsurface waters in the dissolved phase (DP, in pg/L) and suspended particulate matter (SPM, in pg/L) (nd= not detected).

Location	Year	ΣPCBs		ΣDDTs		ΣHCHs		Reference
		DP	SPM	DP	SPM	DP	SPM	
Xiamen Harbour, China	1998	0.1-1.7		1.1-29.1[a]		3.5-27.8[b]		Zhou et al., 2000
Yangtse River, China	1998	2	0.5-1.3	1.9[c]	0.8-1.4[c]	9.9[d]	0.6-1.6[d]	Jiang et al., 2000
Minjiang River, China	1999	204-2473		40.6-234[a]		52.1-515[b]		Zhang et al., 2003
Daya Bay, China	1999	91.1-1355		30-975[a]		35.5-1228[b]		Zhou et al., 2001
Pearl River, China	2001			0.03-0.55[c]	0.13-2.8[c]	14.5-59.1[b]	0.49-4.8[b]	Luo et al., 2004
Pearl River Delta, Macau, China	2001			0.49-2.8[c]	8.1-27.6[c]	5.7-22.3[b]	3.0-8.0[b]	Luo et al., 2004
Pearl River Delta, China	2002	1.13-3.11						Nie et al., 2002
Hong Kong	2002			0.09-0.2[c]		0.08-0.09[d]		Wong et al., 2004
Singapore	2004	0.29-2.9	0.33-1.4	0.03-0.14[a]	0.005-0.05[a]	0.80-3.2[b]	0.05-1.1[b]	Wurl et al. 2005
Hong Kong	2005	0.26-0.41	0.09-0.27	0.8-5.6[a]	0.4-1.4[a]	0.4-0.9[b]	0.03-0.08[b]	this study

[a] Sum of p,p'-DDE, p,p'-DDD and p,p'-DDT

[b] Sum of α-HCH, β-HCH, γ-HCH and δ-HCH

[c] Sum of o,p'-DDE, o,p'-DDD, o,p'-DDT, p,p'-DDE, p,p'-DDD and p,p'-DDT

[d] Sum of α-HCH, β-HCH and γ-HCH

Table VII-3: Comparison of ΣPCBs, ΣDDTs and ΣHCHs in the dissolved phase (DP, in ng/L) and suspended particulate matter (SPM, in ng/L) from various rivers and estuaries in Asia.

Station	1		2		3		4		5	
SML	c_{DP}	c_{SPM}	c_{DP}	c_{SPM}	c_{DP}	c_{SPM}	c_{DP}	c_{SPM}	c_{DP}	c_{SPM}
BDE 28	14.8	42.5	15.4	18.1	nd	nd	nd	nd	30.2	8.1
BDE 47	11.6	26.6	10.4	13.1	nd	nd	nd	nd	23.2	nd
BDE 99	25.3	nd	nd	nd	nd	nd	nd	nd	9.6	nd
BDE 100	23.3	nd	5.4	2.4	nd	nd	nd	nd	nd	nd
BDE 153	45.6	nd	nd	nd	nd	nd	nd	nd	nd	nd
BDE 156	56.5	nd	4.2	nd	nd	nd	nd	nd	nd	nd
BDE 183	51.1	nd	4.8	3.8	nd	nd	nd	nd	nd	nd
BDE 209	tr	tr	tr	tr	nd	nd	nd	nd	tr	nd
ΣPBDEs	228.2	69.1	40.2	37.4	nd	nd	nd	nd	63.0	8.1
Subsurface	c_{DP}	c_{SPM}	c_{DP}	c_{SPM}	c_{DP}	c_{SPM}	c_{DP}	c_{SPM}	c_{DP}	c_{SPM}
BDE 28	32.2	22.1	14.4	nd	nd	nd	nd	nd	5.8	nd
BDE 47	27.5	10.4	8,2	22.4	nd	nd	nd	nd	5.5	nd
BDE 99	2.6	nd	nd	nd	nd	nd	nd	nd	nd	nd
BDE 100	nd	nd	5.3	3.8	nd	nd	nd	nd	nd	nd
BDE 153	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BDE 156	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BDE 183	nd	nd	3.2	nd	nd	nd	nd	nd	nd	nd
BDE 209	tr	nd	tr	nd	nd	nd	nd	nd	tr	nd
ΣPBDEs	62.3	32.5	31.1	26.2	nd	nd	nd	nd	11.3	nd

Table VII-4: Mean concentrations of PBDEs in the SML and subsurface waters in the dissolved phase (DP, in pg/L) and suspended particulate matter (SPM, in pg/L) (tr=traces; nd= not detected).

Literature data on the concentrations of PBDEs in seawater samples are limited and only one recent and more comprehensive study has been conducted in the San Francisco Bay (Oros et al., 2005). Concentrations of ΣPBDE in a range of 3 to 503 pg/L were reported. It was also reported that BDE 99, 100 and 209 were the most abundant congeners present. The congener 209 is considered to undergo rapid degradation and/or bioaccumulation processes in aqueous samples (Söderström et al., 2004). No BDE 209 congeners could be quantified above LOD in Hong Kong's waters, but traces were qualitatively identified. Booji et al. (2002) derived aqueous concentrations of BDE congeners at the Dutch coast based on their accumulation in semi-permeable membrane devices and blue mussels. He reported concentrations of BDE 47, 99, 153 and 209 at 1, 0.5, 0.1 and 4 pg/L, respectively. Concentrations of ΣPBDE in the semi-enclosed waters of the Lake Ontario and Lake Michigan were 6 and 158 pg/L, respectively (Lucky et al., 2001; Stapleton and Baker 2001). All these reported concentrations are in a similar range to that obtained for this study.

VII-3-2-3 Organochlorine pesticides (OCPs)

The major OCPs detected in Hong Kong's subsurface samples were DDT and its metabolites, HCH isomers, trans-Chlordane, Endosulfan I and Endosulfan sulfate. Measured concentrations are given in Table VII-5. DDT and its metabolites were present in substantially higher concentrations than other OCPs, and were in range of 775 to 5583 pg/L for the DP and 359 to 1369 pg/L for the SPM. The samples collected at the entrance to the Aberdeen Typhoon Shelter on the south of Hong Kong Island (Station 5), were highest in DDT contamination. Concentrations among the other stations were at least four times lower. The lowest DDT concentration was detected at Station 3 with a concentration of 775 and 359 pg/L in the DP and SPM, respectively.

Station	1		2		3		4		5	
SML	c_{DP}	c_{SPM}	c_{DP}	c_{SPM}	c_{DP}	c_{SPM}	c_{DP}	c_{SPM}	c_{DP}	c_{SPM}
DDE	138.1	268.4	84.6	200.8	97.1	125.3	107.2	72.2	633.1	464.9
DDD	651.4	1039.1	398.6	344.2	404.8	1160.6	656.5	159.4	5932.9	1328.5
DDT	1329.3	1226.3	837.9	343.6	1347.4	1107.3	1536.5	183.7	16557.0	2453.5
ΣDDTs	2118.7	2533.7	1321.1	888.6	1849.3	2393.2	2300.2	415.3	23122.9	4246.9
α-HCH	125.4	nd	133.6	nd	425.9	33.1	124.8	57.5	96.8	nd
β-HCH	401.0	nd	373.5	nd	398.5	nd	281.0	nd	522.4	nd
γ-HCH	nd	nd	532.8	nd	278.3	nd	89.5	nd	256.8	nd
δ-HCH	nd	nd	80.8	nd	154.3	51.9	95.5	83.9	70.9	nd
ΣHCHs	526.3		1120.6		1256.9	85.0	590.8	141.4	946.9	
Endosulfan I	94.2	89.3	58.3	84.9	64.3	nd	63.7	nd	58.5	60.5
Endosulfate	512.1	189.7	169.7	295.9	450.5	121.5	269.9	nd	475.6	245.1
t-chlordane	77.1	nd	48.6	86.4	59.9	nd	57.1	nd	48.1	52.8
Subsurface	c_{DP}	c_{SPM}	c_{DP}	c_{SPM}	c_{DP}	c_{SPM}	c_{DP}	c_{SPM}	c_{DP}	c_{SPM}
DDE	92.2	133.6	79.0	80.7	54.2	58.0	53.7	57.4	225.6	88.4
DDD	413.8	450.3	311.5	189.9	277.1	140.8	272.0	209.6	1711.3	664.2
DDT	935.2	655.2	501.9	232.0	443.2	159.7	525.1	198.1	3646.4	616.5
ΣDDTs	1441.2	1239.0	892.3	502.6	774.5	358.5	850.7	465.1	5583.3	1369.1
α-HCH	70.9	nd	107.2	32.8	231.0	nd	106.8	nd	78.3	nd
β-HCH	338.8	nd	247.0	nd	302.5	nd	112.9	nd	229.0	nd
γ-HCH	nd	nd	278.6	nd	281.7	nd	149.3	nd	151.3	nd
δ-HCH	nd	nd	55.1	nd	125.1	nd	79.2	nd	64.8	nd
ΣHCHs	409.7		687.8	32.8	940.2		448.1		523.4	
Endosulfan I	45.6	nd	48.1	53.7	54.6	56.7	nd	nd	45.5	nd
Endosulfate	495.3	158.6	136.3	162.5	374.6	107.1	183.5	nd	174.6	102.3
t-chlordane	39.4	nd	40.1	49.1	48.3	50.9	nd	nd	39.3	44.8

Table VII-5: Mean concentrations of OCPs in the SML and subsurface waters in the dissolved phase (DP, in pg/L) and suspended particulate matter (SPM, in pg/L) (nd= not detected).

Concentrations of DDT in the environment of China are high (Wong et al., 2005), and the concentrations in Hong Kong's seawater are relatively low compared to the Daya Bay, located 50 km northeastern of Hong Kong and the Minjiang River (Table VII-3). Concentrations from Macau, China and the PRE were more comparable, even so twenty times higher DDT concentrations in the SPM were detected in Macau, China (Table VII-3). However, the concentrations of DDTs in subsurface samples collected from Singapore's marine environment (Chapter VI) were lower by factors of up to 50. In general, DDT was predominant among its metabolites indicating that fresh inputs of DDT continue to occur into Hong Kong's marine environment.

ΣHCHs varied between 410 and 940 pg/L in the DP, but were detectable in the SPM in only one samples at a low concentration range of 33 pg/L. The highest concentration of ΣHCHs in the DP was found at Station 3, being higher by a factor of 2 compared to other stations. In general, the concentrations of ΣHCHs in Hong Kong's coastal waters can be considered as low by compared to data from the Daya Bay, China, where concentrations of up to a 1300 times higher have been reported (Zhou et al., 2001). Seawater from other coastal regions of China has also been found to be highly contaminated with ΣHCHs (Table VII-3) relative to samples collected in this study. The isomers α-, β- and γ-HCHs were most abundant, whereas δ-HCH was present at lower concentrations (Table VII-5).

Concentrations of Endosulfan I and Endosulfan sulfate are in same range as reported for the Xiamen Harbour, China (Zhou et al., 2000), but endosulfan sulfate levels were two magnitudes higher in the Daya Bay, China (Zhou et al., 2001).

VII-3-3 Concentration of POPs in the sea-surface microlayer (SML)

VII-3-3-1 Polychlorinated biphenyls (PCBs)

Concentrations of PCBs in the SML are given in Table VII-2 and are enriched by factors of between 0.4 and 6.1 compared to the subsurface samples. The enrichment factor (EF) for ΣPCBs ranged between 1.4 to 2.3 and between 1.6 to 2.7 in the DP and SPM, respectively. These values are lower by a factor of three compared to the upper limit values reported for SML samples collected in Singapore (Chapter V and VI). The highest EF values for PCBs associated to SPM were determined at Station 1 and 2 where heavier shipping traffic and lower water depths may lead to more intensive sediment resuspension processes. EF values of PCBs in the SML can be as high as 60 - as reviewed by Wurl and Obbard (2004), but more recent data show that the EF value is more likely to be in the range of 0.5 to 4 (Abd-Allah, 1999; Wurl and Obbard 2005a; Wurl and Obbard, 2006j; Garcia-Flor et al., 2005). The concentrations of PCBs in the DP of the SML varied in a relatively narrow range of between 564 and 610 pg/L, whereas for the SPM the range was 138 to 544 pg/L. This can be explained by the heterogeneous distribution of flocculated particles on the water surface.

VII-3-3-2 Polybrominated diphenyl ethers (PBDEs)

Concentrations ΣPBDE in the SML ranged between 40 and 228 pg/L in the DP, and 8 and 69 pg/L in the SPM (Table VII-4) resulting in EF values of between 1.3 to 5.1, and between 1.4 and 2.1 respectively. As for the subsurface samples, the highest concentrations in the DP and SPM were found at the Station 1 and 2 and were below LOD at Station 3 and 4. The congeners BDE 100, 153, 156 and 183 were detected in the SML collected at Station 1, but were below LOD in the subsurface samples. The EF values for BDE congeners were in the range of 0.4 to >10 in the DP, and of 1.4 to 3.0 in the SPM. Compared to the EF values of the structure-like PCBs, it can be concluded that PCBs and PBDEs have a similar potential to enrich in the SML. Water solubility, n-octanol/water partition coefficient (K_{ow}) and vapor pressure are the key parameters for the enrichment of hydrophobic compounds in the SML. Values of these parameters for BDE and corresponding CB congeners are given in Table VII-6.

	Water solubility [ug/L]	$\log K_{ow}$	Vapor pressure [mPa]
BDE 28	70 [a]	5.94 [c]	2.81 [a]
CB 28	311 [b]	5.68 [d]	27.7 [b]
BDE 47	15 [a]	6.81 [c]	0.19 [a]
CB 47	103 [b]	5.83 [d]	15.1 [b]
BDE 99	9 [a]	7.32 [c]	0.018 [a]
CB 99	35 [b]	6.40 [d]	0.316 [b]
BDE 100	40 [a]	7.24 [c]	0.033 [a]
CB 100	27 [b]	6.17 [d]	0.818 [b]
BDE 153	1 [a]	7.90 [c]	0.0021 [a]
CB 153	13 [b]	6.83 [d]	0.0663 [b]
BDE 156			
CB 156	15 [b]	6.63 [d]	0.0734 [b]
BDE 183	2 [a]	8.27 [c]	0.000468 [a]
CB 183	5 [b]	7.09 [d]	0.0638 [b]
BDE 209		8.7 [e]/ 10 [f]	
CB 209	1 [b]	7.97 [d]	0.00275 [b]

[a] Tittlemier et al., 2002
[b] Holmes et al., 1993
[c] Braekvelt et al., 2002
[d] Makino, 1999
[e] Wania and Dugani, 2003 (model data)
[f] Darnerud et al., 2001 (experimental data)

Table VII-6: Physicochemical properties of BDE and CB congeners.

From these values, it should be expected that BDE congeners are enriched at higher levels in the SML than CB congeners due to the higher K_{ow} and lower water solubility. However, this could not be observed in the samples. The process of enrichment is complex and other factors may play a critical role, such as competing adsorption processes on floating particulates. Beside, the absolute differences of the physicochemical properties at 25°C between BDE and CB congeners, as presented in Table VII-6, may be smaller at the prevailing temperatures during sample collection, i.e. 15°C. However, temperature dependence relationships for these parameters are still unknown for PBDEs.

VII-3-3-3 Organochlorine pesticides (OCPs)

As observed of PCBs in the SML, the concentrations of ΣDDTs in the SML varied in a relative narrow range of 1321 to 2300 pg/L, except at Station 5, where a substantial higher concentration of ΣDDTs in the DP was detected (23,123 pg/L). The concentration range of DDT associated to SPM was wider (415 to 2534 pg/L), probably due to the heterogeneous distribution of flocculated particulates on the water surface. As for the subsurface samples, DDT was detected in higher concentration than its metabolites. The range of enrichment of DDTs in the DP and SPM of the SML were 1.1 to 4.5 and 0.8 to 8.2, respectively. The higher affinity of DDT compounds to particulate matter leads to a higher enrichment of these compounds in the SPM compared to other OCPs. The enrichment of ΣHCHs in the DP of the SML was in the range of 1.2 to 2.5, which is generally similar to levels of enrichment reported in Singapore's SML (Chapter V and VI). This is consistent with the relative high water solubility of HCH isomers and lower K_{ow} values, which results in a lower tendency to accumulate in the SML and adsorb onto SPM. HCH isomers in the SPM of the SML could be detected only in two samples – at

Station 3 and 4 at a concentration of 85 and 141 pg/L, respectively. However, prevailing concentrations of HCHs in Singapore's marine environment can lead to an enrichment of HCHs in the SPM of the SML by up to 7 fold, but were generally in a range of 1.1 to 1.4 (Chapter VI).

The OCPs Endosulfan I, Endosulfan sulfate and trans-Chlordane were enriched in the SML by factors of 1 to 2.7.

VII-3-4 Distribution of POPs between particulate and dissolved phases

VII-3-4-1 Polychlorinated biphenyls (PCBs)

Principal component analysis (PCA) was applied to the prozentual composition of samples normalized to concentration of ΣPCBs and Arochlor composition (Figure VII-2). PCA indicates homogenous PCB contamination among all stations with little variance in the PCB composition for the DP, but slightly higher variances for the SPM. Variability in surface properties, size distribution and carbon content of the SPM among locations of the stations may account for the higher variance observed in PCB composition. The mass percentage distribution of individual CB congeners is shown in Figure VII-3 and VII-4 for Station 1 and 3 respectively. In general, the mass distribution between SML and subsurface waters are similar, and the major detected CB congeners were CB 18, 17+31, 49, 87, 99, 101, 149, 170, 171, 177, 205, 206 and 209. At Station 1 (Victoria Harbour) the PCB content associated to the SPM is higher than at the Station 3 (Deep Bay), but higher chlorinated CB congeners (octa-, nona- and deca-chlorobiphenyls) represent a higher relative contribution on the SPM at Station 3 relative to Station 1 where these congeners dominate in the DP. This may be due to the higher SPM content in the Deep Bay (average 20 mg/L) compared to Victoria Harbour (average 5 mg/L) (EPD, 2003).

The distribution of CB congeners between the DP and SPM were in a range of 40 to 60% associated to SPM in both subsurface and SML samples. Relationship between log Kd' and log Kow are used to examine equilibrium conditions between both phases, as described in more detail in Chapter VI-3-5-1. As observed in the marine environment of Singapore, non-equilibrium conditions were observed in samples with restricted water exchange and higher biological activities, i.e. Station 1 (Victoria Harbour), whereas a weak positive relationship – indicating a closer condition to equilibrium – were observed at the station with oceanic influence, i.e. Station 3.

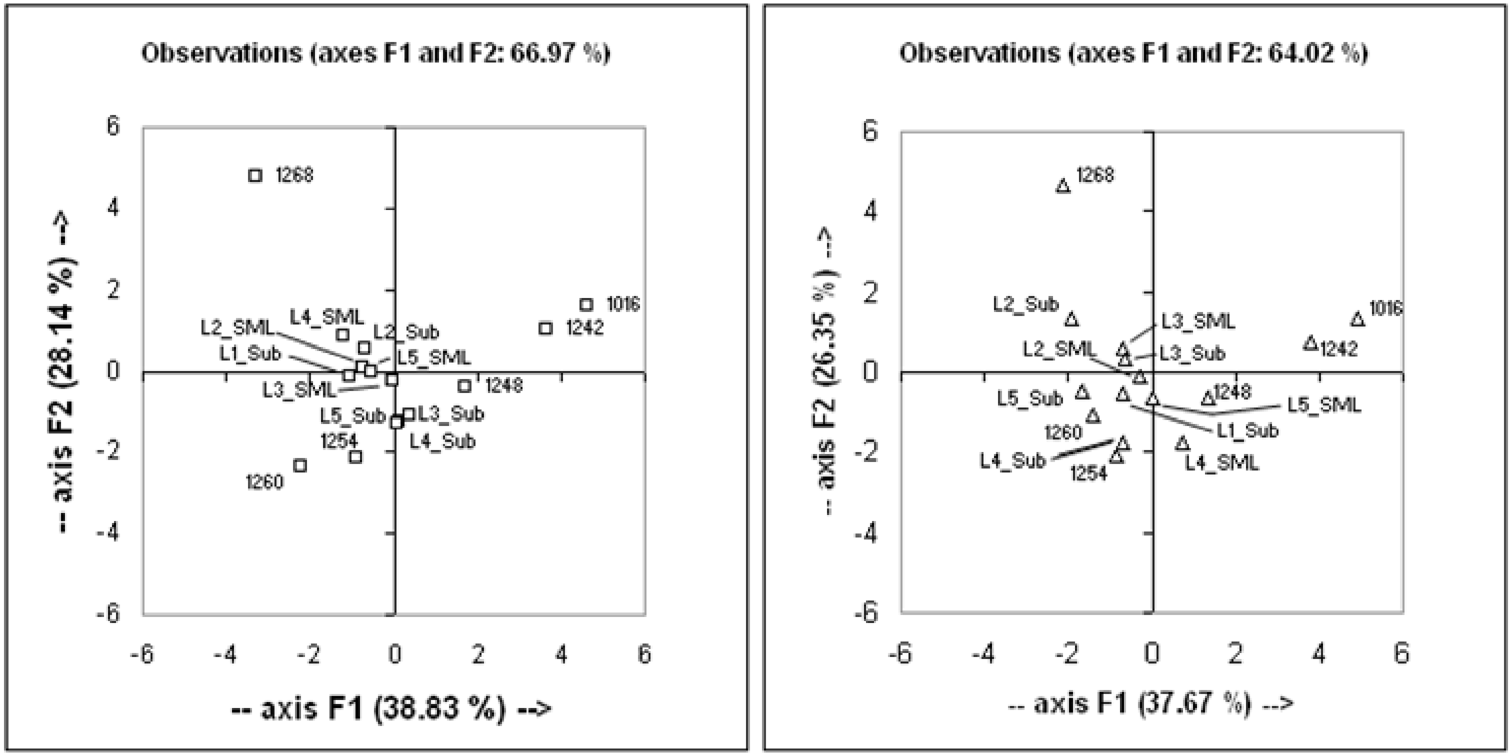


Figure VII-2: PCA score plot for comparison of PCB congeners and Arochlor mixtures in DP (□) and SPM (△).

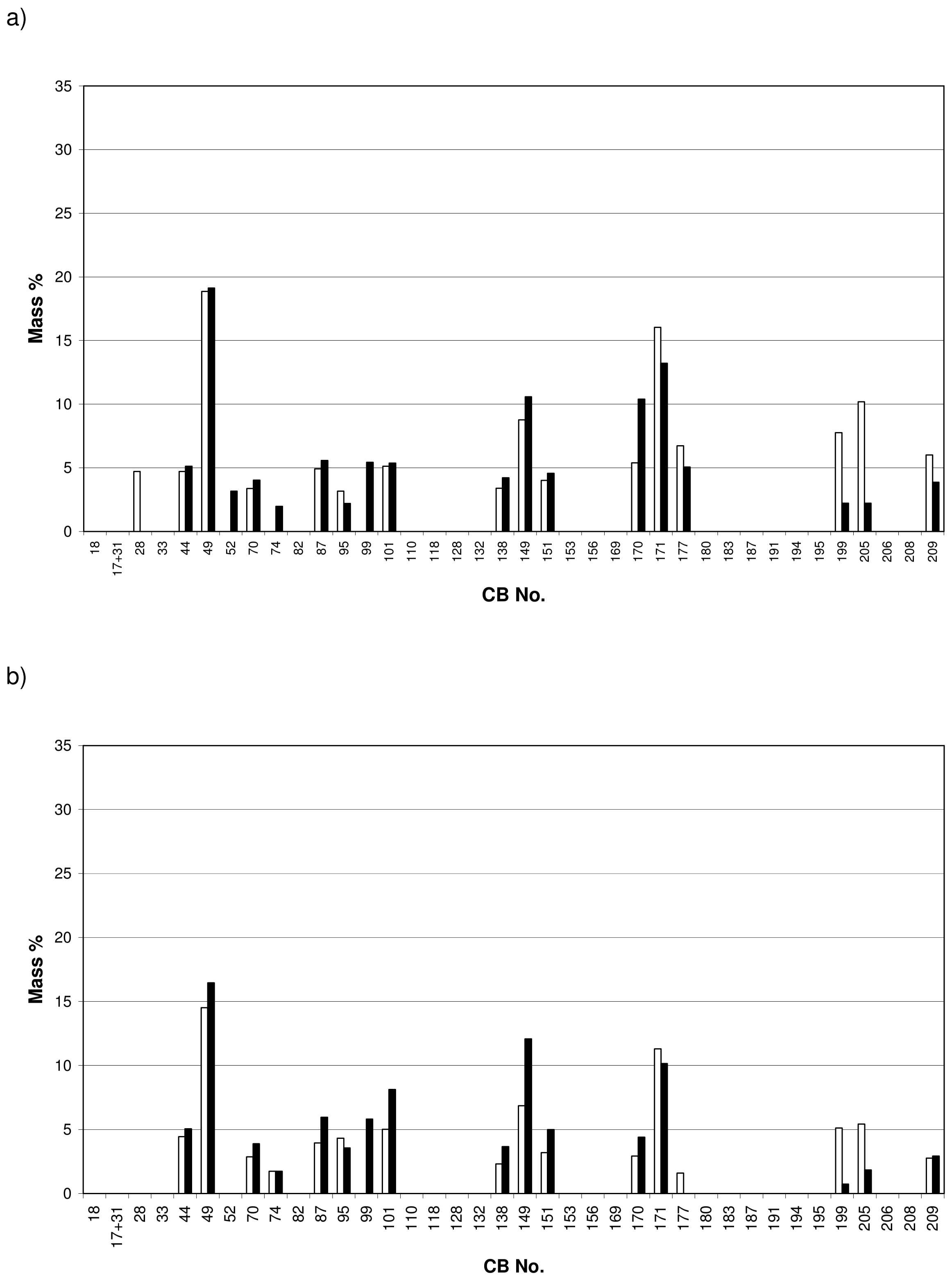


Figure VII-3: Mass distribution of PCB congeners at Station 1 in the DP (☐) and SPM (■) (a) SML, (b) subsurface waters.

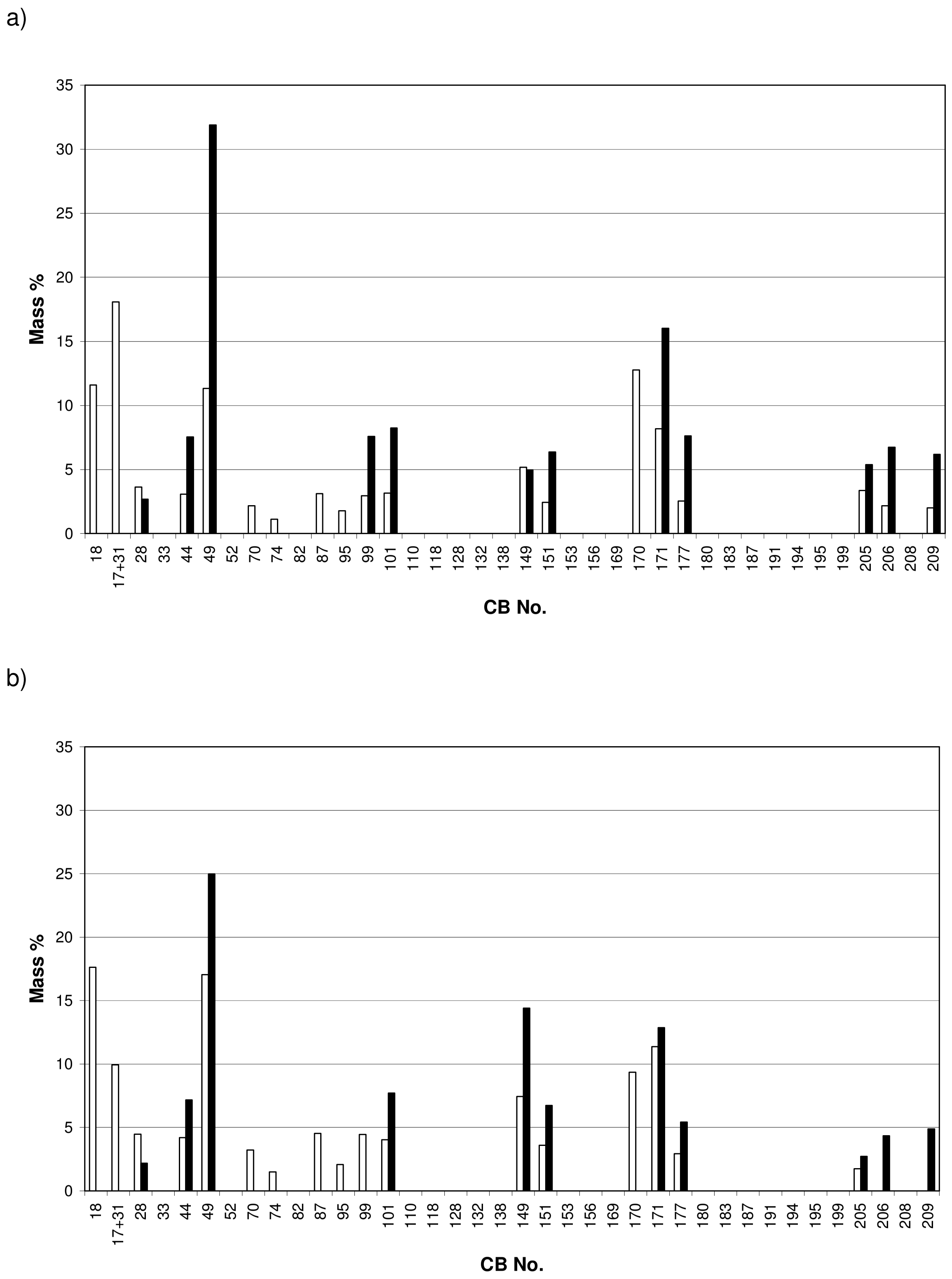


Figure VII-4: Mass distribution of PCB congeners at Station 3 in the DP (□) and SPM (■) (a) SML, (b) subsurface waters.

VII-3-4-2 Polybrominated diphenyl ethers (PBDEs)

Paired concentrations for BDE congeners in the DP and SPM were found in the SML for BDE 28, 47 at Station 1, BDE 28, 100 and 183 at Station 2, and for BDE 28 at Station 5. For subsurface waters, BDE 28 and 47 could be detected in both phases at Station 1, and BDE 47 and 100 at Station 2 (Table VII-4). BDE 209 can be expected to be dominant in the SPM, but probably undergoes photolytic debromination (Söderström et al., 2004) and metabolic degradation (Kierkegaard et al., 1999) to lower brominated BDEs in the marine environment. Suspended particulates may serve as a medium for the biodegradation due to the presence of a microbial film (Aubert and Gauthier, 1977) on the particulate surface. No data could be found in the literature to confirm microbial degradation of PBDEs in the marine environment, however Martin et al. (2004) suggested that microbial transformation is a possible pathway for the fate of PBDEs in the environment. Microbial degradation of PCBs on suspended particulates in aquatic environment has been reported (Sugiura, 1992). In general, the tri-, tetra- and pentabrominated BDE congeners were dominant in the SPM, contributing 70% to the total concentrations (DP+SPM). In contrast, tri-, tetra- and pentachlorinated CB congeners in the SPM were present at less than 50% of the total. This is consistent with a higher K_{ow} value for BDE congeners.

VII-3-4-3 Organochlorine pesticides (OCPs)

DDT compounds are known to associate more strongly with SPM than other OCPs. For example, Luo et al. (2004) reported that 90% of the detected DDT compounds in the PRE were associated to the SPM, whereas this fraction was 40% in the Yangtse River (Jiang et al., 2002) and 54% in coastal waters of Singapore (Chapter V). In this study, the SPM-associated fraction was in a range of 16-56% and 20-48% in subsurface waters and SML, respectively. The lower values determined at Station 4 and 5 are associated with coastal waters of a prevailing oceanic character. At Station 3, the highest distribution to SPM was found, even so this location is subject to hydrodynamic exchange with oceanic waters. This can be explained by the relative high SPM content of 20 mg/L in the waters at this location – four times higher than at the other stations (EPD, 2003).

In a few samples with detectable HCH isomer levels in the SPM, the fraction ranged from 7 to 47% with the upper value of δ-HCH. In Singapore's coastal waters, with a average SPM content of 52 mg/L (Chapter VI), the fraction of HCH isomers associated with the SPM were higher at 72, 52 and 22% for β-HCH, α-HCH and γ-HCH, respectively.

VII-3-5 Sources of POP contaminations

No direct seaward transport of POPs from the PRE to the open South China Sea was suggested by Peng et al. (2005), where submarine outfalls of Hong Kong represent an important contamination source. Chau (2005) suggested that contamination of POPs from the PRE was prevalent in Hong Kong coastal waters. Station 3 may receive such contamination from the PRE, whereas the PRE itself receives contaminants through riverine outflow from Guangdong, southern China (Nie et al., 2005). For example, the Xijiang River is considered to transport high levels of DDTs into the PRE (Luo et al., 2004). Chen et al. (2004) suggested that contamination discharged into Chinese coastal waters from four westerly river tributaries i.e. Yamen, Hufiaomen, Jaimen and Modaomen rivers, is transported away from Hong Kong. However, it was also reported that during the summer months, when a southwesterly monsoon prevails, contamination from the eastern part of the PRE may be carried into Hong Kong's marine environment.

VII-3-5-1 Polychlorinated biphenyls (PCBs)

PCA (Figure VII-2) shows that the PCB composition of all samples in both phases is most similar to the commercial mixtures of Arochlor 1254 and 1248, and similarities between PCB composition of the SPM and Arochlor 1260 exist. The commercial PCB mixture used in China, PCB_3 and PCB_5, are similar in CB congener profile to Arochlor 1242 and 1254 (Qin et al., 2003). The analysis conducted in this study did not include di-chlorobiphenyls, which are part of Arochlor 1242, and this may explain the lower similarity between the samples and Arochlor 1242. Fu et al. (2003) reported that a large number of PCB-containing transformers and capacitors still remain in use in China. The PRE may act as transport pathway for PCBs from the mainland of China to Hong Kong, but local sources cannot be excluded.

VII-3-5-2 Polybrominated diphenyl ethers (PBDEs)

The high import of PBDEs in Asia used as flame retardants (De Wit, 2002) and the shipment of electronic waste to China for disposal are major sources of PBDEs in the environment of China. For example, it was reported that 145 million electronic devices were scrapped in Guangdong Province, southern China in 2002 alone (Martin et al., 2004). However, the concentrations of PBDEs in Hong Kong waters were lower than in the San Francisco Bay by a factor of 2, and are therefore not considered to be heavily polluted with PBDEs. Sediments collected from Hong Kong's marine environment (Liu et al., 2005) were not significantly more contaminated than these collected from San Francisco Bay (Oros et al., 2005) and Singapore (Chapter IV). Mai et al. (2005) reported significantly higher concentrations of PBDEs in river sediments collected from the Dongjiang River and Zhuijing River in Guangdong province compared to the PRE. Zheng et al. (2004) found higher PBDE contamination in the sediments of the northern

PRE compared to the southern part. This may suggest that PBDEs are trapped in river sediments closed to the source in the Guangdong Province.

VII-3-5-3 Organochlorine pesticides (OCPs)

The ratio DDT/(DDE+DDD) is an indication of how recently fresh inputs of DDT into the environment occurred, and were in a range of 1.7 to 2.7 and 1.3 to 1.9 in the DP of the SML and subsurface waters, respectively. These values indicate that inputs of DDT are likely to be ongoing into the marine environment of Hong Kong. The ratio in the SPM ranged between 0.6 and 1.4, and the lower range may be an indication of degradation of DDT to its metabolites in the SPM. The ratio has been reported > 1 in the waters of the Xiamen Harbour (Zhou et al., 2000) and Daya Bay (Zhou et al., 2001), but not for the other Chinese regions listed in Table VII-3. The DDT/(DDE+DDD) ratio in Daya Bay was 230, and is the highest reported in the literature for any environmental compartment. The southwesterly monsoon may transport contamination from Daya Bay to Hong Kong. Recently, it was reported that DDT may still be in use in China, despite a ban imposed in 1983 (Chen et al., 2002). The production and usage of the pesticide Dicofol in China may be another significant source of DDT contamination (Qiu et al., 2004). However, local sediments, inside typhoon shelters, contain historical contamination of pesticides and may act as a continued source to the water column via resuspension processes.

The ratio of α-HCH to γ-HCH ranges between 4 and 15 in technical HCH mixtures, and between 0.2 to 1 for the pesticides Lindane (McConnell et al., 1993). In this study, the ratio ranged between 0.3 and 1.5 (average 0.75) in the DP suggesting lindane as the principal HCH source. The relatively low range of the ratio may indicate a local source or short-range transport of HCH isomers in the marine environment. The ratio was in a similar range of 0.03 to 1.5 reported for Daya Bay (Zhou et al., 2001), 0.7 to 1.5 for the

Macau Harbour (Luo et al., 2004), 1.0 to 2.4 for the Zhujing River (Luo et al., 2004) and 0.5 to 4 in the PRE (Hong et al., 1999).

VII-4 Conclusions

This study presents the first data on POP contamination of the SML in Chinese coastal waters. Seawater samples of Hong Kong's marine environment were relative low in contamination when compared to other coastal regions of China, i.e. concentrations of ΣDDTs, ΣHCHs and ΣPCBs were 180, 1300 and 6000 times lower in Hong Kong's waters. Concentrations and enrichment factors of POPs in the SML are comparable to those reported from Singapore, except for elevated levels of DDT and its metabolites. Indeed, the ratio DDT/(DDD+DDE) suggests recent or ongoing inputs of DDT into Hong Kong's marine environment, which are likely to originate from the mainland of China. The SML was up to 8 times more contaminated than the subsurface waters in Hong Kong, where the highest enrichment was found for POPs associated with the SPM fraction. Despite the growing electronic industry and disposal of electronic waste in the southern provinces of China (i.e. Guangdong), the marine waters of Hong Kong are relatively uncontaminated with PBDEs, suggesting that PBDEs released in the environment are trapped in river and estuarine sediments of the PRE with limited transfer to Hong Kong's coastal waters. However, the PRE is likely to be a major pathway for POPs. The distribution of DDT and PCBs between the DP and SPM suggests that particulate matter may play a critical role in the riverine transport of POPs.

CHAPTER VIII

Persistent Organic Pollutants (POPs) in the Marine Atmosphere of Southeast Asia and the Indian Ocean

VIII-1 Introduction

As discussed in Chapter II-3, POPs are globally distributed through the environment and of great concern due to their effects on ecosystems. Even at the Arctic, effects of POPs on the hormone system of polar bears are evident (Oskam et al. 2004). The atmosphere can be considered as a mobile phase for the transportation of POPs towards the polar regions, where condensation of POPs to the marine environment results in subsequent bioaccumulation in the food chain web. The atmosphere receives input of POPs from the soil and the ocean via evaporation processes. Tropical regions of Asia are considered to be a prime source of many global atmospheric POPs due to their extensive usage in the past three decades (Iwata et al., 1994). Atmospheric data for POPs in Southeast Asia and the Indian Ocean date back at least 15 years (Iwata et al., 1993; Bidleman and Leonard, 1982; Tanabe and Tatsukawa, 1980). Primary emissions of POPs to the atmosphere have changed in recent decades, particularly after the establishment of international regulations on reducing emissions.

This study reports concentrations of polychlorinated biphenyl (PCB) and polybrominated diphenyl ether (PBDE) congeners, and the organochlorine pesticides (OCP) hexachlorocyclohexane (HCH) isomers, dichlorodiphenyltrichloroethane (DDT) and its metabolites, and Chlordanes in atmospheric samples collected at two marine sites of Singapore and over the open Indian Ocean between June 2004 and August 2005. Data were compared with those reported for the mid-1970 and beginning of the 1990's to identify any historical trends in atmospheric POP levels over Southeast Asia and the Indian Ocean.

VIII-2 Materials and Methods

VIII-2-1 Sample collection

Two sampling campaigns were conducted, one locally in Singapore and the other during a sailing cruise across the Indian Ocean. Atmospheric samples in Singapore were collected at the two marine stations, S1 and S2 (Figure VIII-1) from the research vessel *Hammerhead* between June and July 2004. Atmospheric samples over the Indian Ocean were collected from the sailing boat *Jocara* during a cruise from August 2004 to August 2005 from Stations IO1 to IO12, as shown in Figure VIII-2. Samples IO3, IO5, IO10 and IO11 were collected over a transect, and the station locations in Figure VIII-2 represents the mid-point of the transects. During sampling no engine was running onboard the vessels, so as to avoid contamination of samples.

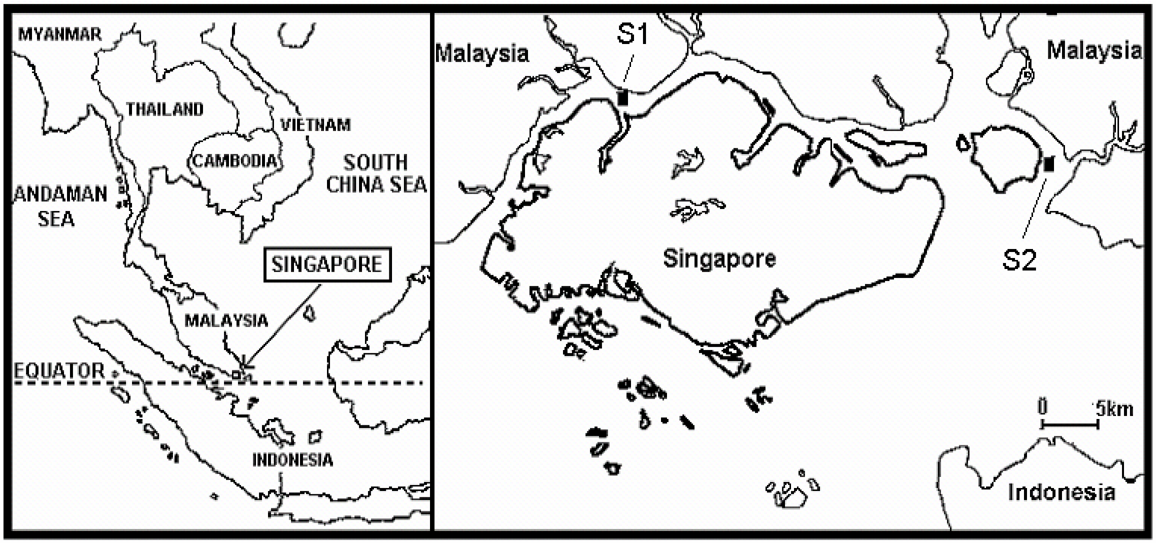


Figure VIII-1: Location of sample Station S1 and S2 located in Singapore.

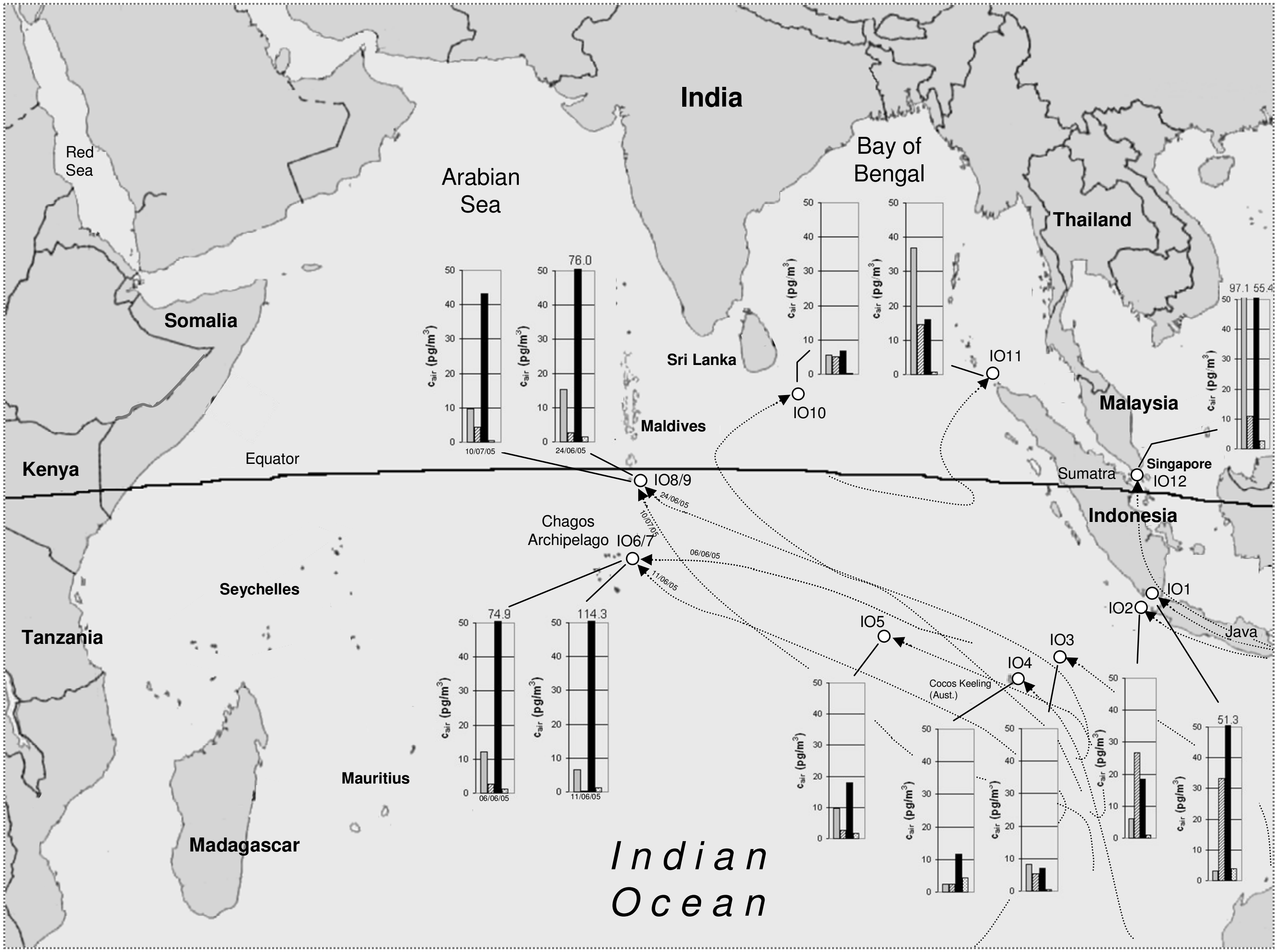


Figure VIII-2: Spatial distribution of ΣHCHs (░), ΣDDTs (▨), ΣPCBs (■) and ΣChlordanes (⁙) at Stations IO1 to IO12 and air mass trajectories.

Atmospheric particulates were collected on a glass fiber (GF) filter of 47 mm diameter (Whatman GF/A, 1.6 μm). Compounds in the gas phase were adsorbed onto PUF plugs. GF/A filters were baked at 450 °C for 16 hrs prior to use. Polyurethane foam (PUF) plugs were pre-cleaned as described by Wurl and Obbard (2005b) and stored in sealed tin container. A GF/A filter and two PUF plugs in series were placed in a dual cartridge stainless steel vacuum flask. A 12 V DC high-volume air pump (H8400B, F&J Specialty Products, Inc., USA) with a fixed flow rate of 55 L/min was initially used during sampling in Singapore and for sample collection sites at Station IO1 to IO5 in the Indian Ocean. Due to a decline in power by 30%, the H8400B air sampler was replaced by a 220V AC H8400TE air sampler with a variable flow rate and thermally protected motor for sample collection at Station IO6 to IO12. The decline in power of the H8400B air sampler and inaccuracy of air flow measurements during collection of samples at Station IO1 to IO5 was accounted for in data processing (see Chapter VIII-3-2). The H8400TE air sampler was operated at a flow rate of 400 mL/min. The collected air volume ranged between 60 to 260 m^3 for all air samples. All air samples were stored at –20 °C after collection. Details of Station IO1 to IO12 are given in Appendix C.

VIII-2-2 Sample treatment and analysis

All blanks, spiked control sample and samples were extracted using a validated and quality assured microwave assisted extraction method, as described by Wurl and Obbard (2005b). All extracts were cleaned-up using a silica gel column and the procedure is described in Chapter III-5. Analysis of samples collected in Singapore between June and July 2004 was performed on a Shimadzu QP5050 GC-MS, according to procedures described in Chapter III-6-1. Samples collected after July 2004 were analysed on a Varian 4000 GC-IT-MSMS according to the procedure outlined in Chapter III-6-2. A few samples were analysed using both analytical systems to cross check the consistency of results.

VIII-3 Results and discussion

VIII-3-1 Quality assurance

All analytical procedures were subject to strict quality assurance and control procedures. Sampling performance was evaluated by analyzing the first and second PUF plug separately. The concentration levels in the second PUF plug should not exceed 10% of that of the first, otherwise excessive breakthrough of POPs is suspected. This criterion was fulfilled for all samples, except for HCH isomers where up to 24% was found in the second plug. Blanks for PUF plugs and GF filters constituted 20% of the total number of samples in order to evaluate contamination during transport and storage of samples. For the air sampling over the Indian Ocean, PUF plugs were spiked with analytes (spiked control samples) and sent together with blanks and PUF plugs for air sampling to assess losses of analytes during transportation and storage. Blanks and spiked control samples were analyzed in the same way as samples. The entire analytical procedure was evaluated by using $^{13}C_{12}$ -labeled PCB surrogate standard. Mean recoveries of surrogate per sample were between 71% and 112%. The values of relative percent difference (RPD) of duplicate samples were between 11 and 58%. Control calibration standards were analysed for every four samples to check performance during analysis.

VIII-3-2 Error Analysis

Due to the decline of the power of the air sampler H8400B during the *Jocara* cruise, some uncertainties in the obtained atmospheric concentrations of POPs may have occurred. To assess these uncertainties a propagation of random errors (Shoemaker et al., 1996) was performed. Uncertainties in the estimated atmospheric concentrations of POPs are derived from errors occurring during sample treatment and analysis, and inaccuracy in the flow rate of air samplers.

$$\sigma^2(C_{air}) = \left(\frac{\delta C_{air}}{\delta F}\right)^2 (\sigma F)^2 + \left(\frac{\delta C_{air}}{\delta c_{measured}}\right)^2 (\sigma c_{measured})^2 \qquad (1)$$

where C_{air} is the atmospheric concentration. Total propagated variance [$\sigma^2(C_{air})$] is the linear combination of the weighted contribution of the variances (σ^2) of the flow rate F and measured concentrations $c_{measured}$.

Uncertainties in the quantification of POPs were estimated from the value of RPD of the analysis of duplicate samples. The uncertainty of the flow rate from the air sampler H8400B was estimated at 15% due to a gradual decline of the flow rate from 55 to 38 L/min. The accuracy of the flow rate of the air sampler H8400TE was estimated to be ±20 L/min at a flow rate of 400 L/min. The overall error of the atmospheric concentrations of POPs was between 22 and 66% (mean 31%), and between 7 and 61% (mean 27%) using the H8400B and H8400TE air sampler, respectively. The highest errors originated from compounds present at the lowest concentrations among samples, thereby resulting in relatively high RPD values for the duplicate samples.

Analytical uncertainty originated from the breakthrough of POPs from the PUF plugs was not accounted for in the error analysis as atmospheric concentrations of POPs were corrected by using a correction factor S, as calculated using a Taylor Series as follows:

$$S = 1 + \frac{1}{k} + \frac{1}{k^2} + \frac{1}{k^3} + \frac{1}{k^4} \ldots \qquad (2)$$

where k is the multiplier between concentrations found on both PUF plugs. Equation 2 can be transformed to

$$S = \frac{k}{k-1} \qquad (3)$$

For the highest breakthrough of 24% (k=4.16) observed in this study, S is calculated as 1.32.

VIII-3-3 Air mass back trajectory analysis

To identify possible sources of atmospheric pollutants, the origins of air masses can be traced back for several days using air trajectory models. In this study the models Meteorological Data Explorer (METEX) obtained from the Centre for Global Environmental Research, Japan (Zeng, 2003) and the HYSPLIT model from the NOAA Air Resources Laboratory (Drawler and Rolph, 2003) were used to perform back trajectories (BTs) for 5 days. Both air trajectory models were needed in order to perform calculations for all atmospheric samples collected over the Indian Ocean since the 1970's. BTs were performed at altitudes between 300 and 1500m and comprised stable atmospheric layers of the same origin, up to an altitude of 1000m. BTs are presented in Figure VIII-2 and VIII-3 at an altitude of 500m for samples collected over the Indian Ocean and Singapore, respectively. Air masses reaching the local stations in Singapore during the sampling events on the 16 June, 23 June and 21 July 2004 originated from the land masses of Java. Samples collected on two sample occasions (7 and 14 July 2004) originated from a relative short distance of 200 km from the west coast of Sumatra. Air collected on a single occasion (30 June 2004) was derived from the open Indian Ocean and may have been affected by passing partly over the Malaysian Peninsula. Air collected during the *Jocara* cruise originated from open ocean areas and sampled air had traveled long distances without impinging upon any land masses (Figure VIII-2). Only air samples collected at the Station IO1, IO2 and IO12 derived from the landmasses of Java, and were partly of terrestrial origin.

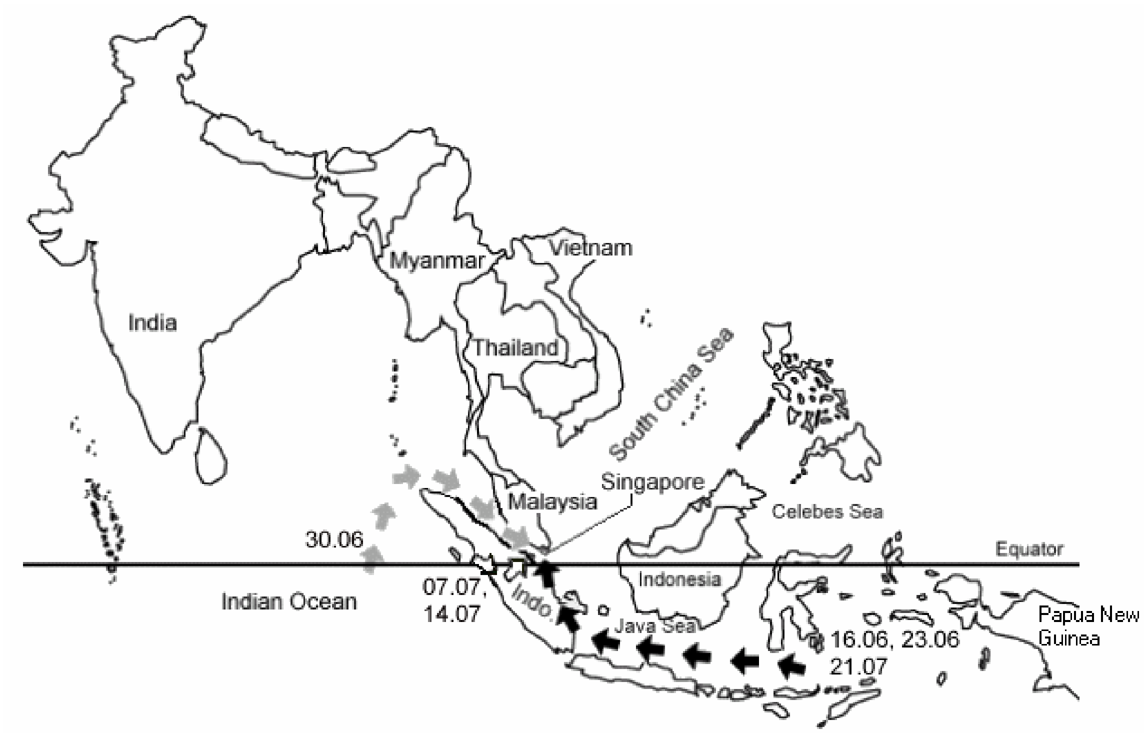


Figure VIII-3: Estimated air mass back trajectories (5 days) for collected air samples in Singapore from 16th June to 21st July 2004 as indicated.

VIII-3-4 Polychlorinated Biphenyls (PCBs)

VIII-3-4-1 PCBs in the marine atmosphere of Singapore

Concentrations of the major PCB congeners detected in the atmospheric gaseous phase are presented in Table VIII-1. At Station S1 and S2 the average concentrations of ΣPCBs were 36 ± 16 pg/m^3 and 29 ± 2.5 pg/m^3 respectively. Due to their higher volatility, only tri-, tetra-, penta-, and hexa-CBs were detectable, whereas the higher chlorinated congeners were below limit of detection (LOD) in all samples. Several data sets are available from the literature reporting atmospheric PCB concentrations over rural areas, e.g. from Ansung, Korea (36 pg/m^3; Yeo et al., 2003), Galveston Bay, Houston, USA (208-4783 pg/m^3; Park et al., 2001), Birmingham, UK (252 pg/m^3; Harrad and Mao, 2004), Kanagawa Prefecture, Japan (10-3290 pg/m^3; Uraki et al., 2004), and a European wide survey of 25 urban and

46 rural sites (20-1700 pg/m^3, Jaward et al., 2004b). These data indicate the continued prevalence of PCBs in the atmosphere over the USA and Europe two decades after their ban. However, concentrations of atmospheric ΣPCBs collected over major cities of Southeast Asia were higher by factors of up to 100 (Iwata et al., 1994) than data reported here. Air samples collected in this study were of oceanic character that originated in Indonesia (Java Sea and Sumatra), and are more comparable to samples collected over the Java Sea in the beginning of the 1990's (Iwata et al., 1993). Iwata reported the concentration of ΣPCBs at 30 pg/m^3 over the Java Sea. The profile of PCB homologs in the air samples included tri-, tetra-, penta-, and hexa-homologs as shown in Figure VIII-4, but were dominated by penta- and hexa-homologs. However, it is expected that lower chlorinated PCBs, particular the tri- and tetra-homologs, are dominant in the gas phase of the atmosphere due to decreasing vapor pressure, and increasing K_{OA} (octanol-air partition coefficient) and K_{OW} (octanol-water partition coefficient). A shift in the PCB congener profiles to the higher chlorinated congeners during summer periods was observed during annual monitoring of PCBs in the air over the Great Lakes (Hoff et al., 1992; McConnell et al., 1998). High ambient air temperatures in tropical climates may result in higher chlorinated PCBs being more readily volatilized, thereby leading to an increase in the gas phase concentrations of these lower vapor pressure compounds. The different PCB congeners profiles in air samples collected from the highly urbanized region of Singapore (S1, S2 and IO12) as well as the oceanic regions (IO1 to IO11) are discussed in the following section.

Compound	Station S1			Station S2		
	16th June	30th June	14th July	23rd June	7th July	21st July
α-HCH	38	175	149	96	140	137
β-HCH	18	121	59	66	33	65
γ-HCH	44	154	92	92	107	48
δ-HCH	3	53	47	48	39	45
ΣHCH	101	503	347	303	318	295
DDE	0.5	0.6	0.5	0.5	0.4	0.5
DDD	1.4	4.6	1.6	2.2	3.4	1.5
DDT	9.9	6.2	5.3	6.6	5.2	1.7
ΣDDT	11.3	11.3	7.4	9.3	9	3.6
CB 18	0.7	1.7	3	3.6	1.8	1.1
CB 17+31	2.3	7.4	3.8	1.9	3.8	2.4
CB 28	< 0.09	1.4	2.3	1	1.9	0.4
CB 44	2.3	< 0.16	3.1	2.9	< 0.16	< 0.16
CB 87	1.5	4.2	2.4	1.2	3.7	< 0.7
CB 110	2.5	4.9	1.4	1.8	1.8	1.1
CB 118	6.7	11.2	4.3	11.8	10.8	19.6
CB 138	10.2	15.7	3.5	4.9	< 0.37	1.2
CB 149	2	6.6	1.4	1.5	1.4	0.9
CB 153	0.9	1	< 0.16	0.2	< 0.16	< 0.16
ΣPCBs	29	55	25	32	25	27

Table VIII-1: Mean concentrations (pg/m3) of HCHs, DDTs and major PCB congeners in marine atmospheric samples from Singapore (2004).

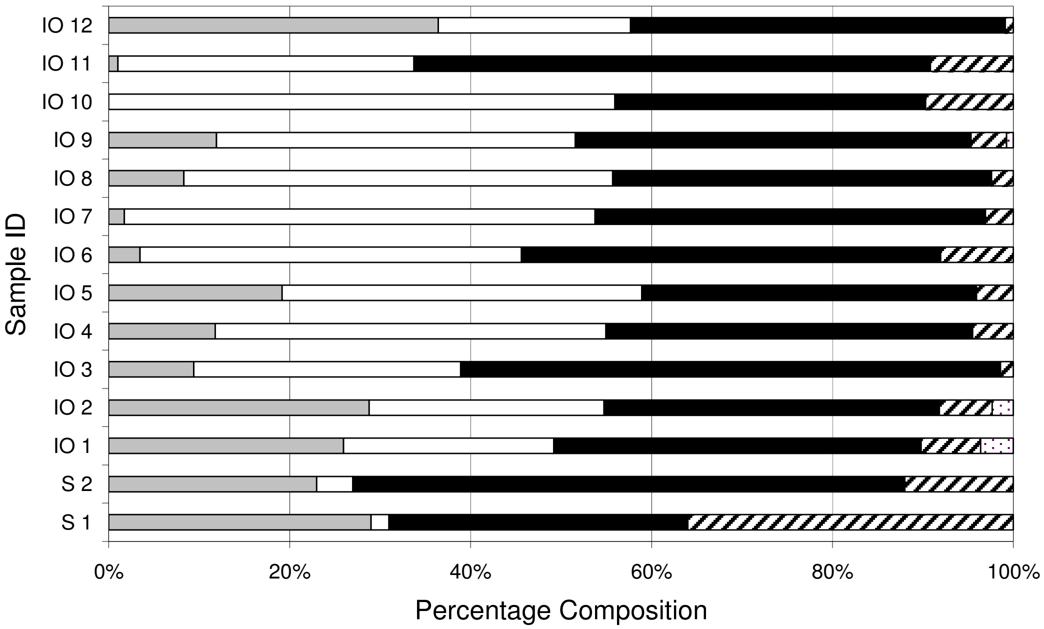


Figure VIII-4: Percentage composition of tri-(▒), tetra-(☐), penta-(■), hexa-(▨) and hepta-CBs (⬚).

VIII-3-4-2 PCBs in the atmosphere over the Indian Ocean

The concentrations of ΣPCBs at the Station IO1 to IO12 were between 7 and 114 pg/m^3 (Figure VIII-2). Mean, minimum, and maximum atmospheric concentrations are given in Table VIII-2. Detailed data on concentration measured at each Station are summarized in Table C-1 in Appendix C. The major congeners were CB 44, 49, 52, 70, 74, 95, 101 and 110/82 with 13.1, 37.7, 43.6, 5.0 and 0.6% as average accounted for tri-, tetra-, penta-, hexa- and hepta-homologs respectively. The homolog compositions between the samples collected in Singapore (S1, S2 and IO12) differ significantly to these from the stations over the Indian Ocean (IO1 to IO11) (Figure VIII-2). The fraction of tetra-homologs were generally higher over the Indian Ocean, but lower for the hepta-homologs. It is suggested that local emission sources at Station S1, S2 and IO12, as well as different rates of atmospheric degradation of PCBs in the atmosphere over urban and oceanic areas, may account for the differences in homolog compositions observed. It is difficult to explain the differences in data values, due to the potentially wide ranging and poorly documented PCB emission sources in the highly urbanized region around Singapore.

The concentrations of ΣPCBs found over the Indian Ocean are lower than for the Atlantic Ocean (Jaward et al., 2004a), which were reported to be in arrange of 12 to 360 pg/m^3. In this study, higher values were observed for samples collected near to the coastline of Indonesia (Station IO1 and IO2), and were probably affected by the proximity to Jakarta and Singapore (Station IO12). However, the highest concentration of atmospheric PCBs was found at the remote Chagos Archipelago in the Indian Ocean. The largest of the islands, Diego Garcia, contains a large joint UK-US naval support facility with about 1500 UK and US military personnel and 2000 civilian contractors, whereas all other islands are uninhabited (CIA, 2004).

Compound	Mean	Minimum	Maximum
CB 18	3.1	< 0.3	20.2
CB 44	2.1	0.2	5.2
CB 49	1.1	0.2	2.4
CB 52	7.7	1.0	21.5
CB 70	2.4	0.4	4.9
CB 74	0.9	0.1	2.4
CB 87	1.8	0.2	3.7
CB 95	4.1	0.3	9.4
CB 101	4.4	0.3	10.6
CB 110/82	3.7	< 0.04	16.3
Σ_{38}PCB	40.9	6.8	114.3
α-HCH	3.2	< 0.2	19.2
γ-HCH	13.8	2.3	80.0
ΣHCHs	18.4	2.4	105.6
p,p'-DDE	2.2	< 0.2	6.3
p,p'-DDD	1.3	< 0.2	4.8
p,p'-DDT	5.9	< 0.2	26.7
ΣDDTs	10.4	2.5	33.2
trans-Chlordane	1.2	0.3	2.7
cis-Chlordane	0.5	< 0.07	2.4
ΣChlordane	1.7	0.3	4.5

Table VIII-2: Mean, minimum, maximum of atmospheric PCB and OCP concentrations at Station IO1 to IO12.

Air masses reaching the Chagos Archipelago traveled at least 5 days over the open ocean prior to sampling, and therefore it is likely that the military activities on Diego Garcia represent a local source of atmospheric PCBs. This observation is supported by other reports of high PCB contamination around military bases elsewhere (Poland et al., 2001; Kuzyk et al., 2005). Concentrations of PCBs in air samples collected on the Addu Atoll, the most southerly atoll of the Maldives with a population of approximately 28,000, were as high as in these collected at the marine stations of Singapore. A former UK military base on the island Gan in the Addu Atoll, closed in 1976, is unlikely to be the source of PCBs when compared within the context of concentrations measured on the Chagos Archipelago and the current activities on Diego Garcia. Air trajectory analysis showed that air masses reaching Gan during sampling events blew from the southeast to south-southeast, and originated over the open ocean. A local source of atmospheric PCB contamination is likely to be the unregulated waste management on the atolls of the Maldives. On average 0.66 kg waste is generated per capita per day on the atolls and burning of household waste is a common practice (UNEP, 2002b) and this can lead to an emission of up to 0.13 mg PCBs / kg of burned material (Lemieux et al., 2004). Assuming that half of the generated waste is combusted (i.e. 28,000 x 0.66 x 0.13/2 = 1.2), a release of approximately 1.2 g of PCBs per day on the Addu Atolls is expected. Based on this calculation, the measured atmospheric PCB concentration over the atoll is comparable when based on the use of a simple fix-box model using this emission rate, an average wind speed of 2 m/s during sampling, and a background concentration of 20 pg/m^3 - as detected at Station IO5. The calculated value of approximately 50 pg/m^3 is comparable to the measured concentrations over Gan, Maldives (Figure VIII-2).

VIII-3-5 DDT compounds

VIII-3-5-1 DDTs in the marine atmosphere of Singapore

Average concentrations of ΣDDTs at the Station S1 and S2 (Figure VIII-1) were 10.0 ± 2.3 pg/m^3 and 6.0 ± 2.9 pg/m^3, respectively, and lower than observed in Ansung, Korea at 60 pg/m^3 (Yeo et al., 2003) and Hong Kong, China at 49 pg/m^3 (Louie and Sin, 2003). Concentrations, higher by a magnitude of two, were reported in the air over the Taihu Lake region, China (mean 1139 pg/m^3; Qui et al., 2004). Officially, DDT has been banned in many countries of Southeast Asia, but evidence of its usage has been reported for China and Vietnam (Monorith et al., 2003). DDT contamination may also originate from the production and usage of the pesticide Dicofol in China (Wan et al., 2005). However, no air masses collected in this study originated from China or nearby regions. Much of the air masses blew over the land masses of Sumatra and Java, Indonesia. Even though it has been reported that DDT was banned in Indonesia in the early 1980's, the usage of DDT continues due to non-existing enforcement, as noted by Shaw (1999). The ratio DDT to the sum of its metabolite products DDD and DDE, can be used to assess how recently DDT inputs occurred to the environment. The ratio DDT:DDD+DDE ranged between 0.9 to 5.2 and may reflect the ratio prior to volatilization from soil, since the significance of DDT photo-degradation processes in the atmosphere are somewhat controversial. Photochemical degradation of DDT has been reported for controlled experiments, but not for the atmosphere (Prakash et al., 1994; Dolinova et al., 2004). Gore et al. (1971) showed that DDT does not absorb significant levels of energy above a wavelength of 290 nm, meaning that gas-phase photolysis of DDT is unlikely to be an important loss process. The ratio of DDT:DDD+DDE determined in this study suggests that not all DDT entering the air mass reaching Singapore has been transformed prior to volatilization. The highest and lowest ratios were determined during sampling on 16th June and 21st July 2004 respectively, for air masses that originated from Java, Indonesia. This may indicate an emission source of DDT, likely due to volatilization and periodical application of DDT.

VIII-3-5-2 DDT in the atmosphere over the Indian Ocean

The highest concentrations of atmospheric ΣDDT were detected in samples collected in the proximity to Indonesia, in a range of 14.5 to 33.2 pg/m^3 (Station IO1, IO2 and IO11 in Figure VIII-2). The concentration of DDT contributed 66 to 86% of ΣDDT, and this indicates that inputs of DDT into the atmosphere continue in the region of Indonesia. This is consistent with the report of Shaw (1999), as pointed out in the previous section, and also to a report on the highest concentrations worldwide of DDT in human milk found in Indonesian women (Shaw et al. 2000). 'Oceanic' concentrations of DDT ranged between

< 0.5 to 5.8 pg/m^3 (mean 3.1 pg/m^3) (Table C-1 in Appendix C). DDTs in samples collected over the open Atlantic Ocean were frequently below the limit of detection at <1.5 pg/m^3, but the levels of the metabolite DDE was as high as 47 pg/m^3 in samples influenced by proximity to Africa and western Europe (Jaward et al., 2004a). Among all samples collected over the Indian Ocean, the ratio DDT:DDD+DDE ranged between 0.2 to 6.2 (mean 1.9). The prevailing concentrations may depend on the origin of the air mass, e.g. the concentrations in samples collected at Station IO6 and IO7 on the Chagos Archipelago were 5.0 and < 0.5 pg/m^3 respectively. Air trajectory analysis for 10 days prior to sampling showed that air masses originated from the northern coastline of Australia and from the southern region of the Indian Ocean (latitude S 45 ^{o}) for these samples, respectively. The photooxidative half-life time for DDT has been estimated at 17 to 177 h in the atmosphere (Mackay et al., 1997), and therefore the atmospheric transport of DDT from continental areas to remote areas with a distance of several thousands of kilometers is feasible, without degradation reducing amounts below LOD.

VIII-3-6 HCH isomers

VIII-3-6-1 HCHs in the marine atmosphere of Singapore

Concentration of ΣHCHs ranged between 101 and 503 pg/m^3 at the Station S1 and S2 (Table VIII-1). These concentrations are in same range as those recorded from over the Java Sea (75 pg/m^3), the Celebes Sea (280 pg/m^3), and the South China Sea (1300 pg/m^3) at the beginning of the 1990's (Iwata et al., 1993). Therefore data indicates no recent decline of ΣHCHs in the atmosphere over Southeast Asia. The high volatilization and water solubility of HCH isomers leads to their global distribution. It is believed, that due to the higher volatilization of γ-HCH (Lindane) and/or its possible photo-transformation to α-HCH, as shown in aqueous solutions under laboratory conditions (Zaleska et al., 2000), in the atmosphere (Willet et al., 1998), both isomers dominate in this study. However, photo-transformation of HCH isomers in the atmosphere is controversial and has not been observed to occur in the atmosphere itself. The ratio α-HCH to γ-HCH ranges from 4 to 15 in technical HCH mixtures, and from 0.2 to 1 in the pesticide lindane (McConnell et al., 1993). These ratios are expected to increase with distance from the source (Ramesh et al., 1989) assuming transformation of γ-HCH to α-HCH. Indeed, the reaction rate with OH radicals was reported to be higher for γ-HCH than α-HCH - leading to atmospheric life times of 96 to 120 days, respectively (Willet et al., 1998). The ratios of samples collected at Station S1 and 2 ranged between 0.9 and 2.9 and suggest lindane as a principal source. The sources are unlikely to be local areas of Singapore, and were most likely transported via the prevailing air masses to the air sampler. Recent use of HCHs as insecticides in Malaysia and India has been reported (UNEP, 2002a; Li, 1999), and is likely to act as a regional source of atmospheric contamination. Indeed, the concentration of ΣHCHs detected on the 30th June 2004 in air blowing partly over Malaysia was 2 to 5 times higher compared to other sampling events. HCHs isomers are banned in Indonesia, as is DDT (UNEP, 2002a), but the control and monitoring programme of used pesticides in this country is lacking (Shaw, 1999). Therefore continue usage of HCH isomers cannot be excluded.

VIII-3-6-2 HCHs in the atmosphere over the Indian Ocean

The concentrations of ΣHCHs were highest at 37 and 97 pg/m^3 at the northern tip of Sumatra (Station IO11) and Singapore (IO12), respectively. In contrast, 'oceanic' air samples contained between 2.4 and 15.2 pg/m^3 of ΣHCHs (Figure VIII-2 and Table C-1 in Appendix C). The relatively low concentrations of ΣHCHs at the Station IO1 and IO2, despite the proximity to Indonesia may reflect the spatial differences in the use of pesticides in this region since the highest concentrations of atmospheric DDT were found at these stations. The air masses reaching Station IO11 during sampling were of oceanic origin, but local emissions of POPs may be associated with prevailing forest fires at the time of sampling in Sumatra. The lowest concentration of ΣHCHs was detected on Cocos Keeling Island (Station IO 4) at 2.4 pg/m^3, and this was lower by a factor of 6 compared to the Chagos Archipelago (Station IO6 and IO7) and Addu Atoll, Maldives (Station IO8 and IO9). The last agricultural activities on Chagos Archipelago, date back 30 years and soils are therefore unlikely to be a continue source of atmospheric HCH contamination. Long-range transport of atmospheric contaminants from continental land masses is more likely.

The α-HCH:γ-HCH ratios were in the range of 0.05 to 0.2, except for the sample collected at IO11, where the ratio was 1.1. The prevailing forest fires along Sumatra's coastline may have altered the ratio at Station IO11. The ratio at Station IO12 (Singapore) was 0.2 and significant lower than in the samples collected a year before at the Station S1 and S2. A reason may be the temporal and spatial variability in the usage of Lindane in countries neighboring Singapore, leading to a relatively wide range of observed ratios. According to the ratios observed in this study, the pesticide Lindane seems to be the primary source of atmospheric HCH contaminations. The relatively low ratios measured, indicate that sampling events were conducted close to the source of Lindane, which is unlikely for the 'oceanic' stations, or that γ-HCH was transported rapidly from the source to the air sampler with little transformation of γ-HCH.

VIII-3-7 Chlordanes in the atmosphere over the Indian Ocean

Samples collected over the Indian Ocean were analyzed for cis- and trans-chordane, but this was not the case for air samples collected from the marine atmosphere of Singapore. The concentrations of ΣChlordane were low among all samples. The highest concentrations were detected at Station IO1 and IO4 (Cocos Keeling) at 3.8 and 4.5 pg/m^3 respectively (Table C-1 in Appendix C).

VIII-3-8 Polybrominated diphenyl ethers (PBDEs) in the atmosphere over the Indian Ocean

Few data are available on atmospheric PBDE levels over the continents in the northern hemisphere, although Jaward et al., (2004a) reported concentrations of up to 250 pg/m^3 in urban areas. This study reports the first data on the atmospheric concentrations of PBDEs in the gas phase collected over the open ocean. The concentration of ΣPBDE ranged from oceanic background concentrations of 1.5 pg/m^3 (Station IO5) to terrestrially affected concentrations of up to 15.6 pg/m^3 (Station IO2) (Figure VIII-5). Samples at Station IO1 and IO2 were influenced partly by terrestrial and oceanic air masses, and may also have been affected by the proximity of Jakarta to the south. The concentrations of ΣPBDE and individual congeners are given in Table C-2 in Appendix C.

The concentration of atmospheric ΣPBDE at Mace Head, Ireland, a European background site, has been reported at a range from 0.2 to 5 pg/m^3 (mean 2.6 pg/m^3) (Lee et al., 2004). This suggests that the air over the Atlantic Ocean reaching Mace Head, has similar levels of PBDEs than over the Indian Ocean (mean 2.5 pg/m^3 of the oceanic Station IO3 to IO9). Air concentrations of ΣPBDE (sum of gaseous and particulate phase) were reported as 8.6 pg/m^3 in the air over a remote site on the island Gotska Sandön in the Baltic Sea (Ter Schure et al., 2004).

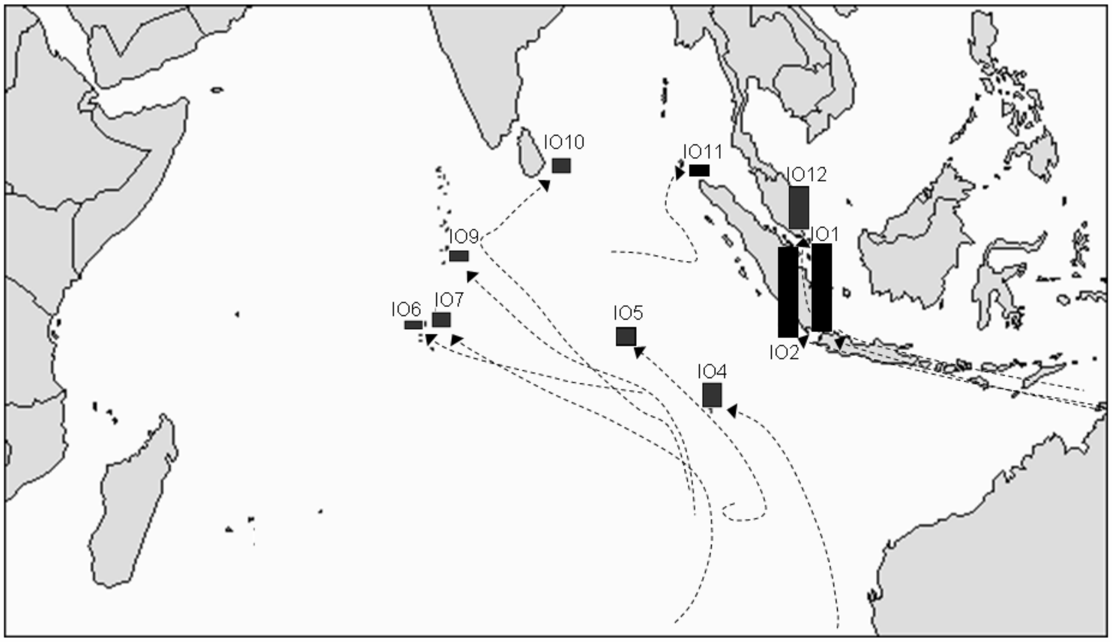


Figure VIII-5: Spatial distribution of ΣPBDE and origin of air masses (5 days back air trajectory). No data are available for Station IO3 and IO8. Key: Largest bar = 15.6 pg/m^3 (Station IO 2); smallest bar = 1.5 pg/m^3 (Station IO 6).

The most abundant congeners were BDE 47 and 100, whereas BDE 183 and 209 were not detectable in any samples. There may be several reasons for the absence of higher brominated PBDEs, particular BDE 209, in the gas phase of the atmosphere - even over urban areas. They may be lost through photolytic degradation or strong association to airborne particles (Lee et al., 2004). Their lower volatility, but higher lipophilicity ($K_{ow} > 8$) compared to lower brominated congeners, may lead to their rapid accumulation within the water phase and low evaporation rate into the atmosphere. The air masses from the Stations IO4 to IO10 were of an oceanic origin, which is consistent with the lower atmospheric concentrations of PBDEs found at these stations. Interestingly, PBDE concentrations have not correlated with the high concentrations of PCBs on the Chagos Archipelagos and Maldives suggesting that the military activities on Diego Garcia and the uncontrolled waste management on the Addu Atoll, Maldives are low sources of atmospheric PBDEs. Detailed, backward air mass trajectory analysis over 10 days prior to sampling, showed that air masses sampled at Stations IO4, IO5, IO7, and IO9 originated from the southeast region of the Indian Ocean from a latitudes of S45°. The air masses had traveled thousands of kilometers without impinging any land masses en-route, thereby indicating a widespread distribution of flame retardants in the atmosphere of the southern hemisphere. It has been shown that lower brominated BDE congeners have a similar potential to undergo long-range atmospheric transport as for higher chlorinated PCB congeners (Wania and Dugani, 2003). Therefore it is possible that PBDEs have been transported as far as Antarctica - as was shown for higher chlorinated PCBs by Kallenborn et al. (1998).

The presence of relatively high concentrations of PBDEs in the atmosphere of the less industrialized southern hemisphere suggests that PBDEs are globally distributed in the atmosphere, with the potential to affect the health of even remote ecosystems.

VIII-3-9 Historical trends of atmospheric POPs over the region of the Indian Ocean

To assess the historical trend of POPs in the atmosphere over the Indian Ocean, previously reported data from Tanabe and Tatsukawa (1980), Bidleman and Leonard (1982) and Iwata et al. (1993) were compared with data obtained in this study. The data cover a time span from 1976 to 2005 and includes time periods of peak usage of HCHs and DDTs in Asian countries, e.g. in India in the early 1980s. It should be noted that the quality and accuracy of the analysis of POPs have risen substantially since the mid of the 1980's due to the availability of more sophisticated analytical techniques and greater awareness of possible contamination sources. Selected sample locations for all four studies are shown in Figure VIII-6 and sample clusters identified representing six regions of the Indian Ocean. Cluster Ia, Ib and Ic include data from 1976 to 2005, Cluster II from 1989 to 2005, and Cluster IIIa and IIIb from 1976 to 1990. All available POP concentration data during these time periods within the respective clusters are summarized in Table VIII-3. For the data reported by Tanabe and Tatsukawa (1982) (indicated with □1-15 in Figure VIII-6) the actual date of sampling was not reported (only month and year), and therefore no air back trajectory analysis could be conducted for these samples. However, such analysis was performed between October and December 1976, over a 24 hr interval for the sample locations □1-15.

VIII-3-9-1 Historical trend of atmospheric PCBs

Data of ΣPCBs are only available from 1989 and 2005. However, Tanabe and Tatsukawa (1980) reported that PCBs were below LOD of < 500 pg/m^3 in all air samples collected over the Indian Ocean in 1976. From 1990 to 2005, atmospheric ΣPCBs declined by a factor of 2 and 100 in the Clusters Ia and Ib, respectively. The concentration of 710 pg/m^3 measured in Cluster Ib in 1990 was the highest amongst all samples collected in a global survey (Iwata et al., 1993) with a range of 19-710 pg/m^3 (mean 270) reported for the Arabian Sea and Bay of Bengal. No clear trend of atmospheric ΣPCBs levels in Cluster II could be observed, and a decline is unlikely to have occurred over the last 15 years. The concentrations of ΣPCBs over Cluster IIIa and IIIb in 1976 were below 500 pg/m^3 and therefore it can be concluded that there has been no significant decline in atmosphere ΣPCB levels between 1976 and 1990. Overall, the atmospheric concentration of ΣPCBs has not significant declined in the clusters adjacent to Indonesia, but levels have been relatively low since the 1990's. The mean concentration for the Arabian Sea and Bay of Bengal from 1990 was 40 times higher than the concentration measured in 2005, but only 2-3 times higher than the concentrations measured at the Chagos Archipelago obtained during this study.

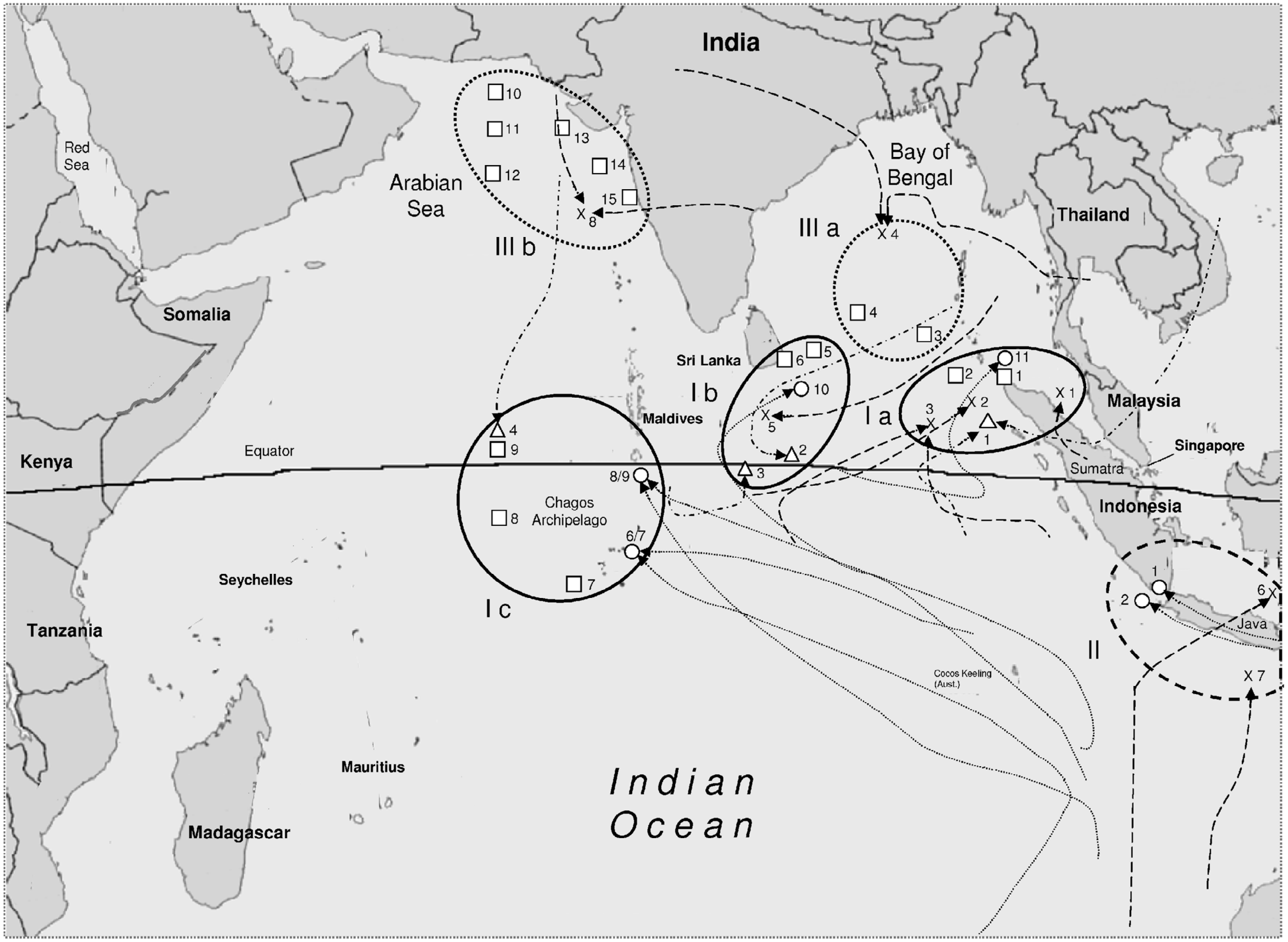


Figure VIII-6: Clusters using mean sample locations from Tanabe and Tatsukawa (□), Bidleman and Leonard (△), Iwata et al. (X) and this study (O) and air masses trajectories.

VIII-3-9-2 Historical trend of atmospheric DDTs

In Cluster Ia the level of atmospheric ΣDDT was in the same range of approximately 250 pg/m^3 in both 1976 and 1989, but had decreased by about 15 times by 2005. The highest concentration of 580 pg/m^3 of ΣDDT was found in air collected at location X1 which is likely to have originated from Sumatra, whereas samples □1 and □2 were likely to be of an oceanic origin. In the Clusters Ib and Ic the decline of atmospheric ΣDDT between 1976 and 2005 is even more significant, with a 40-fold reduction. In contrast to Cluster Ia, a significant decrease in ΣDDT in Cluster Ib between 1976 and 1990 from 200 to 50 pg/m^3 is apparent. All samples in Cluster Ib were of an oceanic origin, but sample □6 could have been affected by air masses originating from Northern India during the last week of December 1976. A 3-fold increase of atmospheric ΣDDT in Cluster II occurred between 1990 and 2005. However, the samples O1 and O2 (2005) were partly terrestrial in origin, whereas the samples X6 and X7 were of a more oceanic character. No significant decline or increase of atmospheric ΣDDT can be identified for Clusters IIIa and IIIb. Cluster IIIb was clearly affected by air masses originating in Pakistan and India, as indicated for sample X8 in Figure VIII-6. The high concentrations found in 1976 and 1990 in Cluster IIIb are consistent with the period of extensive usage of DDT in India. Air at stations nearer to the coastline (□13-15) was substantially more contaminated than at stations located offshore (□10-12). In general, atmospheric ΣDDT concentrations have declined over the past 30 years, but to a higher extent in the oceanic Clusters Ib and Ic. The increase of ΣDDT in the atmosphere over Cluster II may be a result of the varying origin of air masses during sampling in both 1990 and 2004, but also indicate a continued release of DDT compounds into the atmosphere over Indonesia.

	Month/Year	ΣDDT	p,p'-DDT	ΣHCH	α-HCH	γ-HCH	ΣPCBs
Cluster I a							
□1	10-1976	270		360			
□2	10-1976	160		160			
△1	12-1976		4.4	32	30	< 2	
X 1	05-1989	580	220				30
X 2	05-1989	263					34
X 3	05-1989	241					57
O11	08-2005	14.5	12.5	37	19	18	16.1
Cluster I b							
□5	10-1976	150		200			
□6	12-1976	220		140			
△2	12-1976		5.4	208	170	38	
△3	12-1976		4.7	85	79	6.3	
X 5	02-1990	57		827			710
O10	08-2005	5.2	4.2	5.6	0.9	4.7	6.8
Cluster I c							
□7	11-1976	160		280			
□8	11-1976	130		180			
□9	11-1976	100		240			
△4	12-1976		16	1078	922	156	
O 6	06-2005	5	3.8	12.1	1.3	10.8	75
O 7	06-2005	<0.5	0	6.6	0.8	5.8	114
O 8	06-2005	2.6	0	15.2	2	13.2	75
O 9	07-2005	4.5	0.8	9.6	0.9	8.7	43
Cluster II							
X 6	11-1989	5.6	3.4	58	46	12	22
X 7	11-1989	10		181			136
O 1	09-2004	33	27	3.2	0.4	2.8	51
O 2	09-2004	27	18	6.6	0.7	5.9	18
Cluster III a							
□3	10-1976	190		950			
□4	10-1976	170		370			
X 4	02-1990	240		2880			260
Cluster III b							
□10	11-1976	400		3300			
□11	11-1976	240		2100			
□12	11-1976	200		2500			
□13	12-1976	10900		2000			
□14	12-1976	1300		9100			
□15	12-1976	1100		10000			
X 8	02-1990	1000		32000			500

Figure VIII-3: Concentrations of atmospheric POPs (in pg/m^3) over the Indian Ocean from 1976 to 2005.

VIII-3-9-3 Historical trend of atmospheric HCHs

Li et al. (1998) reported a linkage between global usage of ΣHCHs and concentrations in the atmosphere over the Arctic. Two significant decreases in air concentrations of α-HCH occurred in the Arctic in 1983 and between 1990 and 1992. This is consistent with two decreases in global technical HCH usage, one in 1983 with the ban of this insecticide in China; and the other in the early 1990's when India and the Soviet Union banned the use of technical HCH in agriculture. Tanabe and Tatsukawa (1980) reported a 10 times higher concentration of ΣHCHs than Bidleman and Leonard (1982) in the atmosphere over Cluster Ia, which can not be explained by differences in air mass origins or the fact that Tanabe and Tatsukawa defined ΣHCH as sum of four isomers (α-, β-, γ- and δ-HCH), whereas Bidleman and Leonard analysed only the two most common isomers in the atmosphere (α- and γ-HCH). However, due to the high usage of HCHs in Southeast Asia and India, the values reported by Tanabe and Tatsukawa may be more representative of the atmospheric concentrations of ΣHCHs in Cluster Ia for the year 1976. In Cluster Ib, the concentration range of ΣHCHs reported by Tanabe and Tatsukawa (1980), and Bidleman and Leonard (1982) are in the same range, with an average value of 160 pg/m^3, which increased to 827 pg/m^3 in 1990 (Iwata et al., 1993). After 1990, a decrease to 5.6 pg/m^3 has been observed in this study. An increase of atmospheric ΣHCHs by a factor of 3 to 8 between 1976 and 1990 is apparent within Cluster IIIa and IIIb, which is consistent with the peak usage of technical HCH mixture in India in the early 1980's (Li et al., 1998). The elevated concentrations of ΣHCHs over the atmosphere in Cluster IIIa and IIIb were clearly affected by the usage of these compounds in India and the Middle East. A substantial declining trend of atmospheric ΣHCHs is apparent within the 'oceanic' Cluster Ic by a factor of 180 over the last 30 years. It shows that in the 1970's and 1980's, the atmosphere in even remote oceanic regions has been highly affected by POPs originating from the continent, which may have been less significant in recent years due to international regulations controlling the usage of POPs. In Cluster II, the concentration measured in 2004 were 10 to 30 times lower than in 1989, which is consistent with the ban of HCHs isomers in several countries in Southeast Asia. Overall, an increase of HCH isomers in the atmosphere over the Indian Ocean can be observed from the mid-1970 to the early 1990's, but this has been reversed over all clusters by a magnitude of up to two up to 2005. The decrease in atmospheric ΣHCH levels is likely to be due to the restricted usage of these compounds in India since the early 1990's. A change in the ratio α:γ-HCH is apparent between the studies conducted in 1976 and 1989/1990, and this study (Table VIII-3). This may be explained by the declining usage of technical HCH mixtures in India, and the origin of air masses (i.e. southern hemisphere) during sampling in this study.

VIII-4 Conclusions

Atmospheric concentrations of ΣPCBs, ΣDDT and ΣHCHs over the sea of Singapore were in a range of 25 to 55 pg/m^3, 3.6 to 11.3 pg/m^3 and 101 to 503 pg/m^3, respectively, and were much affected by air masses derived partly from both terrestrial and oceanic sources. Even so, a declining trend of atmospheric DDT was observed in the region of Southeast Asia, the ratio DDT/(DDD+DDE) indicates fresh inputs of DDTs to the atmosphere of Singapore - most probably originating from the land masses of Indonesia. Reported usage of HCH isomers in neighboring countries to Singapore may explain moderate levels of atmospheric contamination and the stable trend over the last decade.

The atmospheric concentrations of organochlorine pesticides measured over the Indian Ocean in this study were generally in the same range as reported for the tropical region of the Atlantic Ocean, but were lower by a factor of up to 3 for atmospheric PCBs (Jaward et al., 2004a). Atmospheric concentrations of ΣHCHs have declined by a magnitude of two following the restriction in the usage of these compounds in India. The decrease of atmospheric ΣDDTs was shown for several regions over the open Indian Ocean, but evidence of ongoing usage of DDT in Indonesia is evident from this study. Atmospheric PCBs have not declined significantly over regions of Indonesia, but concentrations have remained relatively low since the 1990's. Overall, the Indian Ocean, surrounded by countries of historical high consumption of organic compounds, is now substantially less contaminated with atmospheric POPs than in the 1970's and even 1990's. However, the potential still exists for Southeast Asia to be an ongoing source in the global distribution of POPs.

CHAPTER IX

The Role of the Sea-Surface Microlayer in the Dynamics of Air-Sea Gas Exchange of Persistent Organic Pollutants

IX-1 Introduction

The world's ocean plays a key role in the global fate and distribution of persistent organic pollutants (POPs) and also acts as a key storage reservoir. The oceans receive inputs from POPs via riverine transport, the resuspension of contaminated sediments, municipal discharge, and atmospheric wet and dry deposition. POPs can also be removed from the ocean via two major mechanisms –adsorption onto particulates and subsequent gravitational settlement, and evaporation into the atmosphere from the ocean surface. Gravitational fluxes of polychlorinated biphenyls (PCBs) on particulates to the deep ocean and bottom sediments were estimated to be 4.4 ng/m^{2}day in the Sargasso Sea (Knap et al., 1986) and about 15 ng/m^{2}day in the Mediterranean Sea and Arabian Sea (Dachs et al., 1996; Dachs et al., 1999). Air-sea gas exchange fluxes of PCBs were 400-2100 ng/m^{2}day in the New York-New Jersey Harbor Estuary (Totten et al., 2001) and -63 to 800 ng/m^{2}day in the Chesapeake Bay (Nelson et al., 1998; a negative flux means absorption to the ocean), 19-141 ng/m^{2}day in the Great Lakes (Baker and Eisenreich, 1990) and 76 ng/m^{2}day in the Kattegat Sea, Sweden (Sundqvist et al., 2004). A reported flux of 1.2 ng/m^{2}day for PCBs from soil to the atmosphere in Sweden (Backe et al., 2004) emphasizes the importance of air-sea gas exchange of PCBs in their global transfer and distribution. Estimation of air-sea gas exchange rates for POPs contains much uncertainty, mainly due to the poor understanding of the relationship between the mass transfer coefficient and environmental parameters, such as prevailing wind speed (Bidleman and McConnell, 1995). However, another uncertainty originates from the existence of the sea-surface microlayer (SML), as pointed out by Mackay et al. (1991), Wania et al. (1998) and Mackay (2001), but this has been largely ignored to date due to the difficulties in quantifying POPs in the SML. Mackay et al., 1991 hypothesized that the storage capacity for POPs in the air-water interface may be large enough to control the air-sea gas exchange of these compounds. The air-water interface is defined as the uppermost boundary layer in the SML.

The objective of this study was to provide the first scientific data on measurements of air-sea gas fluxes of PCBs and hexachlorocyclohexane (HCHs) isomers via the SML, and to evaluate the potential importance of the SML as a controlling interface for the air-sea gas exchange of POPs.

IX-2 Model Description and Data

IX-2-1 Air-sea exchange model

The transfer of a gas across an air-sea interface is illustrated by a classical two-layer model (Liss and Slater, 1974) in Fig IX 1a, which has been used to study air-sea exchange of POPs (Achman et al., 1993; Nelson et al., 1998; Bamford et al., 1999; Zhang et al., 1999; Totten et al., 2001). The flux F of POPs across the air-sea interface is calculated from the mass transfer coefficient (K_{ol}) describing transport across the air-sea interface, and the concentration gradient between the bulk water and air phases.

$$F = K_{ol}\ (c_{truly} - c^{*}) \qquad (1)$$

$$\frac{1}{K_{ol}} = \frac{1}{k_a H'} + \frac{1}{k_w} \qquad \text{and} \quad c^{*} = \frac{c_{air}}{H'} \quad (2)$$

where c_{truly} is the truly dissolved chemical concentration in water (ng/m^3); c^* is the dissolved chemical concentration in equilibrium with the partial pressure of the gas in the atmosphere above (ng/m^3); c_{air} is the chemical concentration in the gas phase (ng/m^3); H' is the dimensionless Henry's Law constant and is related to the Henry's Law constant H (Pa m^3/mol) as H/RT; R is the ideal gas law constant (Pa m^3/ mol K) and T is the temperature near the air-sea interface (K); K_{ol} is the overall mass transfer coefficient (m/h); k_a is the mass transfer coefficient across the air layer (m/h); k_w is the mass transfer coefficient across the water layer (m/h); $1/K_{ol}$ is the total resistance to mass transfer across the air-water interface and is equal to the sum of the resistance across the air layer ($1/k_aH'$) and the water layer ($1/k_w$).

Henry Law constants (H in Pa m^3/mol) for PCBs and HCHs were taken from the literature (Bamford et al., 2002; Sahsuvar et al., 2003). The Henry Law constant was corrected for the prevailing temperature T (Totten et al., 2001; Sahsuvar et al., 2003) and salinity (Jurado et al., 2004).

The mass transfer coefficient $k_{a,comp}$ (cm/s) for a compound in air was calculated using the following equations, as described by Schwarzenbach et al. (2003):

$$k_{a,comp} = k_{a,H_2O}\left[\left(\frac{M_{H_2O}}{M_{comp}}\right)^{0.5}\right]^{0.67} \qquad (3)$$

with $k_{a,H_2O} \approx (0.2 * u_{10}) + 0.3$ and u_{10} as the wind speed at a height of 10 m,

and the molar masses M_{H20} and M_{comp} (g/mol) of water and POP compound respectively.

The wind speed u_{10} (m/s) at a height of 10 m above the sea surface was calculated based on the wind speed measured at a height of 2 m (u_2) using the following equation (Mackay and Yeun, 1983):

$$u_{10} = \left(\frac{10.4}{\ln 2 + 8.1} \right) * u_2 \quad (4)$$

The mass transfer coefficient $k_{w,comp}$ (cm/h) in seawater were calculated using the equation given by Wannickhof et al. (1992).

$$k_{w,comp} = (0.45 * u_{10})^{1.64} * \left(\frac{Sc}{600} \right)^{-0.5} \quad (5)$$

The Schmidt number, Sc, is related to the kinematic viscosity η (cm^2/s) and diffusivity D (cm^2/s) by Sc = η/D of seawater. The kinematic viscosity of seawater was calculated as the quotient of the dynamic viscosity μ (g/cm s) and the density φ (g/cm^3). The equations from Millero (1974) and Millero and Poisson (1981) were used to calculate μ and φ, respectively. The diffusivity, D, was calculated using the Wilke-Chang equation (Wilke and Chang, 1955). Unit conversion was performed for the mass transfer coefficients to the unit m/h.

The net fluxes F are presented in the unit ng/m^2day by unit conversion.

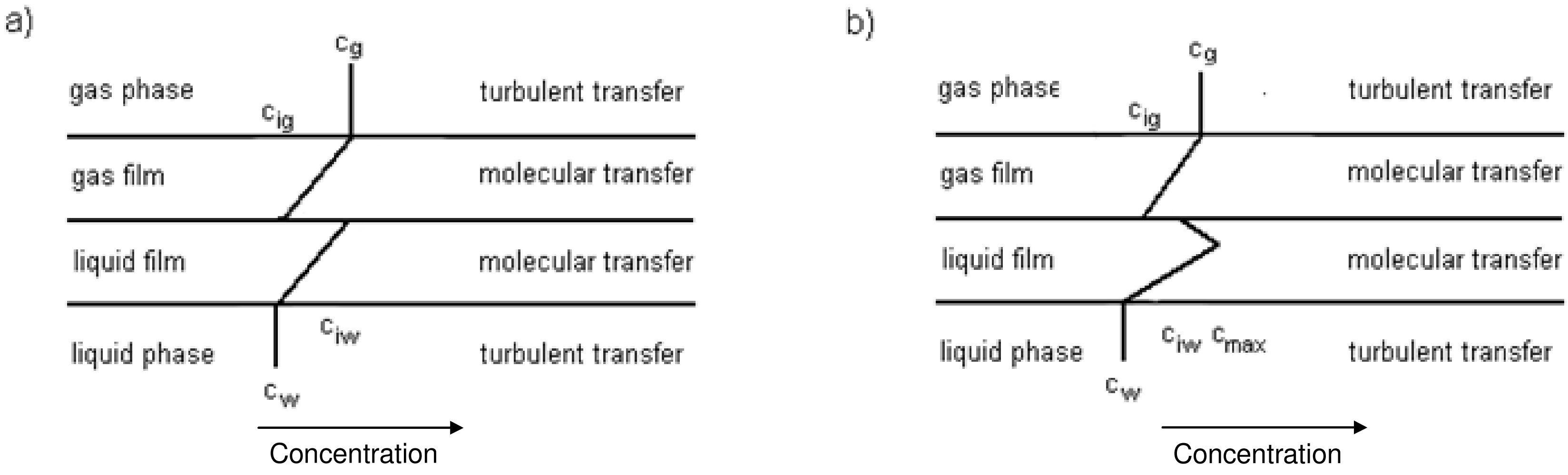


Figure IX-1: (a) classical two-layer model of a gas-liquid interface (Liss and Slater, 1974) and (b) a modified two-layer model with a maximum concentration in the liquid film (SML) (Zhou and Mopper, 1997). c_{iw} and c_{ig} are concentrations in the liquid and gas side interface respectively.

IX-2-2 Aqueous concentration data

Paired concentration levels above detection limits for subsurface, SML and air could be obtained simultaneously for α-HCH, γ-HCH, and for the PCB congeners CB 18, 28, 87, 110, 118, 149 and 153 from two marine sites in Singapore (Station 1 and 2 in Figure VI-1). These compounds were therefore selected to investigate the role of the SML in the air-sea gas exchange of POPs. The data for the aqueous phases are reported and discussed in Chapter VI, whereas the atmospheric data are reported in Chapter VIII. Detailed meteorological data during sampling events can be found in these Chapters. Mean wind speeds ranged from 1.2 to 3.7 m/s and were below the critical wind speed of 4 – 5 m/s at which the SML may be disturbed by turbulence on the sea-surface. Air and water temperature (40 cm depth) were in the range of 26.5 to 32.3 ºC and 28.9 to 30.7 ºC respectively. The water temperature at a depth of 0.5 to 1 cm was 0.2 to 0.6 ºC warmer than the deeper layer and was used as an estimate of the water temperature within the SML itself. The dissolved organic carbon (DOC) concentrations were 2.1 to 25.2 mg\L and 2.7 to 10.9 mg/L in the SML and subsurface water, respectively (Chapter VI).

IX-2-3 Partitioning between truly dissolved and colloidal phases

Operationally defined dissolved concentrations (i.e. sum of truly dissolved and colloidal fractions) for PCBs and HCH isomers in subsurface waters and the SML are reported in Chapter VI and are summarized in Table IX-1. Ranges of dissolved concentrations for ΣPCBs (sum of congeners 18, 28, 87, 110, 118, 149 and 153) were 76 to 468 pg/L (mean 189 pg/L) and 189 to 890 pg/L (mean 482 pg/L) in subsurface water and SML, respectively. The dissolved concentrations of ΣHCHs (sum of α-HCH and γ-HCH) ranged between 72 and 1135 pg/L (mean 449 pg/L), and between 154 and 1010 pg/L (mean 568 pg/L). The mass of PCBs and HCHs adsorbed to DOC were estimated, as described by Totten et al. (17). The dissolved concentration of POPs (C_{Diss}) is the sum in the truly dissolved (C_{truly}) and colloidal (C_{coll}) fractions, as represented by following equation:

$$c_{diss} = c_{truly} + c_{coll} = c_{truly} * \left(1 + K_{OW} * DOC * 10^{-7}\right) \quad (7)$$

where DOC is the concentration of DOC in mg/L and K_{OW} is the n-octanol/water partition coefficient in L/kg. The predicted mean fraction adsorbed to DOC for PCB congeners 18, 28, 87, 110, 118, 149 and 153 in subsurface water was 11.3, 22.3, 18.1, 18.9, 21.3, 44.5 and 22.5 % and in SML 10.3, 27.3, 33.2, 46.2, 48.0, 55.6 and 28.4 % respectively. α- and γ-HCH were adsorbed to DOC as an insignificant mean fraction of 0.4 and 0.3 % in subsurface waters and to 0.7 and 0.5 % in the SML, respectively.

IX-2-4 Gas-phase concentrations

Atmospheric gas-phase concentrations of ΣPCBs and ΣHCHs ranged from 14 to 31 pg/m^3 (mean 21 pg/m^3) and 82 to 329 pg/m^3 (mean 212 pg/m^3) respectively (Table IX-1, Chapter VIII-3-4-1 and VIII-3-6-1). Air mass back trajectories were performed, as described in Chapter VIII. All air masses arriving at the air sampler were partly terrestrial and partly oceanic in origin.

Compund	c_{SML}	c_{Sea}	c_{Air}	$EF_{SML/Sea}$	c_{SML}	c_{Sea}	c_{Air}	$EF_{SML/Sea}$	c_{SML}	c_{Sea}	c_{Air}	$EF_{SML/Sea}$
	Station 1 (16/06/04)				Station 1 (30/06/04)				Station 1 (14/07/04)			
ΣHCHs	1010	1135	82	0.9	779	588	329	1.3	380	227	241	1.7
α-HCH	660	725	38	0.9	264	148	175	1.8	317	126	149	2.5
γ-HCH	350	410	44	0.9	515	440	154	1.2	63	101	92	0.6
ΣPCBs	234	76	14	3.1	232	126	31	1.8	189	114	15	1.7
CB 18	60	7.8	0.7	7.7	12	5.8	1.7	2.1	7	8	3	0.9
CB 28	72	26	< 0.09	2.8	71	31	1.4	2.3	23	15	2.3	1.5
CB 87	7	6	1.5	1.2	19	9	4.2	2.1	34	20	2.4	1.7
CB 110	13	8	2.5	1.6	13	11	4.9	1.2	16	10	1.4	1.6
CB 118	43	12	6.7	3.6	87	54	11	1.6	70	40	4.3	1.8
CB 149	32	11	2	2.9	24	9	6.6	2.7	30	16	1.4	1.9
CB 153	7	5	0.9	1.4	6	6	1	1.0	9	5	< 0.16	1.8
	Station 2 (23/06/04)				Station 2 (07/07/04)				Station 2 (21/07/04)			
ΣHCHs	895	570	188	1.6	191	102	247	1.9	154	72	185	2.1
α-HCH	565	375	96	1.5	155	58	140	2.7	141	66	137	2.1
γ-HCH	330	195	92	1.7	36	44	107	0.8	13	6	48	2.2
ΣPCBs	890	130	21	6.9	666	220	22	3.0	682	469	24	1.5
CB 18	55	25	3.6	2.2	15	14	1.8	1.1	5	5	1.1	1.0
CB 28	43	6.5	1.0	6.6	2.2	51	1.9	0.0	5.2	7	0.4	0.7
CB 87	29	12	1.2	2.4	57	21	3.7	2.7	18	12	< 0.7	1.5
CB 110	22	19	1.8	1.2	87	67	1.8	1.3	12	8.5	1.1	1.4
CB 118	720	43	12	16.7	470	33	11	14.2	610	419	20	1.5
CB 149	8	8	1.5	1.0	14	22	1.4	0.6	17	12	0.9	1.4
CB 153	13	16	0.2	0.8	21	12	< 0.16	1.8	15	5	< 0.16	3.0

Table IX-1: Concentrations of HCH isomers and PCB congeners in the dissolved phase of seawater (in pg/L), SML (in pg/L) and in air in (pg/m^3), and the SML enrichment factor EF.

IX-3 Results and Discussion

IX-3-1 Error estimation

Uncertainty in the estimated air-sea gas exchange fluxes results are derived from systematic and random errors in the analysis, systematic errors in the values of H and, in particular, from uncertainties in the estimation of the mass transfer coefficient. To assess the uncertainty in the air-sea gas exchange fluxes, a propagation of random errors (Shoemaker et al., 1996) was performed:

$$\sigma^2(F) = \left(\frac{\delta F}{\delta K_{ol}}\right)^2 (\sigma K_{ol})^2 + \left(\frac{\delta F}{\delta c_{truly}}\right)^2 (\sigma c_{truly})^2 + \left(\frac{\delta F}{\delta c_a}\right)^2 (\sigma c_a)^2 + \left(\frac{\delta F}{\delta H}\right)^2 (\sigma H)^2 \qquad (8)$$

where F is the instanteous gas flux resulting from the difference in truly dissolved (c_{truly}) and gas phase (c_a) concentrations, accounting for H. Total propagated variance [σ^2(F)] is the linear combination of the weighted contribution of the variances (σ^2) of the mass transfer coefficient, H, and measured concentrations. Uncertainty in the overall mass transfer coefficient K_{ol} was estimated by the errors of the mass transfer coefficients $k_{w,comp}$ and $k_{a,comp}$ and assumed to be 40% (Nelson et al., 1998) as based on the inspection of k_w versus wind speed plots in Wannickhof et al. (1990).. Uncertainties in the quantification of PCB congeners and HCH isomers were estimated at 30% and 20%, respectively and were determined by the values of the relative percent differences of the analysis of duplicate samples. Uncertainty in the values of H was removed from the error analysis, as errors originating from incorrect temperature and salinity corrections of H are assumed to be systematic errors. The overall error of the air-sea gas exchange fluxes ΔE ranged between 52 and 150% (mean 78%). The error of fluxes in this study is higher by 38% than that reported by Nelson et al. (1998). However, in this study, uncertainties in the overall analytical process were considered, whereas Nelson et al. used the uncertainty in the precision of measurement. The error analysis shows that the major source of uncertainty for the air-sea gas exchange flux originates from the mass transfer coefficients, where a better understanding of the mass transfer process will lead to an improved accuracy of flux calculations. Livingstone and Imboden (1993) described the short-term variability in the wind speed on uncertainties in the calculation of mass transfer coefficients using a two-parameter Weibull distribution. However, the wind speed measured during this study are limited to a record of every 10 to 15 mins during each sampling event and may describe the wind speed variability using the Weibull distribution poorly.

IX-3-2 Gas exchange fluxes of PCBs

Fluxes F_{bulk}, using bulk water and gas phase concentrations, of ΣPCBs are shown in Figure IX-2, whereas ΣPCBs are defined as the sum of the congeners CB 18, 28, 87, 110, 118, 149 and 153. The mean flux of ΣPCBs at Station 1 and 2 were 47 and 87 ng/m^{2}day respectively. Fluxes of individual PCB congeners are given in Table IX-2. All fluxes of individual CB congeners are positive indicating volatilization from the sea to the atmosphere. Iwata et al. (1993) reported adsorption of PCBs from the atmosphere to the sea for many oceanic regions, with highest adsorption fluxes in the arctic regions, North Atlantic and Mediterranean Sea (Table IX-4). Flux data of ΣPCBs obtained from the South China Sea and Eastern Indian Ocean 15 years ago were in a range of -7.6 to 17 ng/m^{2}day (mean 5.3) and 6.2 to 35 ng/m^{2}day (mean 13) and indicate adsorption and volatilization of PCBs into or from the atmosphere. It can be concluded that the atmospheric PCB concentrations over the open ocean in Southeast Asia has not declined significantly over the last 15 years based on a comparison of Iwata's data (1993) and those from this study (Chapter VIII). It is also reasonable to assume that the oceanic water concentration of PCBs has not substantially decreased over the last 15 years. Therefore it is suggested that the direction and intensity of air-sea gas fluxes of PCBs may differ between coastal and oceanic regions of Asia, as controlled by the water concentrations.

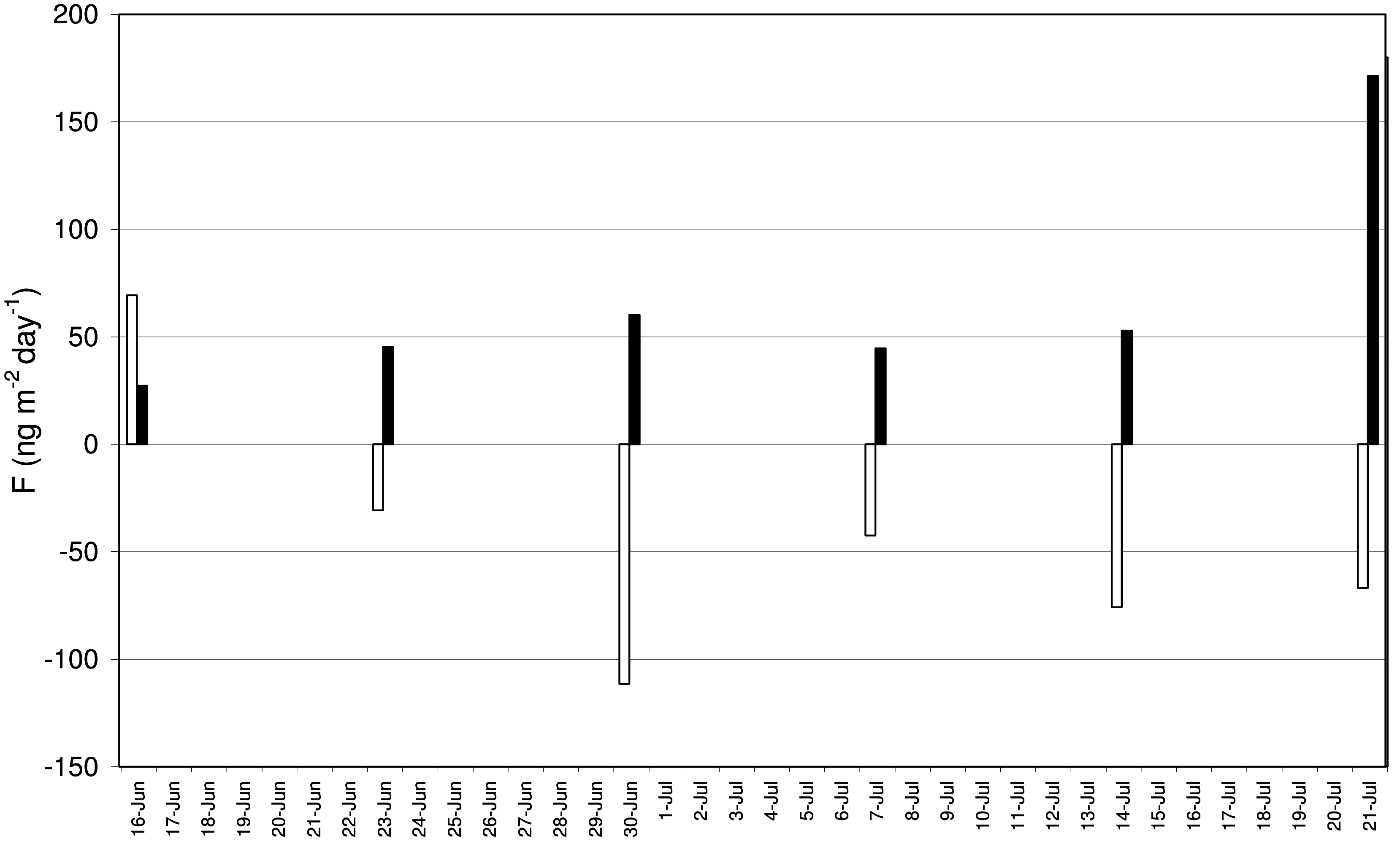


Figure IX-2: Calculated fluxes of ΣHCHs (□) and ΣPCBs (■) across the air-sea interface.

Compund	F_{bulk}	F_{inter}	F_{bulk}	F_{inter}	F_{bulk}	F_{inter}
Station 1						
	16th June 2004		30th June 2004		14th July 2004	
ΣHCHs	69.4	73.8	-111.5	-96.9	-75.7	-62.5
α-HCH	55.4	49.6	-40.2	-27.9	-35.6	-17.6
β-HCH	8.1	21.1	-39.3	-41.0	-12.0	-15.7
γ-HCH	5.9	3.1	-32.0	-28.0	-28.1	-29.1
ΣPCBs	27.3	85.2	60.1	112.1	52.9	87.9
CB 18	2.8	22.0	2.8	5.8	3.7	3.2
CB 28	9.9	27.3	15.7	36.1	7.4	11.3
CB 87	2.1	2.4	4.1	8.9	9.2	15.6
CB 110	2.8	4.6	5.1	6.1	4.6	7.4
CB 118	4.1	15.1	25.3	41.0	18.3	32.2
CB 149	3.9	11.4	4.2	11.4	7.4	14.0
CB 153	1.7	2.5	2.8	2.8	2.3	4.1
Station 2						
	23rd June 2004		7th July 2004		21st July 2004	
ΣHCHs	-30.8	-8.2	-42.5	-37.1	-66.8	-59.5
α-HCH	5.8	21.4	-18.8	-14.1	-31.7	-25.6
β-HCH	-17.6	-16.2	-5.9	-5.0	-20.7	-19.9
γ-HCH	-19.0	-13.4	-17.8	-17.9	-14.4	-14.1
ΣPCBs	45.3	97.5	44.6	133.1	171.3	249.6
CB 18	9.0	19.9	2.9	3.1	1.9	1.9
CB 28	2.4	16.1	10.9	0.4	2.7	2.0
CB 87	4.2	10.1	4.1	11.3	4.4	6.6
CB 110	6.7	7.7	13.5	17.5	3.1	4.4
CB 118	14.8	36.4	6.5	93.7	153.1	223.1
CB 149	2.8	2.8	4.4	2.8	4.3	6.2
CB 153	5.6	4.5	2.4	4.2	1.8	5.4

Table IX-2: Fluxes of ΣHCHs, α-HCH, γ-HCH, ΣPCBs and individual PCB congeners (in ng m^{-2} day^{--1}). F_{bulk} and F_{inter} calculated using a classical and modified two-layer model respectively.

In the urbanized regions, concentrations of POPs in seawater may be significantly higher, thereby driving PCBs from the water into the gaseous phase. The flux data from this study is in a similar range as that for the Chesapeake Bay, USA and Kattegat Sea, Sweden, but significantly lower compared to the New York Harbor Estuary (Table IX-3). It should be noted that Totten et al. (2001) measured the atmospheric concentrations at land-based stations and air samples may have been affected by terrestrial influences.

Compared to the data reported by Sundqvist et al. (2004) from the Swedish West Coast, no significant differences are apparent between the air-sea gas exchange fluxes of PCBs between the northern temperate region of Sweden and the tropical region of Singapore. However, the mean flux data for the Kattegat Sea listed in Table IX-3 is averaged over a year with a peak flux of approximately 350 ng/m^{2}day in May 1999 and a flux of zero (means air-sea gas exchange in equilibrium) in April 1999.

IX-3-3 Gas exchange of HCH isomers

Fluxes F_{bulk}, using bulk water and gas phase concentrations, of ΣHCHs, are shown in Figure IX-2, whereas ΣHCHs are defined as the sum of α-HCH and γ-HCH. The mean flux rates of ΣHCHs at Station 1 and 2 were -39 and -47 ng/m^{2}day respectively. Fluxes of α-HCH and γ-HCH are given in Table IX-2. Fluxes of HCH isomers are negative indicating adsorption of these compounds from the atmosphere to the sea, except for the sampling event on the 16th of June 2004, where a positive flux of 69.4 ng/m^{2}day has been calculated. During this sampling event, the highest water and lowest gaseous concentrations were measured, which resulted in the positive net flux.

Iwata et al. (1993) reported negative fluxes of HCHs in all oceanic regions surveyed indicating adsorption into the ocean. High adsorption fluxes were reported for the Arabian Sea, Bay of Bengal, South and East China Sea (Table IX-3), but these data originated from samples collected prior or during a time of major regulations of the usage of HCHs in India and China (see Chapter VIII-3-9) and are likely to be substantial lower at the present time. The mean adsorption flux of ΣHCHs reported in this study was 4-fold higher than data derived from the Kattegat Sea, Sweden (Sundquist et al., 2004). As for the PCBs, the mean ΣHCH flux for the Kattegat Sea in Table IX-3 is averaged over a year and the flux of ΣHCHs in July 1999 were -35 ng/m^{2}day , and in the same range as the flux data from this study.

Location	Year	α-HCH	γ-HCH	ΣHCH	CB 28	CB 118	CB153	Σ PCB	Reference
Great Lakes, USA	1986							19	Baker et al., 1990
East China Sea	1989/1990	-210	-50	-260				-15	Iwata et al. 1993
South China Sea		-210	-140	-350				5.3	
Eastern Indian Ocean		-2.2	-5.2	-7.5				13	
Bay of Bengal/Arabian Sea		-2200	-310	-2500				4.3	
Chukchi Sea		-47	-8.6	-56				-37	
Bering Sea		-57	-17	-73				-53	
Gulf of Alaska		-29	-16	-45				-17	
North Atlantic		-69	-27	-96				-54	
North Pacific		-49	-13	-62				2.9	
Mediterranean Sea		-43	-24	-67				-40	
Southern Ocean		-11	-6.1	-17				-2.7	
Chesapeake Bay, USA	1993							96	Nelson et al., 1998
New York, USA	1998							1250	Totten et al., 2001
Kattegat Sea, Sweden	1998/1999	-4.2	-6.6	-11	4.9	4.4	21	76	Sundquist et al., 2004
Singapore	2004	-11	-17	-43	8.2	37	2.8	67	this study

Table IX-3: Air-sea gas fluxes of HCHs and PCBs (mean values in ng/m^{2}day) in different regions of the world.

IX-3-4 Importance of the SML in air-sea gas exchange of POPs

It has been shown that air-water transfer velocities can be reduced for water soluble gases, i.e. CO_2, in the presence of organic films and the SML may represent a layer of resistance for the air-sea gas exchange of such gases (Frew, 1997; Asher, 1997). However, for hydrophobic compounds, the SML is likely to behave as a storage reservoir due to the enrichment of these compounds, as suggested by Mackay et al. (1991). However, to date, no attempt has been undertaken to investigate the effects of the SML on this process.

To evaluate the importance of the SML in the air-sea gas exchange of POPs, a modified two-layer model was used as described by Zhou and Mopper (1997), as shown in Figure IX-1b. Due to the enrichment of POPs in the SML, the maximum concentration is likely to occur near the air-sea interface within the SML, and therefore the truly dissolved concentrations of PCBs and HCHs in the SML are used for the calculation of the fluxes F_{inter} , as given in Table IX-2.

The SML receives organic matter, including POPs, from both benthic sediments and the underlying water column by upwelling, convection, diffusion and bubble formation. The accumulation of micro bubbles at the air–sea interface is known to be a significant transport vector of organic matter to the sea-surface, particularly for the removal of small particles from the water column (Hardy, 1982). The increasing enrichment of OCs after heavy rainfall events (see Chapter V) provides supporting evidence that the SML receives a significant amount of organic contaminants via atmospheric wet deposition.

The fluxes F_{inter} for PCBs were significantly higher compared to those derived from the bulk seawater - due to the increasing concentration gradient of PCBs between ocean and atmosphere. Due to the enrichment of PCBs in the SML, one would expect that molecular transfer would go in both directions, i.e. into bulk seawater and into air. However, as the PCB molecule approaches the SML its chemical potential is lowered to a preferred stage (Valsaraj, 1994). In other words, it is apparent that there is an energy barrier to the desorption of the molecule from the SML to the bulk seawater, unless mixing of the SML with the bulk seawater occurs, or the molecule is associated with sinking particulates. In this discussion an undisturbed SML and molecular transfer of truly dissolved molecules are considered, and therefore it is suggested that the desorption from the SML to the bulk seawater is negligible.

The residence time of the selected PCB congeners is calculated by the ratio of the surface concentration in the SML (e.g. $c_{truly} * \gamma$, with γ as thickness of collected SML given in Table VI-1) divided by the air-sea gas flux F_{inter}. The calculated residence times in SML varied between 0.3 to 0.6 minutes among sampling events. The residence times among the selected CB congeners varied insignificantly during a single sampling event. This may indicate that the physicochemical properties do not affect the air-sea gas flux of PCBs to a significant extent. For example, the vapor pressure varies over a magnitude of three between tri- and hexa-CBs (Table II-1), but the residence times changed only by maximum ±10% among the CB congeners.

It has been recognized that the impact of surfactant films, or in other words the SML, in retarding gas exchange is hydrodynamic in nature and does not involve the formation of a barrier layer at the air-sea interface impeding gas diffusion (Davis, 1966; Tsai, 1998). A barrier effect is highly dependent in surfactant film type and requires a rigid, close-packed lattice characteristic of a condensed, insoluble monolayer. Under typical conditions of turbulence found at the sea surface, a close-packed configuration would not be maintained in the presence of wind and breaking waves (Liss, 1983). Indeed, a linear relationship was found between the average residence times of the selected PCB congeners and the reciprocal of the wind speed u_2 (Figure IX-3). That means that the higher the wind speed the shorter is the residence time of PCB congeners in the SML. This is consistent with a less close-packed surfactant film and therefore a more permeable SML at higher wind speeds.

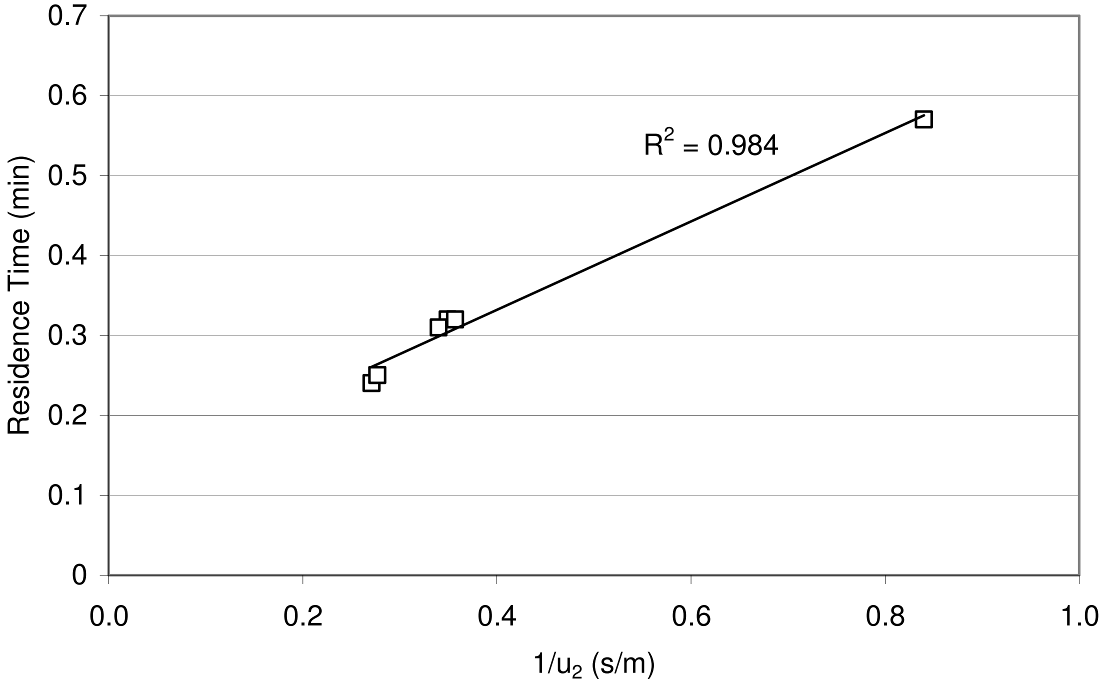


Figure IX-3: Mean residence times of PCB congeners versus reciprocal of the wind speed (u_2) for the sampling events between 16th June to 21st July 2004.

The residence times for α-HCH and γ-HCH were in a range between 0.6 to 3.0 and 0.3 to 2.8 minutes. The higher residence times compared to those for PCB congeners originate from the disproportionally higher concentrations of HCH isomers in the bulk water and SML relative to their fluxes. The relationship between residence times of HCHs in the SML and the reciprocal of the wind speed is non-linear.

However, the air-sea gas exchange process of HCH isomers through the SML may be different to the process governing the transfer of PCBs across the SML. HCH isomers are substantial less hydrophobic and therefore have a lower tendency to accumulate in the SML. The enrichment of the truly dissolved concentration of HCHs has not exceeded 1.2 and for a few occasions enrichments were below unity - indicating a depletion of these compounds in the SML. The molecular transfer of HCH isomers between the SML and bulk water may be significant due to the lower or non-existing energy barrier for the transfer of hydrophobic compounds between the SML and bulk water (Valsaraj, 1994). The energy barrier becomes larger with an increasing molecular size - as observed for a series of hydrocarbons (Valsaraj, 1988).

To investigate the air-sea gas exchange through the SML in more details, a parameterization of the transfer process between bulk water and SML needs to be developed. This requires intensive experimental and modeling work, and could not be conducted within this study. For example, no measured interfacial partition coefficients for POPs were available and the attempt to predict the coefficient using four different methods (Hoff et al., 1993; Valsaraj et al., 1993; Goss 1994; Goss 1997) gave poor results within two to three orders of magnitude differences.

IX-4 Conclusions

A classical and modified two-layer model for the air-sea gas flux calculation was used to investigate the effects of the SML on the air-sea gas exchange of selected POPs. Concentration data of PCB congeners and HCH isomers were obtained by simultaneous measurement of these compounds in the bulk seawater (1m depth), SML and atmosphere. The average fluxes of ΣPCBs and ΣHCHs were 60.3 ng/m^{2}day (volatilization) and -60.7

ng/m^{2}day (adsorption) respectively using the classical model. These fluxes are compared with data from other regions of the world and are generally in a comparable range. The modified model gave average fluxes of ΣPCBs and ΣHCHs of 127.6 and -31.7 ng/m^{2}day by assuming that the maximum concentration of the compound near the surface will be present within the SML closed the air-water interface. The residence time of PCB congeners within the SML were 0.3 to 0.6 minute and evidence is presented that hydrodynamics near the surface plays an important role in the air-sea gas exchange of PCBs. The residence times of HCH isomers were higher by a factor of 3 and the different behavior of these less hydrophobic compounds in the air-sea gas exchange is discussed.

CHAPTER X

Summary of Major Conclusions and Suggestions for Further Research

X-1 Summary of Major Conclusions

In conclusion, this work has fulfilled its objectives and provides new insights into the fate and distribution of persistent organic pollutants (POPs) in Southeast Asia, the region of the Indian Ocean and Hong Kong, China, with particular focus on the sea-surface microlayer (SML). These studies serve as a solid base for further work on the understanding of the global distribution of POPs and the role of Asian regions, particularly the tropical regions of Southeast Asia. The investigations undertaken have shown that the SML plays a critical role in the distribution of POPs in the marine environment. The main conclusions obtained from this research are summarized as:

Chapter IV. Occurrence of Persistent Organic Pollutants (POPs) in Singapore's Coastal Marine Sediments and Ecotoxicological Assessment.

Refer to Chapter I-2 for research objectives. POPs were detected in Singapore's marine sediments and levels reflect the ubiquity of such pollutants (Wurl and Obbard. 2005c).

(a) Polychlorinated biphenyls (PCBs) and organochlorine pesticides, such as DDTs, Chlordanes and HCHs, were detected in Singapore's marine sediments in 2003. For the first time, polybrominated diphenyl ethers were detected in marine sediments from Southeast Asia. Compared to other Asian countries, Singapore's marine sediments can be classified as moderately contaminated with POPs.

(b) The study showed that recent inputs of the pesticide HCH to the marine sediments is likely, but not for DDTs. PCB congeners were present from low to high chlorination grades, indicating diverse inputs that most likely originated from ship traffic emissions, municipal discharge and the petroleum industry.

(c) An ecotoxicological assessment showed that contamination of POPs in the sediments is likely to induce ecotoxicological impacts to the marine environment of Singapore.

Chapter V. Occurrence of Persistent Organic Pollutants (POPs) in the Sea-Surface Microlayer (SML) and Seawater during the Northeast Monsoon in Singapore

Refer to Chapter I-2 for research objectives. SML samples were successfully collected with a self-designed glass drum sampler. POPs were quantified in the SML and seawater from Singapore's marine environment between October 2003 and March 2004, and this represents the first data on the enrichment of POPs in the SML for Asia (Wurl and Obbard, 2005a).

(a) POPs were generally found to be enriched in the SML, by a factor of up to 7, compared to bulk seawater. The enrichment factors (EF) were lower compared to previously reported data from temperate regions, but more comparable to subtropical regions. Concentrations of POPs in seawater were comparable to other regions of Southeast Asia.

(b) Atmospheric wet deposition was identified as an important source of POPs to the SML during the wet season. The concentrations of POPs in the SML increased by a factor of up to 6 after heavy rainfall events, but no increase was observed for the bulk seawater.

Chapter VI. Distribution of Persistent Organic Pollutants (POPs) in the Sea-Surface Microlayer (SML), Water Column and Sediment of Singapore's Marine Coastal Environment

Refer to Chapter I-2 for research objectives. POPs were quantified in the dissolved (DP) and suspended particulate matter (SPM) phase in the SML and water column collected at several marine locations in Singapore, and results confirm the ubiquity of POPs in the coastal environment. Even so, the concentrations are significantly lower when compared to data for bulk seawater reported for other regions of Asia, i.e. China (Wurl and Obbard, 2006j).

(a) It was observed that the more water soluble HCH isomers are only weakly associated to the SPM, but nonetheless the SPM plays an important role in the distribution of DDT and PCBs in the water column. The SPM-associated fractions of POPs were lower at the marine location influenced by stronger water dynamics.

(b) Vertical profiles show the unique distribution between the DP and SPM of PCBs, DDTs and HCHs and their enrichment in the two boundary layers of the water column i.e. the SML and near-bottom water layer.

(c) Evidence is presented to show that sediment resuspension processes release PCB and DDT contamination to the water column. It has also been ascertained that the SML receives inputs of POPs via atmospheric wet and dry deposition.

Chapter VII. Occurrence and Distribution of Persistent Organic Pollutants (POPs) in the Sea-Surface Microlayer (SML) and Seawater in Hong Kong, China.

Refer to Chapter I-2 for research objectives. The concentrations of POPs, including polybrominated diphenyl ethers (PBDEs), were determined in SML and seawater samples collected at five locations in Hong Kong, China (Wurl et al., 2006e; Wurl et al., 2006f)

(a) PCBs, PBDEs, DDTs, and HCH isomers were the major POPs present in SML and seawater samples collected. The data represent the first reporting the occurrence of PBDEs in the SML. Seawater samples from Hong Kong were lower in concentration by a magnitude of 2-3 fold compared to other coastal regions of China.

(b) EF values of POPs in the SML were up to 8, and comparable to these found in Singapore. The highest EF values were found for POPs associated with the SPM i.e. DDT and PCB compounds.

(c) From the data it can be deduced that fresh inputs of DDT continue to be introduced to Hong Kong's marine environment, which is consistent with the evidence provided in the literature that DDT continues to be used in several regions of China.

(d) PBDEs were detected in samples collected at stations with low water dynamics and which are influenced by runoff from urban areas. EF values of PBDEs in the SML were similar to these found for PCBs.

(e) The Pearl River Estuary (PRE) is a major pathway of POPs from mainland China to Hong Kong. Despite of the growth of electronic industries in the region of the PRE, the concentrations of PBDEs in Hong Kong's waters are considered to be low to intermediate, probably due to the potential of river systems to trap PBDEs via sedimentation before entering the PRE.

Chapter VIII. Persistent Organic Pollutants (POPs) in the Marine Atmosphere of Southeast Asia and the Indian Ocean

Refer to Chapter I-2 for research objectives. This chapter reports rare atmospheric data for prevailing levels of POPs over Southeast Asia and the Indian Ocean. Atmospheric samples were collected during a sailing expedition, and include the first data on PBDEs in air over the open ocean (Wurl and Obbard, 2005b; Wurl et al., 2006g; Wurl et al., 2006h).

(a) Concentrations of PCBs and DDTs were relatively low in the marine atmosphere of Singapore, but moderate levels were detected for HCH isomers.

(b) Relatively high concentrations of atmospheric PCBs were found on the remote islands of Chagos Archipelago and Gan, Maldives, most likely originating from military activities and uncontrolled waste management, respectively.

(c) DDT concentrations in air samples collected in proximity to Indonesia's coastline were high, and data indicated fresh emissions of DDT into the atmosphere over Indonesia.

(d) Air mass back trajectory analysis showed that POPs, including PBDEs, traversed for at least 5 days over the open ocean prior to collection, indicating long-range transport of these compounds and a large spatial distribution over the southern hemisphere.

(e) PBDE concentrations in air collected over the open Indian Ocean were as high as levels reported from a remote coastline in Europe, thereby indicating a relatively high concentration of PBDEs in the atmosphere in the southern hemisphere and a ubiquitous global atmospheric distribution.

(f) Comparison of atmospheric data collected over the last 30 years with those reported in this study show a significant decline in levels of DDTs and HCHs in the atmosphere over the Indian Ocean, which is most likely due to the restricted usage of these pesticides in India the recent years. However, no clear trend in the level of atmospheric PCBs over the Indian Ocean could be observed.

Chapter IX. The Role of the Sea-Surface Microlayer in the Dynamics of Air-Sea Gas Exchange of Persistent Organic Pollutants (POPs)

Refer to Chapter I-2 for research objectives. The controlling function of the SML on the mass transfer of POPs between the ocean and atmosphere was investigated for the first time, as based on a modification of a classical two-layer model. The simultaneous measurements of PCBs and HCH isomers in seawater, SML and the atmosphere provided the concentration data used in the model (Wurl et al., 2006i).

(a) Air-sea gas exchange fluxes using a classical two-layer model were in a similar range to flux data reported for the Great Lakes, USA and Sweden.

(b) A modified two-layer model, based on the assumption that the maximum concentration of the compound is present within the SML adjacent to the air-water interface, showed that fluxes were higher by a factor of up to 3 for the air-sea gas exchange of POPs - particularly for the more hydrophobic compounds.

(c) Evidence is presented that hydrodynamics near the ocean surface play an important role in controlling the air-sea gas exchange of the more hydrophobic POPs.

X-2 Suggestions for Further Studies

Specific recommendations for future studies include:

(a) To determine the concentration of POPs, including PBDEs, in the SML in different regions of the world, and to include the SML as a separate environmental compartment for investigations on the fate of these compounds.

(b) To study the fate and distribution of POPs in other tropical regions of the world. For example, data are lacking from Africa and Central America, where POPs may still be in use in many developing countries.

(c) Physical, chemical and biological parameters, such as wave height, surfactant concentrations and biological activity likely affect the formation of the SML, and therefore the extent that POPs are enriched in the SML and controlled by air-sea gas exchange processes. There is an urgent need to understand the influence of such parameters in more detail in order to gain a better understanding of the global fate and distribution of POPs.

(d) Further studies on the environmental pathways of PBDEs are needed in order to understand their global distribution. In particular, studies on the bioaccumulation of PBDEs in marine biota and environmental degradation processes are rare, but comprehensive investigations are necessary to serve as inputs to environmental fate models.

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Appendix A

GC-MS Parameters Using EI-SIM Mode

Analyte	Retention time (min) [a]	Quantification ion	Confirmatory ion
HCHs	16.1 to 21.5	181	219
PCNB	18.9	237	235
Heptachlor	24.2	100	66
Heptachlor epoxide	31.5	81	353
Chlordanes	34.2 to 35.7	373	375
Endosulfan I & II	35.5, 43.2	195	239, 195
Dieldrin	38.9	79	82
p,p'-DDE	39.4	246	248
p,p'-DDD	45.2	235	237
Endrin Aldehyde	45.4	67	250
Endosulfan sulfate	48.9	272	237
p,p'-DDT	50.7	235	237
Endrin Ketone	55.4	67	317
Methoxychlor	60.8	227	228
3-CBs	19.5 to 24.0	256	258
4-CBs	26.4 to 32.6	290	292
5-CBs	32.7 to 43.6	324	326
6-CBs	41.4 to 61.5	360	362
7-CBs	52.7 to 60.0	394	396
8-CBs	62.6 to 66.5	430	428
9-CBs	64.8 to 68.2	464	462
10-CB	69.4	498	500
BDE-47	34.2	326	484
BDE-99	40.2	404	567
BDE-100	39.0	404	567

[a] Example of retention times obtained using GC program as described in Section III-6-1, Chapter III.

Appendix B

GC-IT-MSMS Parameters Using EI-MSMS Mode

Analyte	Retention time (min) [a]	Quantification ion
HCHs	26.7 to 33.2	183.0
Heptachlor	38.0	237.0
Heptachlor epoxide	47.9	262.9
Trans-, cis-chlordanes	51.3, 53.2	300.1, 372.9
Endosulfan I & II	53.1, 60.4	301.0, 267.0
Dieldrin	57.0	241.0
p,p'-DDE	56.7	246.0
p,p'-DDD	61.1	200.2
Endrin Aldehyde	61.7	245.1
Endosulfan sulfate	63.5	237.0
p,p'-DDT	63.9	200.1
Endrin Ketone	66.6	281.0
Methoxychlor	67.5	212.2
3-CBs	31.0 to 37.4	186.1
4-CBs	40.7 to 48.9	292.0
5-CBs	49.1 to 60.3	324.9
6-CBs	58.7 to 69.2	358.8
7-CBs	64.9 to 68.2	393.8
8-CBs	69.7 to 72.3	429.6
9-CBs	71.3 to 73.7	465.7
10-CB	75.0	497.8
BDE-28	10.7	167.1
BDE-47	12.4	219.1
BDE-99	13.6	563.6
BDE-100	14.0	563.6
BDE-153	14.9	481.8
BDE-156	15.4	481.8
BDE-183	16.5	482.8
BDE-209	21.0	796.1

[a] Example of retention times obtained using GC program as described in Section III-6-2, Chapter III.

Appendix C

Details of Station IO 1 to IO 12 for Collection of Atmospheric Samples over the Indian Ocean

Station	Date	Location	ΣPCBs	ΣHCHs	α-HCH	γ-HCH	ΣDDTs	DDT	ΣChlordane
IO 1	13/09/2004	6° 06' S 105° 26' E	51	3.1	0.3	2.8	33.2	27.7	3.8
IO 2	15/09/2004	6° 45' S 105° 14' E	28.3	6.1	0.5	5.6	26.6	17.7	1.1
IO 3	19/09/2004	10° 46' S 99° 00' E to 11° 58' S 97° 05' E	7.5	8.8	1.1	7.7	5.8	3.2	0.5
IO 4	26/09/2004	12° 06' S 96° 53' E	11.8	2.4	0.2	2.2	2.5	< 0.2	4.4
IO 5	08/10/2004	13° 52' S 87° 39' E to 14° 09' S 86° 44' E	16.5	9.1	1.6	7.0	2.5	1.7	1.7
IO 6	06/06/2005	5° 20' S 72° 16' E	74.6	12.1	1.2	10.5	5.0	3.8	1.3
IO 7	11/06/2005	5° 21' S 72° 13' E	114.3	6.6	0.8	5.8	< 0.5	< 0.2	1.3
IO 8	24/06/2005	0° 41' S 73° 9' E	75.2	15.2	2.0	13.2	2.6	< 0.2	1.4
IO 9	10/07/2005	0° 41' S 73° 9' E	43.2	9.6	0.9	8.7	4.5	0.8	0.6
IO 10	15/08/2005	4° 45' N 83° 20' E to 4° 53' N 84° 9' E	6.8	5.6	4.0	0.8	5.2	4.2	0.3
IO 11	22/08/2005	5° 59' N 95° 24' E to 6° 02' N 96° 16' E	16.1	37.0	19.3	17.8	14.5	12.5	0.8
IO 12	29/07/2005	1° 14' N 103° 55' E	55.4	97.1	9.7	80.1	11	< 0.2	2.7

Table C1: Details on sample stations and concentrations (pg/m^3) of ΣPCBs, ΣHCHs, α-HCH, γ-HCH, ΣDDTs, DDT and ΣChlordane

Station	Date	Location	ΣPBDE	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 156	BDE 183	BDE 209
IO 1	13/09/2004	6° 06' S 105° 26' E	14.2	< 0.3	12.7	< 0.08	1.5	< 0.7	< 0.7	< 0.1	< 0.6
IO 2	15/09/2004	6° 45' S 105° 14' E	15.6	5.2	10.2	< 0.08	0.2	< 0.7	< 0.7	< 0.1	< 0.6
IO 3	19/09/2004	10° 46' S 99° 00' E to 11° 58' S 97° 05' E	no data								
IO 4	26/09/2004	12° 06' S 96° 53' E	4.1	< 0.3	1.7	< 0.08	2.4	< 0.7	< 0.7	< 0.1	< 0.6
IO 5	08/10/2004	13° 52' S 87° 39' E to 14° 09' S 86° 44' E	2.6	0.5	< 0.4	< 0.08	2.1	< 0.7	< 0.7	< 0.1	< 0.6
IO 6	06/06/2005	5° 20' S 72° 16' E	1.5	0.3	1.1	0.1	0.1	< 0.7	< 0.7	< 0.1	< 0.6
IO 7	11/06/2005	5° 21' S 72° 13' E	2.6	0.6	< 0.4	0.7	< 0.08	1.3	< 0.7	< 0.1	< 0.6
IO 8	24/06/2005	0° 41' S 73° 9' E	no data								
IO 9	10/07/2005	0° 41' S 73° 9' E	1.9	< 0.3	1.9	< 0.08	< 0.08	< 0.7	< 0.7	< 0.1	< 0.6
IO 10	15/08/2005	4° 45' N 83° 20' E to 4° 53' N 84° 9' E	2.7	0.6	2.1	< 0.08	< 0.08	< 0.7	< 0.7	< 0.1	< 0.6
IO 11	22/08/2005	5° 59' N 95° 24' E to 6° 02' N 96° 16' E	1.8	< 0.3	0.5	0.1	1.2	< 0.7	< 0.7	< 0.1	< 0.6
IO 12	29/07/2005	1° 14' N 103° 55' E	7.6	< 0.3	1.5	0.7	5.4	< 0.7	< 0.7	< 0.1	< 0.6

Table C2: Details on sample stations and concentrations (pg/m^3) of ΣPBDEs and individual congeners

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