

**Distribution and Debromination of Polybrominated Diphenyl Ethers  
(PBDEs) in Tropical Asian Countries**

**Thesis is in partial fulfillment of the requirements for the degree of  
Doctor of Philosophy**

**Submitted to**

**Symbiotic Science of Environment and Natural Resources  
United Graduate School of Agricultural Science  
Tokyo University of Agriculture and Technology**

**2014**

**Charita Saloma KWAN**

**Distribution and Debromination of Polybrominated Diphenyl Ethers  
(PBDEs) in Tropical Asian Countries**

**Thesis is in partial fulfillment of the requirements for the degree of  
Doctor of Philosophy**

**Submitted to**

**Symbiotic Science of Environment and Natural Resources  
United Graduate School of Agricultural Science  
Tokyo University of Agriculture and Technology**

**Signature of  
Author**

---

**Charita Saloma Kwan**

**Signature of  
Supervisor**

---

**Prof. Hideshige Takada**

## 学 位 論 文 要 旨

### **Distribution and Debromination of Polybrominated Diphenyl Ethers (PBDEs) in Tropical Asian Countries**

(熱帯アジア諸国における臭素化ジフェニルエーテル類 (PBDEs) の分布と  
脱臭素化)

Charita Saloma Kwan

Polybrominated diphenyl ethers (PBDEs) are extensively used as additive flame retardants in polymers for the manufacture of many consumer products. Tetra- to hepta-BDE congeners have been regulated under the Stockholm Convention because of their persistence, toxicity, potential to bioaccumulate and their capacity for long-range environmental transport. However, deca-BDE has not been regulated. Although there have been indications of the debromination of deca-BDE to lower and more toxic congeners, the evidences have been limited. Thus, the present study focussed on providing evidence on the debromination of deca-BDE through environmental observation.

Another focus of this study is the relationship between socio-economic setting and pollution. Tropical Asian countries have experienced unprecedented population and rapid economic growths in the last decade. These are driving factors in the consumption of PBDE-laden goods, e.g. electrical and electronic equipment. Consequently, high volumes of PBDE-containing wastes may be generated in the region. Some tropical Asian countries may be recipients of electronic waste. Thus, there is a need to reveal the environmental distribution of PBDEs, and to understand the transformation processes of deca-BDE in these environments.

This study investigated the distribution, transport and fate of PBDEs, including debromination in eight tropical Asian countries and their highly urbanized cities, such as Lao People's Democratic Republic (Vientiane), Cambodia (Phnom Phen), Vietnam (Hanoi and Can Tho), India (Kolkata, Chennai

and Mumbai), Indonesia (Jakarta), Thailand (Bangkok), the Philippines (Metro Manila) and Malaysia (Kuala Lumpur). The study covered three topics: PBDEs in the leachates of municipal solid waste dumping sites (MSWDS), sedimentary PBDEs in the canals or rivers of urban areas, and understanding the historical trends of PBDE emissions in tropical Asian coastal environments using sediment cores. Twenty three to 46 PBDE congeners were measured in 24 leachate samples from 10 MSWDS, and in 44 surface sediment samples collected from rivers, and coastal waters among the 8 countries. Forty five PBDE congeners were measured in sediment cores from Manila Bay, Philippines and the upper Gulf of Thailand.

The total PBDE concentrations in the leachates from the MSWDS ranged from 3.7 to 133,000 ng/L. The total PBDE concentrations in the sediments ranged from 0.83 to 3,140 ng/g dry wt. The PBDE concentrations in most of the leachates from the MSWDS, and the sedimentary BDE-209 concentrations showed a trend toward higher concentrations in the more industrialized Asian countries, and were similar to or higher than those reported for highly urbanized and industrialized countries worldwide. Thailand, Cambodia, India, the Philippines and Malaysia are possible hot spot areas of PBDE pollution.

The PBDE congener profiles in the leachates and in the sediments reflected the composition of the technical penta-, octa- and deca-BDE products, and the higher importation of technical deca-BDE than octa- and penta-BDE products into Asia. The occurrence of congeners which are not contained, or in trace concentrations, in the technical PBDE products (e.g., BDEs 208, 207, 206, 202, 188, 49, 17/25, 8, 1) was observed in most of the leachate samples and surface sediments, suggesting the occurrence of debromination of BDE-209 in the MSWDS and in the sedimentary environments of tropical Asian countries. Increasing ratios of BDE-202/209, 206/209, 207/209 and decreasing % BDE-209 down the core layers (relative to their proportions in the technical deca-BDE mixtures) provided further evidence in the anaerobic debromination of BDE-209. Debrominated higher PBDE congeners can be the source of lower but more bioavailable and toxic congeners to the environment.

PBDEs were predominantly found in the adsorbed phase of the leachates. Partitioning of PBDEs in the dissolved phase in some leachates was associated with the presence of dissolved organic matter (DOM). Dissolution of PBDEs with DOM in the leachates may facilitate the transport of PBDEs from the MSWDS to the aquatic environments.

The historical trends of PBDE emissions in typical tropical Asian environments were captured by the sediment cores. Increasing concentrations of total PBDEs toward the surface suggested increasing consumption of PBDEs. The doubling times of total PBDEs (6–7 years) and BDE-209 (6–7.5 years) were comparable to or faster than those reported in other water bodies around the world

## *Acknowledgement*

I would like to express my sincerest gratitude and appreciation to the many individuals and institutions both in Japan and in the Philippines who have helped me in many ways.

Foremost, Prof. Dr. **Hideshige Takada**, my dissertation advisor for all the unwavering support at all stages of my study, and for providing all the logistical support during my stay in Japan.

Dr. **Evangeline C. Santiago**, my home advisor and immediate work supervisor for the moral support and for providing the local logistics.

Prof. Dr. **Kazuhiko Narisawa**, Prof. Dr. **Shinso Yokota**, Prof. Dr. **Shiro Hatakeyama**, and Prof. Dr. **Mitsunori Tarao**, reviewers of my dissertation for their constructive suggestions and comments.

Asst. Prof. Dr. **Kaoruko Mizukawa** for providing me the analytical training, and all possible technical assistance. Dr. **Mahua Saha** for the training on general laboratory protocols and the preparation for my defense, and together with Dr. **Unnikrishnan** for helping me adjust to the living conditions in Japan. Dr. **Rei Yamashita** for helping me with the data cluster analysis. Ms. **Maiko Torii**, Ms. **Maki Ito** and Mr. **Tatsuya Koike** for providing the necessary assistance in some of the auxiliary experiments. Dr. **M. Yoh** and Dr. **K. Koba** for the measurement of the particulate and dissolved organic carbon in the leachate samples. Dr. **Yoshihisa Kato** for the measurement of the  $^{137}\text{Cs}$  and  $^{210}\text{Pb}$  activities in the sediment core samples. Dr. **Rinawati**, Dr. **Le Quang Dung**, Dr. **Pauzi** for providing the samples from their respective countries, and to the many scientists from the different tropical Asian countries who have provided assistance in collecting the samples.

To the many **Undergraduate and Graduate Students at the TUAT Laboratory of Organic Geochemistry** who have provided the necessary assistance during sampling and who have extended their friendship especially Rina, Morita-ku, Masaki, Maybelline, Hiroaki, Kyao, Akiko, Mai, Toshiko, Kosuke, Sae, Yasuko, Ruko, Tokuma, Junki, Saya, Yukari, Yohee and Saito. Kitamura-san and Imamura-san for the logistical support.

Dr. Ernelea P. Cao, Dr. Windell L. Rivera and my co-staff at the UP NSRI for the moral support and the assistance, especially to Jena, Raian, Chescel, Romy, Liezel, Floyd and Jenny.

Dr. Ruchaya Boonyatumanond for the help during the application process of the fellowship, Mrs. Esmeralda Cuizon and Mr. John Garcia for securing some documents, and to all my Friends for their kind wishes.

The **Japan Society for the Promotion of Science** for granting me the JSPS RONPAKU Dissertation PhD fellowship. The **Department of Science and Technology of the Philippines** and Staff for coordinating all the requirements of the JSPS during the application process and the conduct of my research visits.

The **University of the Philippines Diliman** through the **Office of the Chancelllor** and the **Natural Sciences Research Institute** for allowing me to undertake the PhD fellowship.

The **Quezon City Controlled Disposal Facility** for the logistical support during sampling at the Payatas dumpsite. The Officers and Men of the **Philippine Coast Guard** for the use of the BRP-EDSA II (SARV-002), and the assistance during sampling in Manila Bay and in the Pasig River. The **Local Governments of Cavite City, and Barangay 128 of the City of Manila** for the assistance during sampling in Cavite City and in the Smokey Mt. dumpsite, respectively.

I am also very grateful for the moral support of the Saloma and Kwan Families, for the values of hard work, and perseverance instilled by my parents, and most especially for the loving support of my husband, **Yefey**, and my daughter, **Kay**.

To the **Almighty God**, all praise and thanksgiving.



## DEFINITION OF ACRONYMS AND TERMS

ABS	Acrylonitrile-Butadiene-Styrene
APIC	Asia Petrochemical Industry Conference
ASE	Accelerated Solvent Extraction
BCFs	Bioconcentration Factors
BDE	Brominated Diphenyl Ether
BFRs	Brominate Flame Retardants
BSEF	Bromine Science and Environmental Forum
CBs	Chlorinated Biphenyls
DOC	Dissolved Organic Carbon
DCM	Dichloromethane
DOM	Dissolved Organic Matter
ECD	Electron Capture Detector
EE	Electrical and Electronic
EEE	Electrical and Electronic Equipment
EMB	Environmental Management Bureau
E-waste	Electronic waste
FRs	Flame Retardants
GC	Gas Chromatography
GC/MS	GC/Mass Spectrometry
GDP	Gross Domestic Product
GMC(s)	Geometric Mean Concentration(s)
HBCD	Hexabromocyclododecane

HIPs	High Impact Polystyrene
I/E ratios	Concentration ratios of the Internal isomers to the External isomers of linear alkylbenzenes
IIS	Injection Internal Standard
IUPAC	International Union of Pure and Applied Chemistry
LABs	Linear alkylbenzenes
LAS	Linear Alkylbenzene Sulfonates
LOD	Limit of Detection
$\log K'_{oc}$	Apparent organic-carbon normalized partition coefficient
$\log K'_{ow}$	Octanol-water partition coefficient
MC(s)	Median Concentration(s)
MSWDS	Municipal Solid Waste Dumping Sites
NA	Not Analyzed
ND	Non-Detection/Not Detected
NSO	National Statistics Office
OC	Organic Carbon
OECD	Organisation for Economic Co-operation and Development
PAS	Passive Air Sampler
PBBs	Polybrominated Biphenyls
PBDEs	Polybrominated Diphenyl Ethers
PDR	People's Democratic Republic
PCBs	Polychlorinated Biphenyls
POC	Particulate Organic Carbon
POPs	Persistent Organic Pollutants



PUF	Polyurethane Foam
RSD	Relative Standard Deviation
SRM	Standard Reference Material
SS	Suspended Solids
TBBPA	Tetrabromobisphenol A
UNEP	United Nations Environment Programme
UNDESA	United Nations Department of Economic and Social Affairs
UR	Upper Range
WEEE	Waste Electrical and Electronic Equipment



## LIST OF FIGURES

- Fig. 1.1. Chemical structure of PBDEs.
- Fig. 1.2. Chemical structure of PCBs.
- Fig. 2.1. Distribution of PBDEs in the adsorbed and dissolved phases of the leachate samples from tropical Asian countries.
- Fig. 2.2. Apparent organic-carbon normalized partition coefficients ( $K'_{oc}$ ) of PBDE congeners in the landfill leachates from tropical Asian countries compared to the corresponding octanol-water partition coefficients ( $K_{ow}$ ). Solid line relationship is based on equilibrium partitioning (Ref.: Seth et al. 1999).
- Fig. 2.3. Average congener profiles of the PBDEs in the adsorbed phase of landfill leachates, by clusters. Cluster 1 is consist of CP-1, IK-1, IJ-1, IJ-2, IJ-3, PMP02-1, PMP10-1, PMP10-2, MK03-1, MK04-1 and MK04-2; Cluster 2 is consist of LV-1, LV-2, LV-3, CP-2, VC-1, VH-1, TB-1, TB-2, TB-3, PMS02-1 and PMP02-2. Error bar represents the standard deviation.
- Fig. 2.4. Relative abundance of the non- or trace technical mixture component congeners in the adsorbed phase of landfill leachate samples from tropical Asian countries. Non-technical mixture component congeners: BDEs 179, 202; trace technical mixture component congeners: Br1-Br3 congeners, 49, 206, 207, 208. Red lines indicate the relative abundance of the congeners in the technical mixtures as reported by La Guardia et al. (2006). For BDEs 206, 207 and 208, their respective abundance in the technical deca-BDE mixture is indicated.

Fig. 2.5. (a) BDE208/BDE209 and BDE207/BDE209 ratios, (b) BDE208/BDE209 and BDE206/BDE209 ratios, and (c) BDE206/BDE209 and BDE207/BDE209 ratios in the landfill leachate samples from tropical Asian countries.

Fig. 2.6. Concentrations of PBDE congeners in the leachates from MSWDS in Manila, Philippines: Smokey Mt. in 2002 and 2009, and Payatas in 2002 and 2010.

Fig. 2.7. Concentrations of total PBDEs in the adsorbed phase of landfill leachate samples from tropical Asian countries.

Fig. 2.8. Concentrations of PBDE congeners in the adsorbed phase of landfill leachates and downstream river sediments in Manila, Philippines. Leachate samples from an operational MSWDS: PMP02-1, PMP02-2, PMP09-1, PMP09-2. Sediment samples from the Pasig River: PR2, 3, 7, 8, 12 (information on sampling locations is available in Annex Table 2.1).

Fig. 3.1. Distribution of PBDE congeners in the sediments from urban cities of tropical Asian countries and Japan. \*Estimated from the consumption pattern of the technical PBDE mixtures in Asia (BSEF, 2012) and the composition of the technical mixtures (La Guardia et. al., 2006).

Fig. 3.2. Comparison of the concentrations of BDEs 47, 99, 153, 183 and 209 in the sediments from urban areas of tropical Asian countries and Japan, and with those from other locations around the world.

\*This study: Lao PDR (S1) to Japan (S9).

\*\*References: (R1) Beijiang River – Chen et al., 2009; (R2) Pearl River Delta –Zheng et al., 2004; (R3) Marine – Liu et al., 2005; (R4) Surabaya rivers, (R5) Surabaya coasts – Ilyas et al., 2011; (R6) Bays: Busan, Ulsan and Jinhae – Moon et al., 2007; (R7) Southeast and Northeast coasts – Wurl and Obbard, 2005; (R8) Industrial and urban –

Toms et al., 2008; (R9) Scheldt Estuary – Verslycke et al., 2005; (R10) Coastal – Eljarrat et al., 2005; (R11) Polyurethane foam manufacturing facility – Hale et al., 2002; (R12) Niagara River – Samara et al., 2006; (R13) San Francisco Bay – Klosterhaus et al., 2012.

Fig. 3.3. Total PBDEs in the sediment samples from tropical Asian countries and Japan.

Fig. 3.4. Total PBDEs in sediments vs. (a) urban population, and (b) GDP per capita of the selected tropical Asian countries.

\*Geometric mean of all samples per country.

\*\*Based on available data (<http://www.unstats.un.org>).

\*\*Geometric mean in year 2000 and 2010 (World Bank, 2010).

Fig. 3.5. Total PBDEs in sediments vs. total adsorbed PBDEs in the landfill leachates from the selected tropical Asian countries. Data of total adsorbed PBDEs in the landfill leachates can be found in Chapter 2 Table 2.3a.

\*Geometric mean of all samples per country.

Fig. 3.6. Spatial distribution of sedimentary BDE-209, total PBDEs without BDE-209, and total PBDEs in the Philippines (Pasig River System and Manila Bay).

\*Manila Canals: MC 1, 2, 3, 6 are tributaries of the Pasig River.

\*\*Pasig River: upstream to downstream, PR 12, 8, 7, 3, 2, 1 flowing towards Manila Bay.

\*\*\*Manila Bay: near-shore to off-shore from Pasig River, MB 1, 4, 17, 18.

Fig. 3.7. Comparison of the concentration ratios of BDE208/209, BDE207/209 and BDE206/209, % BDE49 and % Br1-Br3 in the sediments from tropical Asian countries and from Japan, to the corresponding ratios and % in the technical deca-BDE mixture.

\*From the compositional analysis of the technical deca-BDE mixture (indicated by red lines; La Guardia et al., 2006).

- Fig. 3.8. Debromination indices of BDEs 206, 207, 208, 209 in the sediments and in the landfill leachate samples from Lao PDR, Cambodia, India, Thailand, the Philippines and Malaysia. Debromination index for each of the nona-BDEs is computed as the ratio of the concentrations of BDEs 206, 207, 208 to BDE-209 in the sample. The ratios of BDE206/209 (0.023), BDE207/209 (0.0025), BDE208/209 (0.00062) and the % BDE-209 (91.6) in the technical deca-BDE mixture (La Guardia et al., 2006) are indicated by red lines in the corresponding plots.
- Fig. 3.9. I/E ratios vs. % BDE-209 in the sediment samples from tropical Asian countries. I/E ratio is the concentration ratio of the internal (I) isomers (i.e., isomers in which the substitutional positions are near the center of the alkyl chain) to the external (E) isomers (i.e., isomers in which the phenyl substitutional positions are near the terminal end of the alkyl chain) of linear alkyl benzenes in the sediments.
- Fig. 4.1. Vertical profiles of the total PBDEs and PCBs in the sediment core samples from the Philippines.
- Fig. 4.2. Vertical profiles of the total PBDEs and PCBs in the sediment core sample from Thailand.
- Fig. 4.3 Concentrations of PCBs in beached plastic resin pellets and in air from the Philippines (Cavite in Manila Bay area), Malaysia, Vietnam and Japan.  $\sum$ PCBs is the sum of the concentrations of CBs 66, 101, 105, 110, 118, 128, 138, 149, 153, 170, 180, 187 and 206. PCBs in air were obtained by passive air sampling using PUF disks.
- Fig. 4.4. Concentrations of BDE-209 in the sediment core samples from the Philippines and Thailand as a function of depth and year of deposition.
- Fig. 4.5. Concentrations of detectable PBDE congeners in the sediment core samples from the Philippines and Thailand as a function of depth and year of deposition. BDEs 30, 32,

17/25, 33/28, 35, 37, 75, 49, 71, 116, 118, 126 and 203 were not detected in the sediment core samples.

Fig. 4.6. Vertical profiles of BDEs 209, 99, and 47 in the sediment cores from the Philippines. Blue or vertical lines without symbols indicate the corresponding PBDE concentrations in the blank sample.

Fig. 4.7. Vertical profiles of BDEs 209, 99, and 47 in the sediment core sample from Thailand. Blue or vertical lines without symbols indicate the corresponding PBDE concentrations in the blank sample.

Fig. 4.8. Vertical profiles of the concentration ratios of BDE202/209 and % BDE-209 in the sediment cores from the Philippines and Thailand. \*From the compositional analysis of the technical deca-BDE mixture (indicated by the red or vertical lines without symbols; La Guardia et al., 2006).

Fig. 4.9. Comparison of the concentration ratios of BDE207/209 and BDE206/209 in the sediment cores from the Philippines and Thailand. \*From the compositional analysis of the technical deca-BDE mixture (indicated by the red or vertical lines without symbols; La Guardia et al., 2006).

Fig. 4.10. Comparison of the concentration ratios of BDE196/209 and % Br1-Br3 in the sediment core samples from the Philippines and Thailand. %Br1-Br3 includes BDEs 3, 7, 15. \*From the compositional analysis of the technical deca-BDE mixture (indicated by red lines; La Guardia et al., 2006).

Fig. 4.11. Debromination indices of BDEs 202, 206, 207, and 209 in the landfill leachates, river sediments, and in the sediment core samples from the Philippines and Thailand. The ratios of BDE-206/209 (0.023), BDE-207/209 (0.0025), and % BDE-209 (91.6) in the technical deca-BDE mixture (La Guardia et al., 2006) are indicated by the horizontal

red lines in the corresponding plots. BDE-202 was not detected in the technical octa- and deca-BDE mixtures (Kohler et al., 2008).



## LIST OF TABLES

Table 1.1	PBDE congener composition in the technical PBDE mixtures.
Table 1.2	Socio-economic information for the selected tropical Asian countries.
Table 2.1	Information on the selected MSWDS of tropical Asian countries and sampling conditions.
Table 2.2	Sample information on the leachate samples from the selected MSWDS of tropical Asian countries.
Table 2.3	Validation of the analytical method for extraction of adsorbed PBDEs in the leachate samples: recovery and reproducibility, and analysis of the standard reference material NIST SRM 1941b (Marine Sediment).
Table 2.4a	Concentrations of adsorbed PBDEs in the leachate samples from tropical Asian countries.
Table 2.4b	Concentrations of dissolved PBDEs in the leachate samples from tropical Asian countries.
Table 2.4c	Concentrations of $\sum \text{PBDEs}_{\text{Adsorbed+Dissolved}}$ in the leachate samples from tropical Asian countries.
Table 2.5.	Comparison of the PBDE concentrations in the leachate samples with concentrations reported for other countries.
Table 3.1	Sample information for the sediment samples from tropical Asian countries.
Table 3.2	Statistical evaluation of the concentrations of BDE-209 and the ratios of BDE 207/209 and BDE 206/209 in the NIST SRM 1941b marine sediment analyzed in 2004 and 2012.

Table 3	Sedimentary PBDEs in rivers, canals and coastal areas in urban cities of tropical Asian countries including Japan.
Table 4.1	Sampling information for the sediment cores from the Philippines and Thailand.
Table 4.2	Concentrations of PBDEs in the sediment core samples from the Philippines.
4.2a	MB17
4.2b	MB18
Table 4.3	Concentrations of PBDEs in the sediment core sample from Thailand.
Table 4.4	Concentrations of PCBs in the sediment core samples from the Philippines.
4.4a	MB17
4.4b	MB18
Table 4.5	Concentrations of PCBs in the sediment core sample from Thailand.
Table 4.6	Comparison of the surface fluxes, inventories and doubling time of PBDEs and PCBs in Manila Bay, Philippines and in the upper Gulf of Thailand with those from other locations worldwide.

## Table of Contents

	Page
Abstract	i
Acknowledgement	iii
Definition of Acronyms and Terms	v
List of Figures	ix
List of Tables	xv
<b>Chapter 1    General Introduction</b>	<b>1</b>
1.1. Introduction	3
1.1.1. Integration of the flame retardants into the polymer or plastic industry	3
1.1.2. Brominated flame retardants	4
1.1.3. The PBDE flame retardants	5
1.1.4. Physico-chemical properties of PBDEs and their occurrence in the environment	7
1.1.5. Historical information on PBDEs using sediment cores	8
1.1.6. PBDEs classified as POPs by the Stockholm Convention	9
1.1.7. Debromination of PBDEs	11
1.2. Tropical Asian countries	12
1.3. Objectives and scope of the study	14
<b>Chapter 2    PBDEs in Leachates from Municipal Solid Waste Dumping Sites in                 Tropical Asian Countries: Phase distribution and debromination</b>	<b>19</b>
2.1. Introduction	21

2.2. Materials and methods	23
2.2.1. Sample collection	23
2.2.2. Analytical method	24
2.2.3. Quality assurance and quality control protocols	26
2.2.4. Statistical analysis	27
2.3. Results and discussion	27
2.3.1. Phase distribution of PBDEs in the leachates	28
2.3.2. Possible indicators of debromination	28
2.3.2.1. Congener profiles of PBDEs	28
2.3.2.2. Temporal trend of PBDEs in the MSWDS	31
2.3.3. Variability in PBDE concentrations among countries and MSWDS	32
2.3.4. Tropical Asian MSWDS as potential sources of PBDEs in aquatic environments	33
2.4. Conclusion	34
<b>Chapter 3 Sedimentary PBDEs in Urban Areas of Tropical Asian Countries</b>	<b>55</b>
3.1. Introduction	57
3.2. Materials and methods	59
3.2.1. Sample collection	59
3.2.2. Analytical method	59
3.2.3. Quality assurance and quality control protocols	60
3.3. Results and discussion	62
3.3.1. Congener profiles in the sediments from tropical Asian countries and Japan	62

3.3.2. Sedimentary PBDE levels in tropical Asian countries, in comparison with those in other countries	63
3.3.3. Occurrence of PBDEs in the sediments from tropical Asian countries	63
3.3.4. Spatial distribution of sedimentary PBDEs in the Philippines	65
3.3.5. Indicators of debromination in the sediments from tropical Asian countries	66
3.4. Conclusion	69
<b>Chapter 4 Historical occurrences of Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls in Manila Bay, Philippines and in the upper Gulf of Thailand</b>	<b>85</b>
4.1. Introduction	87
4.2. Materials and methods	89
4.2.1. Study areas	89
4.2.2. Sampling	90
4.2.2.1. Sediment cores	90
4.2.2.2. Confirmatory samples for analysis of PCBs in Asian coastal waters: Plastic resin pellets and PUF disks in passive air sampler	90
4.2.3. Analytical methods	91
4.2.3.1 Bulk density, water content, and organic carbon	91
4.2.3.2. Sedimentation geochronology measurements	92
4.2.3.3. PBDEs and PCBs	92
4.2.4. Quality assurance and quality control protocols	93
4.2.5. Air Volumes Derived from Depuration Compounds	94

4.3. Results and discussion	95
4.3.1. Occurrences of PBDEs and PCBs in the sediment cores	95
4.3.2. PBDE congener profiles in the sediment cores	98
4.3.3. Debromination of BDE-209 in the sediments cores	100
4.4. Conclusion	101
 <b>Chapter 5    General Discussion and Conclusion</b>	 123
5.1. General discussion	125
5.2. General conclusion	128
5.3. Recommendation	129
 <b>References</b>	 133
<b>Annex</b>	147

**Chapter 1**  
**General Introduction**

## **1.1. Introduction**

Consumer products have become basic necessities in today's modern living, particularly the many kinds of electrical and electronic equipment (EEE) such as computers, cellular phones, TV, refrigerators, washing machines, air conditioners, including the furnishings in homes and buildings. Most of these products contain plastic or polymers such as polyvinyl chloride, polystyrene, polymethyl methacrylate, polyethylene, polypropylene, polyamide, polyacrylonitrile, acrylonitrile-butadiene-styrene (ABS) which were commercially developed since the 1930s to the 1970s. Due to their lightness, durability and resistance to corrosion, these plastics or polymers became widely acceptable as raw materials, even substituting the traditional materials, such as cotton, metals and wood (<http://www.plasticsindustry.org>). However, the major drawback of these plastics or polymers is their flammability since they are petroleum-based, e.g., the feed stock ethylene is sourced from natural gas and crude oil (Alaee et al., 2003). In order to use these materials safely, their flammability needs to be controlled.

### **1.1.1 Integration of the flame retardants into the polymer or plastic industry**

Flame retardants (FRs) have been used to reduce the flammability of all kinds of combustible materials, e.g., wood, textiles, paper, including plastics and polymers, in order to reduce the risk of fires (BSEF, 2012). FRs act by reducing the amount of fuel supplied to the flame, and/or the amount of oxygen in the air (OECD, 1994). There are four major groups of FRs: the inorganic (e.g., antimony, aluminum, magnesium), the organophosphorus, the nitrogen-based, and the halogenated (chlorine and bromine) organic chemicals (OECD, 1994; Alaee et al., 2003). Halogenated FRs act directly on the flame in which highly oxidizing H and OH free radicals formed during combustion are trapped by the halogen released from the flame retardant, thereby reducing the rate of combustion and dispersion of the flame (Rahman et al., 2001; Alaee et al., 2003). Of the two halogenated FRs, brominated FRs (BFRs) are widely used (OECD, 1994; BSEF, 2013) because of their higher trapping efficiency and lower decomposing temperature (Alaee et al., 2003).



### **1.1.2. Brominated flame retardants**

In the plastic or polymer industry, BFRs were first used in cellulose nitrate which is extremely flammable (BSEF, 2013). Since then, BFRs have been used in many polymers, e.g., the copolymers ABS and ethylene-vinyl acetate, epoxy and phenolic resins, polyacrylonitrile, polyamide, polyethylene, polypropylene, polyvinyl chloride, polystyrene, high impact polystyrene (HIPS), polyurethane, polyamide, polybutylene and polyethylene terephthalates, and in unsaturated polymers or thermosets (OECD, 1994; Rahman et al., 2001; BSEF, 2012). Therefore, BFRs have a very wide range of applications in many consumer products, such as those in EEE as housings and molded parts in computers, TVs and other household appliances, electrical installations, communication equipment, automotive parts; in printed circuit boards; in electrical and optical cables, connectors and components; in polyurethane foams for sound insulation, as cushion for automotive parts and in upholstered furniture; in textile products such as back-coating of furniture and automotive seating, carpets, drapes, beddings, military safety clothing; in synthetic rubber for conveyor belts; in paints and lacquers, and in wood and composite materials (OECD, 1994; Rahman et al., 2001; BSEF, 2012). With the increasing development and discovery of new products using polymers or plastics, the use of FRs have also increased since the early 1970s, particularly with the growing popularity of the use of personal computers and other electronic devices (OECD, 1994; Covaci et al., 2005).

BFRs are classified into three subgroups according to the mode of integration into the polymers, i.e., the brominated monomers, the reactive, and the additive BFRs. Brominated monomers (e.g., brominated styrene, brominated butadiene) are used in the production of brominated polymers (e.g., brominated epoxy, brominated polystyrene, brominated polycarbonate polybrominated acrylate, brominated polyols; Alaei et al., 2003). Reactive BFRs are chemically bonded into the polymers, and are produced by direct bromination of organic molecules, e.g., tetrabromobisphenol A (TBBPA). Additive BFRs are produced by adding or dissolving bromine in the polymer, e.g., the polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD), and the polybrominated biphenyls (PBBs) (Rahman et al., 2001; de Wit, 2002; Alaei et al., 2003). PBBs were banned in the early 1970s because of its widespread contamination in animal feeds in the U.S (de Wit, 2002). Since then, TBBPA, HBCD and PBDEs have been the three major

types of commercial BFRs (de Wit, 2002; BSEF, 2012). The kind of BFR to be used would depend on the compatibility between the FR and the polymer, and the required level of fire safety (BSEF, 2013). TBBPA are used in epoxy, unsaturated polyesters polycarbonate resins, while HBCD is used in polystyrene foam. PBDEs are extensively used in many kinds of polymers; therefore, they are used in many consumer products (Rahman et al., 2001, de Wit, 2002; Alaei et al., 2003).

### **1.1.3. The PBDE flame retardants**

PBDEs are estimated to constitute one third of the world's production of BFRs (Darnerud, 2003), at 67,000 metric tons/year (BSEF, 2012). Polymer-based products may contain as much as 30% PBDEs by weight (Hale et al., 2002). PBDEs are generally produced by the bromination of diphenyl ether in the presence of a Friedel-Crafts catalyst, such as  $\text{AlCl}_3$  using dibromomethane as solvent (de Wit, 2002; Alaei et al., 2003). Alternatively, PBDEs can also be synthesized by coupling phenol and bromobenzene, and further bromination by refluxing with the Friedel-Crafts catalyst,  $\text{FeBr}_3$  (Rahman et al., 2001). The diphenyl ether molecules contain 10 hydrogen atoms in which any or all may be replaced with bromine (Fig. 1.1), resulting in 209 possible congeners (i.e., the total number of isomers for mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona- and deca-BDEs are 3, 12, 24, 42, 46, 42, 24, 12, 3 and 1, respectively; Rahman et al., 2001). The numbering of individual PBDE congeners followed the IUPAC nomenclature similarly used for polychlorinated biphenyls (PCBs; Fig. 1.2), i.e., based on the position of the bromine atoms on the rings (de Wit, 2002; Alaei et al., 2003). However, the bromination of diphenyl ether would be specific because of steric hindrance and the directing properties of oxygen, resulting in the formation of a limited number of PBDE congeners (Alaei et al., 2003), i.e., approximately about forty are detected in the commercial products (La Guardia et al., 2006) and in the environment (Ross et al., 2009). There are normally three different degrees of bromination: the penta-, octa- and deca-BDEs, which correspond to the commercial or technical products available in the market, i.e., the commercial or technical penta-, octa- and deca-BDE products or mixtures (Alaei et al., 2003). The technical penta-, octa- and deca-BDE products contain mostly the penta-, octa- and deca-BDEs, respectively, but they also contain other PBDEs (de Wit, 2002). PBDEs have been manufactured

since the 1970s (Hardy, 2002); however, the technical penta- and octa-BDE products were phased-out in Europe and in the U.S. since 2004 (BSEF, 2012).

The technical penta-BDE product is a viscous liquid containing 24% to 43% tetra-BDEs (47, 66, 49), 35% to 60% penta-BDEs (99, 100, 85), 2.5% to 8% hexa-BDEs (153, 154, 138) and <0.2% tri-BDEs (17 and 28), where BDEs 47, 99 and 100 are the dominant congeners (Table 1.1; de Wit, 2002; Alaei et al., 2003; La Guardia et al., 2006). The tri-BDEs 17 and 28 are the precursors in the formation of BDE-47, where continued bromination would yield BDE-99 and BDE-100. Further bromination of the tetra- and penta-BDEs would yield BDE-153 and BDE-154 (Alaei et al., 2003). Penta-BDE technical products were used in epoxy and phenolic resins, polyesters, polyurethanes, polyvinylchloride, textiles, paints/lacquers, and in synthetic rubber for conveyor belts, flooring and sheeting (OECD, 1994; Rahman et al., 2001; de Wit, 2002; Alaei et al., 2003).

The technical octa-BDE product is a white powder containing 44% hepta-BDEs, with BDE-183 as the major congener, 31% to 35% octa-BDEs (196, 197, 203), 10% to 12% hexa-BDEs (153, 154), 10% to 12% nona-BDEs (206, 207, 208), and <1 % deca-BDE (Table 1.1; de Wit, 2002; Alaei et al., 2003; La Guardia et al., 2006). Though, it was mainly used in the ABS copolymers, it was also used in polystyrene/HIPs, polyamide, polybutylene terephthalate and polycarbonate. Its major application was in EEE and as housing for computers (OECD, 1994; Rahman et al., 2001; de Wit, 2002; Alaei et al., 2003).

The technical deca-BDE product is the only PBDE product remaining in the market. It is a white powder mainly containing 91% to 98% BDE-209 and small amounts of nona-BDEs (0.3-5%) (Table 1.1) (de Wit, 2002; Alaei et al., 2003; La Guardia et al., 2006). Deca-BDE is considered as a general purpose FR because it is used in many types of polymers (Alaei et al., 2003), such as in polystyrene/HIPs, epoxy and phenolic resins, polyacrylonitrile, polyamide, polybutylene and polyethylene terephthalates, polycarbonates, polyesters, polyethylene, polyolefins, polypropylene and polyvinyl chloride. Its primary application is in the thermoplastics (e.g., the styrenes) used in EEE as housing, printed circuit boards, plugs, switches and connectors (OECD, 1994; Rahman et al., 2001; de Wit, 2002; Hardy, 2002; Alaei et al., 2003). It is also widely used in upholstery

textiles as back coatings (Hardy, 2002; Guzzela et al., 2008), and in synthetic rubber, paints and lacquers (Rahman et al., 2001; de Wit, 2002).

#### **1.1.4. Physico-chemical properties of PBDEs and their occurrence in the environment**

The physico-chemical properties of PBDEs influence their distribution in the environment. Generally, PBDEs have lower vapor pressures that decrease with increasing degree of bromination; thus the largest congener deca-BDE-209 is not expected to volatilize readily from the surfaces of plastics and polymers (Hardy, 2002; Zegers et al., 2003). PBDEs are hydrophobic (Rahman et al., 2001) and have low solubility in water (de Wit, 2002); therefore, they are easily removed from the aqueous environment (Rahman et al., 2001). In particular, the high octanol-water partition coefficient,  $\log K_{ow}$  of BDE-209 ( $\sim 10$ ; Watanabe and Tatsukawa, 1990) would enable it to partition preferentially to particles in water (Rahman et al., 2001; Hites, 2004; Ross et al., 2009), which would eventually sink as sediment (Hites, 2004). Thus, sediments have become reservoirs of PBDEs, particularly BDE-209 (de Wit, 2002; Hites, 2004; Johannessen et al., 2008; Ross et al., 2009).

As additive BFRs, PBDEs are not chemically bound to the material into which they have been added; thus, they may leach out from the surfaces of polymers, plastics and textiles (de Wit 2002). Release of PBDEs into the environment can occur during its initial synthesis, incorporation into polymers, the usage or lifetime, recycling, and eventual disposal of consumer products (Rahman et al., 2001; de Wit, 2002; Hale et al., 2003). PBDEs can then be readily mobilized in various compartments of the environment through runoff from domestic and industrial sources, dispersion into the atmosphere (as dusts), through atmospheric deposition, and as leachates in landfills or municipal solid waste dumping sites (MSWDS) (Rahman et al., 2001; de Wit, 2002; Noël et al., 2009). Leachates from landfills or MSWDS have been identified as one of the significant sources of PBDE emissions in the environment (Rahman et al., 2001).

The various uses of PBDEs and its long historical usage in the manufacture of a wide range of industrial and consumer products, many of which are still in use, would ensure the proliferation of these compounds in the environment. As a consequence, they have become ubiquitous in the environment, and have been detected worldwide. Many studies have reported increasing

concentrations of PBDEs in biota (both humans and wildlife), sediments and sewage sludge, and in air (de Wit, 2002; Hites, 2004; Wang et al., 2007; Ross et al., 2009). They have been detected even in remote areas (Rahman et al., 2001; Noël et al., 2009) such as those reported in the Arctic (Stern et al., 2005; Evenset et al., 2007) and in a pristine lake in the Tibet Plateau (Wang et al., 2007). The high concentrations of PBDEs in sperm whale blubber indicated that PBDEs have reached deep ocean waters (Rahman et al., 2001).

#### **1.1.5. Historical information on PBDEs using sediment cores**

Historical information on the occurrences and emissions of persistent organic contaminants in the environment has been revealed using sediment cores, in which the chronology of contamination is linked to the measurement of  $^{210}\text{Pb}$  or  $^{137}\text{Cs}$  activities in the sediment layers as a function of depth and time (Hites, 2004; Covaci et al., 2005; Stern et al., 2005; Kohler et al. 2008). This approach allows tracking the rate of increase in the concentrations of contaminants in sediments (Hites, 2004), which can further be correlated to other factors, such as production and usage, rates of urbanization and industrialization (Zegers et al., 2003; Boonyatumanod et al., 2007; Hong et al., 2010). Thus, sediment cores can be used to predict future trends on the accumulation of contaminants in the environment (Boonyatumanond et al., 2007).

The pioneering study by Hites et al. (1977) on the historical record of sedimentary polycyclic aromatic hydrocarbons ushered the use of sediment cores to trace the history of accumulation of PCBs, organochlorine pesticides, dioxins, and furans (Covaci et al., 2005; Boonyatumanond et al., 2007; Zennegg et al., 2007; Kohler et al., 2008) in many aquatic ecosystems around the world. Historical deposition of PBDEs using sediment cores has also been reported in Europe (Nylund et al., 1992; Zegers et al., 2003; Guzzella et al., 2008; Kohler et al., 2008), in the Arctic (Stern et al., 2005; Evenset et al., 2007), Canada (Stern et al., 2005; Johannessen et al., 2008), the USA (Song et al., 2004; 2005a,b; Zhu and Hites, 2005), China (Chen et al., 2007), India (Binelli et al., 2007), Japan (Minh et al., 2007) and South Korea (Hong et al., 2010). So far, only three studies on the historical occurrences of organic contaminants using sediment cores in tropical Asian waters have been reported, (i.e., in Thailand (Boonyatumanond et al., 2007), India (Binelli et al., 2007, and Indonesia (Rinawati et al., 2012). I applied the approach

of using sediment cores in this study in order to understand the occurrence and emission of PBDEs in typical tropical Asian coastal environments.

#### **1.1.6. PBDEs classified as POPs by the Stockholm Convention**

Tetra-, penta-, hexa- and hepta-BDEs have been found to meet the criteria for persistence, bioaccumulation, toxicity and susceptibility to long range transport; thus, they were classified as persistent organic pollutants (POPs) by the Stockholm Convention in 2009 (Stockholm Convention, 2012). The Stockholm Convention on POPs is a global treaty under the United Nations Environment Programme (UNEP) with the main objective of identifying, evaluating and eliminating POPs from the environment (Stockholm Convention, 2012). The inclusion of these lower brominated PBDE congeners in the list of POPs verifies their environmental threats and health risks.

Tetra- and penta-BDEs refer to BDEs 47, 99, and other tetra- and penta-BDEs present in the technical penta-BDE mixture. Hexa- and hepta-BDEs include the hexa-BDEs 153, 154 and the hepta-BDE-183, and other hexa- and hepta-BDEs present in the technical octa-BDE mixture. The octa- and nona-BDEs present in the technical octa-BDE mixtures are not classified as POPs (Stockholm Convention, 2012) because they are considered less bioaccumulative.

PBDEs are lipophilic (i.e., with log  $K_{ow}$  of 5.9-6.2 for tetra-BDEs, 6.5-7.0 for penta-BDEs, 8.4-8.9 for octa-BDEs and ~10 for BDE-209 (Watanabe and Tatsukawa, 1990)); thus, they are expected to bioaccumulate especially in aquatic organisms (Rahman et al. 2001; de Wit, 2002; Hites, 2004). However, bioaccumulation of lower brominated congeners were found to be greater than the higher brominated congeners, as indicated by their higher concentrations in biological samples, including humans (Rahman et al, 2001; de Wit, 2002; Hites, 2004; Mizukawa et al., 2009). The lower brominated congeners (of the penta-BDE products) have also been found to have endocrine disrupting effects including neurobehavioral development (de Wit, 2002; McDonald, 2002; Darnerud, 2003; Costa and Giordano, 2007). Many studies have reported the toxicity of the lower brominated congeners to animals and humans targeting the thyroid gland, liver and kidney

(Rahman et al. 2001; de Wit, 2002; McDonald, 2002; Darnerud, 2003; Costa and Giordano, 2007; Ross et al., 2009).

On the other hand, pharmacokinetic studies of deca-BDE in rats have indicated that it was poorly absorbed from the gastro-intestinal tract, and was rapidly excreted through the feces (Hardy, 2002; McDonald, 2002). These results were associated to the large molecular size and weight of BDE-209 at 959 g/mole (Hardy, 2002). Although the bioconcentration factors (BCFs) of PBDEs were correlated to the bromination number, and hence with the hydrophobicity or  $\log K_{ow}$ , Mizukawa et al. (2009) observed that BCFs decreased at  $\log K_{ow} > 7$ , (i.e., octa-BDEs to BDE-209 are less bioaccumulative). PBDE congeners with higher  $\log K_{ow}$  have more bromine atoms which increase their molecular size, therefore inhibiting their permeation through cell membranes and their partitioning into tissues (Mizukawa et al., 2009). In addition, the toxicity of deca-BDE to the thyroid gland, liver and kidney was observed only at very low doses (Darnerud, 2003).

To date, evidences on the bioaccumulative potential and the toxicology of deca-BDE have not been conclusive (BSEF, 2013). On these accounts, deca-BDE is not regulated by the Stockholm Convention, although the POP Review Committee has decided to draft a risk profile for the commercial deca-BDE in October 2013 (BSEF, 2013). In addition, it has become a concern that chemical transformation (i.e., debromination of deca-BDE) converts deca-BDE to lower brominated congeners which are more bioaccumulative and toxic; however, the evidences are limited. More evidences on the transformation of deca-BDE through debromination to lower but more toxic and bioavailable brominated congeners in the environment are necessary. Hence, I examined the environmental transformation of PBDEs particularly deca-BDE, specifically in the tropical Asian environment, where studies on PBDEs are generally limited. The results of my study can contribute to the regulation of deca-BDE.

It is also important to note that while deca-BDE is not yet classified as a POP, developed countries have already implemented restrictions on the use of deca-BDE, e.g., in EEE in the European Union since 2008. Bromine science and environmental forum member companies in the U.S. have also voluntarily phased-out the production and use of deca-BDE for the U.S. and Canadian markets in 2012, with a one year extension for transportation and military applications (BSEF, 2013).

In Asia, only Japan, China and India have implemented restrictions on the use of deca-BDE. Japan requires reporting the volumes of deca-BDE produced, imported and released in the environment. China enforced legislation on electronic waste (e-waste) in 2011, and restricted the use of deca-BDE in mobile and fixed phones, and printers. India also restricted PBDEs in EEE in 2012 (BSEF, 2013). Generally, there is no restriction on the use of deca-BDE in most tropical Asian countries. Thus, I also conducted this study to provide information on the environmental distribution of deca-BDE in tropical Asian countries, which can be utilized as basis for assessment on the use of technical deca-BDE products in the region.

#### **1.1.7. Debromination of PBDEs**

PBDEs are suspected to be more susceptible to environmental degradation than PCBs because the carbon-bromine bond is weaker than the carbon-chlorine bond (Rahman et al., 2001). Transformation of BDE-209 in the environment through debromination (i.e., bromine atoms are sequentially removed from the parent molecule) has an important implication because it can be a source of the lower PBDE congeners which are more toxic and bioaccumulative (Rahman, et al., 2001; de Wit, 2002; Tokarz et al., 2008; Mizukawa et al., 2009).

Deca-BDE has been found debrominated through photolysis both by UV radiation (de Wit, 2002; Söderström et al., 2004; Christiansson et al., 2009) and natural sunlight (Söderström et al., 2004; Kajiwara et al., 2008; Stapleton and Dodder, 2008); and under anaerobic microbial conditions (Gerecke et al., 2005; He et al., 2006; Robrock et al., 2008; Tokarz et al., 2008). Redox conditions in underground environment of MSWDS can become anaerobic due to degradation of organic matter in the waste, as manifested by the generation of methane (Ngoc and Schnitzer, 2009). There is still limited knowledge on the behavior, transport and environmental fate of PBDEs in landfills or MSWDS; thus, I also investigated the distribution and the occurrence of debromination of PBDEs in selected MSWDS of tropical Asian countries.

Similarly, bottom sediments in aquatic environments are mostly anaerobic. Thus, debromination of BDE-209 would likely occur, although predicted at a slower rate due to its hydrophobicity or their strong adsorption to organic matter (Tokarz et al., 2008). Many studies have observed the predominance of BDE-209 in sediments (e.g., Eljarrat et al., 2005; Moon et al., 2007;



Tokarz et al., 2008; Toms et al. 2008; Chen et al., 2009); although, it was not observed in a few studies (Hale et al., 2003; Liu et al., 2005; Oros et al., 2005). With this contrasting observation on the behavior of BDE-209 especially in sediments, it may be inferred that the fate of PBDEs in the aquatic environment is not fully understood. The presence of high concentrations of BDE-209 in sediments may pose some concern if they break down to the more toxic lower brominated congeners (Tokarz et al., 2008; Ross et al., 2009). Therefore, I also examined the occurrence and debromination of PBDEs in the sediments of rivers and canals in tropical Asian countries.

## **1.2. Tropical Asian countries**

The market demand for the technical PBDEs in Asia was estimated at 23,000 metric tons deca-BDE in 1991 and 2001; 2,000 and 1,500 tons octa-BDE in 1991 and 2001, respectively; and 150 tons penta-BDE in 2001 (de Wit 2002; Hites 2004). In 2001, the consumption of technical penta-, octa- and deca-PBDE products in Asia was 1.8%, 40% and 41% of the world's total production, respectively (Hites, 2004; BSEF, 2012). Most tropical Asian countries, such as India, Indonesia, Malaysia, the Philippines, Thailand and Vietnam have experienced unprecedented population growth over the last decade (Table 1.2; UNDESA, 2010). The combined population of these tropical Asian countries, including Lao People's Democratic Republic (PDR) and Cambodia, has accounted for roughly 25% of the world's population since 2000 (UNDESA, 2010). These countries have also experienced rapid economic growth (Table 1.2; World Bank, 2010) since the 1960s, although shortly interrupted by the Asian financial crisis in 1997 (Lloyd and MacLaren, 2000; Burke and Ahmadi-Esfahani, 2006). These are driving factors in the consumption of more PBDE-laden consumer goods. Thus, it may be deduced that significant amounts of these goods, particularly EEE may have been produced and consumed; and consequently, considerable volumes of PBDE-containing wastes or e-waste may have been generated in the region. For examples, most of the 9.3 million units of television sold in the Philippines from 1990 to 2000 may have been all discarded after a life span of ~12 years, or due to product obsolescence (Peralta and Fontanos, 2006).

In addition, most of the solid wastes disposed in the MSWDS of tropical Asian countries are not segregated. That is, plastics and metals are dumped together with organic wastes such as kitchen

wastes. The increasing population, rapid urbanization and economic growth in these countries can lead to large volumes of unsegregated wastes (Table 1.2), i.e., with a high proportion of degradable organic matter, resulting in highly anaerobic conditions in the MSWDS of these tropical Asian countries (Koh 2007; Ngoc and Schnitzer, 2009). Together with the high and prolonged levels of solar radiation in tropical Asian countries, the enhanced anaerobic conditions in the MSWDS may facilitate the debromination of PBDEs, particularly BDE-209.

On top of the domestic production and consumption of PBDE-laden products, some of these tropical Asian countries may be recipients of used e-products and e-waste. E-waste or also known as waste electrical and electronic equipment (WEEE) has been identified as one the fastest growing waste streams worldwide, especially due to the high obsolescence rate of EEE (UNEP, 2007). According to the EU directive on e-waste, EEE refers to equipment which is designed to work on electrical currents or electromagnetic fields with a voltage rating not exceeding 1000 volts for alternating current and 1500 volts for direct current. Thus, e-waste encompasses almost all kinds of EE products that are near or at the end of their useful life and are discarded by their users (UNEP, 2007).

Although it is illegal under the Basel Convention (i.e., a UNEP initiative which controls the trans-boundary movement and trade of hazardous waste in developing countries; <http://www.unep.org>), many developed countries export e-waste rather than recycle it within their own borders due to the associated hazards (i.e., from Pb, Cd, Cr, Hg, Sb, Ni, PBDEs) and strict environmental regulations (Wang et al., 2007; Robinson, 2009). Because of the prospects for material recovery especially for components with economic value (e.g., Fe, Cu, Al, Ag and Au, including plastics (~constituting 21%)), e-waste has become a trading commodity (UNEP, 2007). Huge volumes of e-waste may have been exported by developed countries to developing countries, especially to Asia, such as China, India, Pakistan including Southeast Asian countries (Martin et al. 2004; Wong et al., 2007), (e.g., 80% of e-waste from North America is exported to Asia; Wong et al., 2007). E-waste recycling operations (such as those in China) have been identified as emission sources of PBDEs (Wang et al., 2007; Wong et al., 2007). Thus, additional amounts of PBDEs may be distributed in tropical Asian environments during usage of used e-products, recycling operations

and disposal of e-waste in landfills or MSWDS. However, the pollution status of PBDEs in Asia and their potential connection with e-waste has not been documented yet.

These economic and social factors (Table 1.2) may enhance the vulnerability of tropical Asian countries to PBDE pollution. Only a few studies on the status of PBDE contamination including historical occurrences, emissions and deposition trends in tropical Asian countries have been published. There is a need to identify and quantify their sources, and to examine the transformation or debromination processes of deca-BDE in these environments, where both anaerobic and photolytic conditions are considerably present. This study covered eight tropical Asian countries and their highly urbanized cities, such as Lao PDR (Vientiane), Cambodia (Phnom Penh), Vietnam (Can Tho and Hanoi), India (Kolkata, Chennai and Mumbai), Indonesia (Jakarta), Thailand (Bangkok), the Philippines (Metro Manila) and Malaysia (Kuala Lumpur).

### **1.3. Objectives and Scope of the Study**

The main objective of this study is to understand the distribution of PBDEs in the tropical Asian aquatic environment, and to examine the occurrence of debromination in this environment. The specific objectives are described in the following three chapters:

Chapter 2: To investigate the status, fate and possible transport mechanism of PBDEs in leachates from MSWDS of the selected tropical Asian countries including their phase distribution and the occurrence of debromination through examination of the PBDE congener profiles. Partitioning of PBDEs between the dissolved and adsorbed phases of the leachates may influence their fate and transport mechanism in the aquatic environment. No in-depth study on the partitioning of PBDEs in leachates has been previously conducted.

Chapter 3: To examine the levels and fate of sedimentary PBDEs in selected urban areas of tropical Asian countries. Sedimentary PBDEs, particularly debrominated BDE-209 can become potential sources of bioavailable and toxic congeners to overlying waters in the aquatic environment, and consequently to aquatic organisms.

Chapter 4: To understand the historical trend of PBDE emissions in tropical Asian coastal environments through comparison with the historical production of the technical PBDE products and with the historical deposition of PCBs by using radio-dated sediment cores from Manila Bay, Philippines and from the upper Gulf of Thailand.

The outcomes of the study would provide a solid basis for the formulation of effective policies and regulations for PBDEs especially deca-BDE, and in predicting potential increase of PBDE pollution in the tropical Asian region.

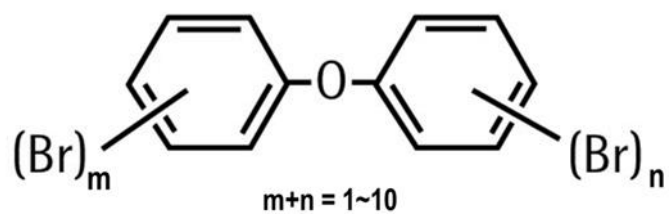


Fig. 1.1. Chemical structure of PBDEs.

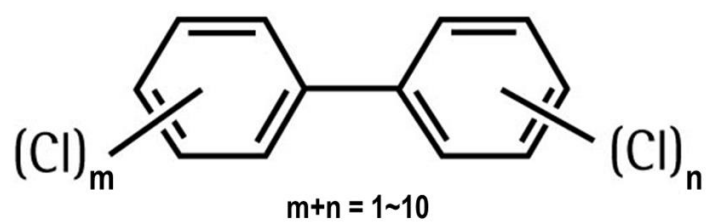


Fig. 1.2. Chemical structure of PCBs.

Table 1.1. PBDE congener composition in the technical PBDE mixtures.

PBDEs			% Composition in the Technical PBDE Mixtures					
Homologue	Congener	IUPAC Nomenclature	Penta-BDE		Octa-BDE		Deca-BDE	
			Ref. (1) <sup>a</sup>	Ref. (2) <sup>b</sup>	Ref. (1) <sup>a</sup>	Ref. (2) <sup>b</sup>	Ref. (1) <sup>a</sup>	Ref. (2) <sup>b</sup>
Tri-	BDE-17	2,2',4-tri-	< 0.2 (tri-)	0.05 - 0.07				
	BDE-28	2,4,4'-tri-		0.1 - 0.25 (BDE-28/33)				
		2',3,4-tri- (BDE-33)						
Tetra-	BDE-47	2,2',4,4'-tetra-	24 - 42 (tetra-)	38.2 - 42.8 (BDE-47/74)				
		2,4,4',5-tetra- (BDE-74)						
	BDE-66	2,3',4,4'-tetra-		0.21 - 0.53 (BDE-66/42)				
		2,2',3,4'-tetra- (BDE-42)						
	BDE-49	2,2',4,5'-tetra-		0.36 - 0.74				
	BDE-75 <sup>b</sup>	2,4,4',6-tetra-		ND - < 0.02				
	BDE-51 <sup>b</sup>	2,2',4,6'-tetra-		ND - < 0.02				
Penta-	BDE-48/71 <sup>b</sup>	2,2',4,5-tetra- (BDE-48)	35 - 60 (penta-)	ND - < 0.02				
		2,3',4',6-tetra- (BDE-71)						
	BDE-99	2,2',4,4',5-penta-		44.8 - 48.6				
	BDE-100	2,2',4,4',6-penta-		7.82 - 13.1				
	BDE-85	2,2',3',4',5-penta-		2.16-2.96				
Penta-/Hexa-	BDE-102 <sup>b</sup>	2,2',4,5,6'-penta-	2,2',3',4',5-penta- (BDE-97)	ND - 0.15				
	BDE-97/118 <sup>b</sup>	2,2',3',4',5-penta- (BDE-97)		<0.02 - 0.12				
		2,3',4,4',5-penta- (BDE-118)						
Hexa-	BDE-126/155 <sup>b</sup>	3,3',4,4',5-penta- (BDE-126)	2,2',4,4',6,6'-hexa- (BDE-155)	0.21 - 0.67				
		2,2',4,4',6,6'-hexa- (BDE-155)						
Hexa-	BDE-153	2,2',4,4',5,5'-hexa-	2.5 - 8 (hexa-)	5.32 - 5.44	10 - 12 (hexa-)	0.15 - 8.66		
	BDE-154	2,2',4,4',5,6'-hexa-		2.68 - 4.54				
	BDE-138	2,2',3,4,4',5'-hexa-		0.53 - 0.73				
	BDE-139	2,2',3,4,4',6-hexa-		0.38 - 0.8				
	BDE-140	2,2',3,4,4',6'-hexa-		0.1 - 0.17				
	BDE-144	2,2',3,4,5',6-hexa-				0.1 - 0.12		
Hepta-	BDE-183	2,2',3,4,4',5',6'-hepta-	0.1 - 0.33 (BDE-75/183)	44 (hepta-)	12.6 - 42 (BDE-175/183)			
	BDE-184	2,2',3,4,4',6,6'-hepta-		ND - < 0.02				
	BDE-171	2,2',3,3',4',4',6'-hepta-				0.17 - 1.81		
	BDE-180	2,2',3,4,4',5,5'-hepta-				ND - 1.7		
	BDE-191	2,3,3',4,4',5',6'-hepta-				ND - 0.02		
Octa-	BDE-197	2,2',3,3',4,4',6,6'-octa-	31-35 (octa-)	10.5 - 22.2				ND - 0.03
	BDE-196	2,2',3,3',4,4',5,6'-octa-		3.12 - 10.5				ND - 0.46
	BDE-203	2,2',3,4,4',5,5',6'-octa-		4.4 - 8.14				ND - 0.07
	BDE-194	2,2',3,3',4,4',5,5'-octa-		ND - 0.02				
	BDE-201	2,2',3,3',4,5',6,6'-octa-		<0.02 - 0.78				
Nona-	BDE-206	2,2',3,3',4,4',5,5',6'-nona-	10-11 (nona-)	1.38 - 7.66		0.3 - 3 (nona-)		2.19 - 5.13
	BDE-207	2,2',3,3',4,4',5,6,6'-nona-		11.2 - 11.5				0.24 - 4.1
	BDE-208	2,2',3,3',4,5,5',6,6'-nona-		<0.02 - 0.19				0.06 - 0.07
Deca-	BDE-209	2,2',3,3',4,4',5,5',6,6'-deca-	< 1	1.31 - 49.6		97 - 98		91.6 - 96.8

<sup>a</sup>Combined from de Wit (2002) and Alaei et al. (2003).<sup>b</sup>From the compositional analysis of the technical PBDE products by La Guardia et al. (2006). BDEs 3, 7, 15, 32, 35, 37, 77, 101, 119, 120, 116, 128, 156, 166, 173, 181, 182, 185, 190, 192, 198, 204, and 205 were not detected in the technical PBDE mixtures based on analysis of available standards (La Guardia et al., 2006).

Table 1.2. Socio-economic information for the selected tropical Asian countries.

Country	Total Population in 2010 <sup>a</sup> (thousands)	Annual Population Growth Rate (2010-15) (%)	GDP per capita in 2010 <sup>b</sup> (USD)	Estimated 2025 Urban MSW <sup>c</sup> Generation <sup>d</sup> (kg/capita/day)
Lao PDR	6,201	1.695	1,177	0.8
Cambodia	14,138	1.501	795	0.52 <sup>e</sup>
Vietnam	87,848	1.138	1,224	0.7
India	1,224,614	1.470	1,410	0.7
Indonesia	239,871	1.085	2,946	1
Thailand	69,122	0.572	4,608	1.5
Philippines	93,261	1.835	2,140	0.8
Malaysia	28,401	1.671	8,373	1.4

<sup>a</sup>UNDESA, 2010.

<sup>b</sup>World Bank, 2010.

<sup>c</sup>Municipal solid waste.

<sup>d</sup>World Bank Urban Development Division, 1999.

<sup>e</sup>Ngoc and Schnitzer, 2009.

## **Chapter 2**

### **PBDEs in Leachates from Municipal Solid Waste Dumping Sites in Tropical Asian Countries: Phase distribution and debromination**



## 2.1. Introduction

Polybrominated diphenyl ethers are ubiquitous in the environment, as a consequence of their use as flame retardants in many consumer products. Technical PBDE products are additives in many polymers and resins used in the manufacture of EE parts, textile coatings, paints, lacquers, packaging materials, upholstered furniture and automotive parts (Rahman et al., 2001; de Wit, 2002; Alaee et al., 2003; BSEF 2012). While PBDEs are intended to be beneficial, studies have indicated their adverse effects on humans and the environment, ranging from bioaccumulation (Rahman et al., 2001; de Wit, 2002; Hites, 2004; Mizukawa et al., 2009) and persistence (Rahman et al., 2001; de Wit, 2002) to toxicity (Rahman et al., 2001; de Wit, 2002), especially the lower brominated congeners. Tetra-, penta-, hexa- and hepta-BDEs were listed in the Stockholm Convention on POPs in 2009 (Stockholm Convention, 2009). The production of technical penta- and octa-BDE products was discontinued in Europe and in the U.S. in 2004, and the use of deca-BDE in EE equipment was restricted in Europe since 2008. The production and use of deca-BDE would be voluntarily phased-out in the U.S. by the end of 2012. Currently, there is no regulatory restriction on the use of deca-BDE in Asia (BSEF, 2012).

The market demand for technical PBDEs in Asia was estimated at 23,000 metric tons in 1991 and 2001 for deca-BDE, 2,000 and 1,500 tons in 1991 and 2001, respectively for octa-BDE, and 150 tons in 2001 for penta-BDE (de Wit, 2002; Hites, 2004). In addition to the domestic production in Asia, a large volume of electronic products and e-waste is suspected to have been exported to tropical Asian countries (Martin et al., 2004), and this will eventually be disposed in MSWDS. Since PBDEs are not chemically bound to the material to which they have been added (de Wit, 2002), they can be released into the environment during usage and disposal in landfills or dumping sites. Leaching of PBDEs from plastics has been confirmed, both in a leaching test (Kim et al., 2006) and in a landfill site (Osako et al., 2004). Landfill leachates have been identified as possible sources of PBDEs in the environment (Rahman et al., 2001). Martin et al., (2004) suspected that PBDEs may be sequestered in the Asian environment, and noted the need to identify and quantify their sources, and to study the transformation and decomposition processes of deca-BDE.

The occurrence of PBDEs in landfill leachates has been reported in the U.S. (Oliaei 2002), Canada (Danon-Schaffer, 2010; Li et al., 2012), Sweden (Öman and Junestedt, 2008), Japan (Osako et al., 2004), Indonesia (Ilyas, 2010) and South Africa (Odusanya et al., 2009; Daso, 2012). Concentrations were scattered over a wide range, with some of the PBDE congeners in the thousands of ng/L range (Oliaei, 2002; Osako et al., 2004; Öman and Junestedt, 2008; Odusanya et al., 2009; Danon-Schaffer, 2010; Daso, 2012). The concentration levels in the landfills were generally higher than those found in rivers and coastal waters. Though the congener profiles also varied widely among these countries, the predominance of BDE-209 was observed in many cases. The detection of BDEs 47, 99, 100, 153, 154 and 209 was ascribed to the technical PBDE mixtures (i.e., penta-BDE, octa-BDE and deca-BDEs). Only a few studies (Danon-Schaffer, 2010; Ilyas, 2010) have associated the congener profiles of the leachates with debromination. Danon-Schaffer (2010) suggested that debromination had occurred in soil samples obtained from landfill sites in Canada, when the ratios of BDE-47/BDE-99 and BDE-47/BDE-100 differed from those of the commercial penta-BDE.

Laboratory studies have also confirmed the debromination of BDE-209 to the more toxic lower brominated congeners through anaerobic microbial degradation (Gerecke et al., 2005; Robrock et al., 2008; Tokarz et al., 2008). Redox conditions in the underground environment of dumping sites can become anaerobic due to degradation of organic matter in the waste, as manifested by the generation of methane. Highly anaerobic conditions may be expected in the dumping sites of developing countries, for example in tropical Asian countries, where increasing population (UNDESA, 2010) and rapid urbanization can produce large volumes of solid waste (mostly non-segregated), resulting in a high proportion of degradable organic matter (Koh, 2007; Ngoc and Schnitzer, 2009). Such heightened anaerobic conditions, as conjectured in the case of tropical Asian MSWDS, may facilitate the debromination of PBDEs. Photolytic debromination of BDE-209 (Christiansson et al., 2009) may also occur in tropical Asian MSWDS, due to the high and prolonged levels of solar radiation.

Since PBDEs are hydrophobic, they are expected to be present in the adsorbed rather than in the dissolved phase (Osako et al., 2004). However, a positive correlation between PBDE

concentrations and the amount of organic matter in the leachates has been reported (Osako et al., 2004; Odusanya et al., 2009). Thus, PBDEs may occur in the dissolved phase (operationally defined as materials passing through a filter with nominal pore size of 0.45  $\mu\text{m}$  (Horowitz et al., 1996) or 1  $\mu\text{m}$  (Osako et al., 2004)) in the presence of dissolved organic matter (DOM). Partitioning of PBDEs between the dissolved and adsorbed phases may influence their fate and transport mechanism in the aquatic environment. However, no in-depth study on the partitioning of PBDEs in leachates has hitherto been conducted.

The objectives of the present study are: (1) to determine the concentration and nature of PBDEs in leachates from MSWDS of eight tropical Asian countries, and to evaluate the propensity of MSWDS to become sources of PBDEs in aquatic environments; (2) to examine the debromination of PBDEs in the MSWDS of tropical Asian countries through assessment of the respective congener profiles; and (3) to examine the partitioning of PBDEs in leachates, by calculating the individual partition coefficients of the PBDE congeners and comparing the values with their octanol-water partition coefficients.

## **2.2. Materials and methods**

### **2.2.1. Sample collection**

Leachate samples ( $n = 1$  to 3) were collected from selected MSWDS in the mega-cities of several tropical Asian countries (Vientiane (Lao PDR), Phnom Penh (Cambodia), Can Tho and Hanoi (Vietnam), Kolkata (India), Jakarta (Indonesia), Bangkok (Thailand), Metro Manila (Philippines) and Kuala Lumpur (Malaysia)) from 2002 to 2010. These MSWDS received predominantly untreated and non-segregated domestic or household waste (Annex Figs. 2.1a and 2.1b). All were operational at the time of sampling, except for Tay Mo (Hanoi, Vietnam), Kukot (Thailand) and Smokey Mountain (Philippines), which were closed in 1999, 2000 and 1993, respectively (Annex Fig. 2.1b). The sampling locations and conditions are summarized in Table 2.1. The leachate samples were grab-collected in solvent-washed amber glass bottles from streams, pools, impounded tanks in the MSWDS (Table 2.1, Annex Fig. 2.1b). In Kukot dumpsite in Thailand, leachate samples were collected by pumping from dumped garbage. In the Smokey

Mountain dumpsite in the Philippines, leachate samples were collected as drippings from garbage in 2009 (Annex Fig. 2.1b). The electrical conductivity, pH and temperature of the leachate samples were determined on site (Table 2.2). High electrical conductivity (3.0-26.3 mS/cm) and the dark brown color confirmed the samples as leachates. The leachates were kept cold (i.e., ~4°C by packing in ice) during transport to the local laboratory. A 20 to 1,000 mL volume of each leachate (depending on the observed turbidity) was filtered through a pre-baked and pre-weighed glass fiber filter (Whatman GF/F, 0.7 µm nominal pore size, 90 mm i.d.). The glass fiber filter containing the sorbed PBDEs was wrapped in aluminum foil and placed in a Ziploc bag.

An aliquot of each filtrate, ranging from 20 to 400 mL, was passed through a methanol-conditioned solid phase extraction SEP-PAK tC<sub>18</sub> plus column cartridge to retain the dissolved PBDEs. The C<sub>18</sub> cartridge containing the dissolved PBDEs was wrapped in aluminum foil and placed in a Ziploc bag. Both the glass fiber filter and the C<sub>18</sub> cartridge were packed in dry ice during transport to the laboratory of TUAT. The samples were stored in the freezer at -30°C until further analysis.

Sediment samples were also collected from five downstream locations of a river in the vicinity of a MSWDS (i.e., the Pasig River and Payatas dumping site in the Philippines), to determine whether leachates from dumping sites could be sources of PBDEs in aquatic environments. The sediment samples were collected using an Ekman dredge, during the same time period as the leachate samples (September 2002). The sampling details are listed in Annex Table 2.1.

### **2.2.2. Analytical method**

The glass fiber filters were freeze-dried and weighed, to calculate the amount of suspended solids (SS). The particulate organic carbon (POC) was measured in an aliquot of the SS using a CHN analyzer (FLASH EA1112, Thermo Scientific). Dissolved organic carbon (DOC) in the filtrates was measured in leachates PMP11-1 to 11-3 using a total organic carbon analyzer (Shimadzu TOC-500).

The filter-sorbed PBDEs were extracted with acetone/dichloromethane (DCM; 1:3 v/v) using a Dionex ASE-200 accelerated solvent extractor. The dissolved PBDEs contained in the filtrates were eluted from the C<sub>18</sub> cartridge with 20 mL of methanol. The methanol extract was concentrated by rotary evaporation, and the solvent was exchanged with DCM.

The adsorbed and dissolved concentrates were spiked with surrogate standards (<sup>13</sup>C-labeled BDEs 3, 15, 28, 47, 99, 154, 153, 183, and f-BDE-208 (4'-fluoro-2,2',3,3',4,5,5',6,6' -nona-bromodiphenyl ether)) and subjected to a two-step column chromatography cleanup. The first cleanup step utilized a 5% H<sub>2</sub>O-deactivated silica gel column in which non- and slightly polar compounds, including the PBDEs, were eluted with hexane/DCM (3:1 v/v). The cleaned-up extract containing the adsorbed fraction was treated with activated Cu whenever sulfur crystals were formed during concentration. Enough Na<sub>2</sub>SO<sub>4</sub> was added to the cleaned-up extract of each dissolved fraction to ensure complete dehydration. After this, both the adsorbed and dissolved cleaned-up extracts were concentrated and then subjected to a second-step cleanup using fully activated silica gel columns. The alkane fraction was first eluted with 4 mL of hexane, followed by elution of the PBDEs with 10 mL of hexane/DCM (3:1 v/v). The PBDE fraction was then concentrated to dryness under a stream of nitrogen gas, and redissolved in 100 µL of isooctane containing <sup>13</sup>C-BDE-139 as an injection internal standard (IIS). All extracts were analyzed by gas chromatography (GC)/mass spectrometry (MS) and GC with electron capture detector (ECD). A total of 36 mono- to hepta-BDEs (1, 2, 3, 7, 8, 10, 11, 12/13, 15, 17/25, 30, 32, 33/28, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 116, 118, 119, 126, 138, 153, 154, 155, 166, 181, 183, 190) were analyzed using a Thermo Scientific Trace GC Ultra, Ion Trap ITQ 1100 MS with 1100 AS Triplus Autoinjector GC/MS system in the selected reaction monitoring mode. The GC was equipped with an Agilent Technologies HP-5MS capillary column (30 m x 0.25 mm i.d. x 0.25 µm film thickness). A total of 10 hepta- to deca-BDEs (179, 188, 196, 197, 202, 203, 206, 207, 208, 209) were quantified using an Agilent Technologies 7890A GC System and 7683 Series Injector with µECD system. The GC was equipped with a shorter J&W Scientific DB-5 fused silica capillary column (15 m x 0.25 mm i.d. x 0.25 µm film thickness). Details of the instrumental conditions are found in Annex Tables 2.2a-2.2b.

The PBDEs in the river sediments were analyzed using 1-2 g dry wt. samples and the same procedure as for the adsorbed PBDEs.

### **2.2.3. Quality assurance and quality control protocols**

A method blank (i.e., a sample that contains all the solvents except the actual sample (leachate) and processed together with the real samples) was included in every batch of 5-7 samples analyzed. The concentrations of the PBDEs in the blank sample defined the limit of detection (LOD), taken as three times the concentration observed in the blank. Concentrations below the LOD were reported as <LOD. The analytical results for each PBDE homologue series analyzed by GC/MS were corrected using the recovery of the corresponding <sup>13</sup>C-labeled homologue PBDE surrogate standard. The PBDE congeners analyzed in the GC-ECD were corrected based on the recovery of f-BDE-208.

The accuracy and precision of the analytical procedures for the adsorbed and dissolved PBDEs in the leachates were also evaluated based on the % recoveries and % relative standard deviation (RSD) of the native PBDEs (tri- to deca-BDEs 28, 47, 99, 154, 153, 183, 188, 179, 202, 197, 203, 196, 208, 207, 206, 209) spiked into the sediment and leachate extracts. The mean % recoveries and % RSD of the native PBDEs ranged from 85-124% and 2-15%, respectively, in the adsorbed fractions (n = 4) (Table 2.3); and 69-123% and 0-12%, respectively, in the dissolved fractions (n = 2) (Annex Table 2.3).

In order to analyze compounds with diverse polarities, methanol was used to elute the organic compounds from the C<sub>18</sub> cartridge. However, due to the hydrophobic nature of the PBDEs and the polarity of methanol, the latter's efficiency as an eluting solvent was verified in combination with DCM using leachate sample PMP10-1. PBDEs sequestered by the C<sub>18</sub> cartridge were eluted successively with 20 mL of methanol followed by 20 mL of DCM, and analyzed using the procedure described in Section 2.2.2. Most of the dissolved PBDEs were found in the methanol fraction (66-100% of the total dissolved PBDEs; Annex Table 2.3). Therefore, methanol can be an effective solvent in the elution of dissolved PBDEs trapped by the C<sub>18</sub> cartridge.

Since the surrogates were spiked into the extracts after accelerated solvent extraction (ASE) of the samples, we examined the efficiency of the method used in the analysis of the PBDEs through analysis of a standard reference material (NIST SRM 1941b). As indicated in Table 2.3, the results obtained for the SRM showed good agreement with the mean values of the interlaboratory comparison exercise (Stapleton et al. 2007), indicating sufficient extraction of the PBDEs from the solid particles in the leachate samples using our analytical method.

In addition, debromination of the PBDEs was examined throughout the analytical procedure. An analytical standard of BDE-209 was subjected to the full analytical procedure, including ASE. Nona- and octa-BDEs were not generated, indicating that debromination of BDE-209 to lower brominated congeners did not occur during the analytical procedure.

#### **2.2.4. Statistical analysis**

The computer software SPSS 14.0J was used for statistical analysis. The leachate samples were classified through cluster analysis of the PBDE profiles (ratio of individual BDE congener concentration to total PBDE concentration) by the Ward method with squared Euclidean distance.

### **2.3. Results and discussion**

This study analyzed 46 PBDE congeners in 24 leachate samples collected from the MSWDS of selected tropical Asian countries. Because PBDEs were expected to be predominantly present in the adsorbed phase due to their hydrophobic nature, the study focused on this phase. To examine their partitioning, however, PBDEs in the dissolved phase were also analyzed in 16 samples with different concentrations of suspended solids (Table 2.2). The adsorbed, dissolved and total concentrations of the PBDE congeners in the leachate samples are summarized in Tables 2.4a, 2.4b and 2.4c, respectively. The total concentrations of the 46 congeners in the leachates (adsorbed + dissolved phases) ranged from 3.7 ng/L (PMS02-1) to 133,000 ng/L (TB-2).

### **2.3.1. Phase distribution of PBDEs in the leachates**

Adsorbed PBDEs were more abundant than dissolved PBDEs in many samples (Fig. 2.1), which is reasonable due to the hydrophobic nature of the PBDEs and the high concentrations of SS in the leachates (ranging from 62 to 61,600 mg/L, and more than 100 mg/L in most of the samples (Table 2.2)). However, a considerable proportion of PBDEs was also found in the dissolved phase of some leachate samples, particularly those from Lao PDR, Philippines PMP02-1 and Malaysia (where the concentrations of SS were relatively lower at 62-380 mg/L).

The apparent organic carbon-normalized partition coefficients,  $K'_{oc}$ , of the PBDEs were calculated to investigate further the partitioning of PBDEs in the leachate samples. The  $K'_{oc}$  values range from  $10^3$  to  $10^4$ , and did not show significant correlation to the degree of bromination. These values were 2 to 4 orders of magnitude lower than the published  $K_{ow}$  and the  $K_{oc}$  predicted according to Seth et al. (1999) (Fig. 2.2, Annex Table 2.4). The substantial proportion of PBDE congeners in the dissolved phase would account for these results, and suggests the contribution of DOM (such as humic matter) in the dissolution of PBDEs in the aqueous phase. Although DOC was not measured in all the samples, higher concentrations of DOC (596-964 mg/L) as compared to POC (29-55 mg/L) were confirmed in the leachate samples from Philippines PMP11-1 to 11-3 (Table 2.2). Dissolution of PBDEs by DOM may facilitate the dispersion or transport of such highly hydrophobic compounds to the aquatic and terrestrial environments. More studies are needed to verify the association of PBDEs with DOM.

### **2.3.2. Possible indicators of debromination**

#### **2.3.2.1. Congener profiles of PBDEs**

The congener profiles were highly variable among the MSWDS (Annex Figs. 2.2a-2.2g), and even among samples taken from the same sites. For example, two sample pairs taken from different locations in the same sites, showed BDE-47 and BDE-99 predominant in one leachate (CP-1, PMP-02-1), and BDE-209 predominant in the other (CP-2, PMP-02-2), as shown in Annex Figs. 2.2b, 2.2e. This variability may be due to the heterogeneous nature of the waste, and the original composition of the flame retardants used.



To quantitatively group the PBDE congener profiles in the leachate samples, cluster analysis was applied to the relative compositions of the PBDEs, and this resulted in two major groups (Fig. 2.3). Cluster 1 includes samples with a predominance of BDE-99 and BDE-47, followed by BDEs 209, 206, 203, 183, 153, 196, 208, 207, 154 and 49. Cluster 2 includes samples with a predominance of BDE-209. These predominant congeners are components of the technical penta-, octa- and deca-BDE mixtures (Alaee et al., 2003; La Guardia et al., 2006).

The congener profiles of the samples in Cluster 1 could be attributed to the major contribution of the technical penta-BDE mixture (BDEs 99, 47, 100, 153, 154, 85, 49, 66, 155, 183, 28, 17), and some contribution of the technical deca-BDE (BDEs 209, 206, 207, 208, 196, 203, 197) and the technical octa-BDE mixture (BDEs 183, 197, 196, 203, 206, 207, 208, 209, 153, 154, 190). Cluster 2 may reflect the composition of PBDEs typically used in Asia (i.e., the predominance of the technical deca-BDE mixture with minor contributions of the technical penta- and octa-BDE mixtures (de Wit, 2002; Hites, 2004).

Some congeners which are not contained in the technical mixtures (e.g., BDEs 202, 179, 188, 37, 32, 15, 12/13, 8, 7, 3, 2, 1) were substantially detected in some of the leachate samples. Similarly, congeners present only in trace proportions in the technical mixtures (e.g., BDEs 208, 207, 206, 49, 28, 17) appeared to be proportionately more abundant in the leachates than in the technical mixtures (Fig. 2.4). These results would suggest the occurrence of debromination in the leachates. Microbial debromination of BDE-209 to BDEs 207, 208 and possibly BDE-202 has been reported under laboratory-controlled anaerobic conditions (Gerecke et al., 2005); and to BDEs 206, 207, 208 in anaerobic sediment microcosms, where BDEs 206, 207 were further degraded to BDEs 196, 197, 191, 184, 154, 128, 119, 99, 66, 47, 49, 28, 17 (Tokarz et al., 2008). Debromination of BDE-99 to BDE-66 and BDE-28, and of BDE-47 to BDE-17 have also been reported (Tokarz et al., 2008). Anaerobic conditions in the MSWDS may have facilitated the debromination. During microbial decay of organic matter in anoxic underground environments (e.g., in MSWDS), microorganism can utilize carbon including those in halogenated organic compounds as alternate electron acceptors during the formation of methane. As electron acceptors, the halogenated organic compounds (e.g., PBDEs) will undergo reductive dehalogenation under anaerobic conditions (Sims

et al., 1991). Moreover, halogenated organic compounds such as PBDEs are relatively oxidized due to the presence of halogen substituents, which are highly electronegative; thus, they will be more susceptible to reduction (Sims et al., 1991; He et al., 2006). The pH values of most of the leachate samples (n = 16; Table 2.2) were within the range of 7.5 – 9.0 for landfills in the methanogenic phase (Ehrig, 1989), suggesting anaerobic conditions in most of the MSWDS included in this study.

The occurrence of BDE-202 in the leachates may also indicate photolytic debromination in the MSWDS in tropical Asian countries, due to the high and prolonged levels of solar radiation. Debromination of deca-BDE under sunlight in sediments was estimated to take 96 hours, compared to 238 days in sewage sludge under dark conditions (Guzzela et al., 2008). BDE-202 was proposed as a debromination marker (Gerecke et al., 2005; Tokarz et al., 2008) through photolysis of BDE-209 (Christiansson et al., 2009).

The suspected debromination products in the leachates (BDEs 208, 202, 179, 49, 32, 17, 12/13, 8, 7, 3, 2, 1) exhibited the absence of bromine at the para position. However, debromination at the meta (BDE-207), ortho (BDE-206), and both meta and ortho positions (BDEs 153, 154, 37, 28, 15) also occurred. The linear correlation between BDE-208/209 and BDE-207/209 (Fig. 2.5a) indicated concurrence of debromination of BDE-209 at the para and meta positions in the leachates, except in the case of leachate IK-1 where the para position was preferred. Robrock et al. (2008) observed debromination pathways with preferential removal of para and meta bromines. Probable debromination of BDE-209 at the ortho position (BDE-206) also occurred in the same proportion as the para (BDE-208/209) and meta positions (BDE-207/209) (Figs. 2.5b, 2.5c). However, the ortho position was preferred in leachates CP-1, VH-1, IK-1, resulting in varied concentrations of BDE-206 in the samples. Debromination to BDE-206 has also been reported in anaerobic sediment (Tokarz et al., 2008). However, most of the debromination reported in other environmental settings is position-selective (e.g., meta position in some species of freshwater fish (Roberts et al., 2011; Stapleton et al., 2006), and meta and para positions in sewage sludge (Gerecke et al., 2005)). Non-position-selective debromination may be a characteristic of dumping sites possibly due to the highly anaerobic conditions in the MSWDS (especially in tropical Asian countries where degradable organic waste are commonly mixed with plastic waste that may contain PBDEs). In addition,

microbial specificity (e.g., the dehalogenating bacteria *Dehalococcoides* species, *Dehalobacter restrictus* and *Desulfotobacterium hafniense* preferred removal at the meta and para positions; Robrock et al., 2008) has been suggested in the anaerobic debromination of PBDEs (He et al., 2006; Robrock et al., 2008; Tokarz et al., 2008). Further studies are needed to examine the presence of microorganisms that may be indigenous in the MSWDS of tropical Asian countries, and which may facilitate the debromination of deca-BDE regardless of the position of the bromine atom. Debromination at all positions would facilitate the cascade of BDE-209 to lower brominated and more biologically active congeners.

It is possible that debromination may occur in consumer products long before their disposal in MSWDS (e.g., during manufacture, usage and e-waste treatment, through photolysis by UV light (de Wit, 2002; Fang et al., 2008) and/or natural sunlight (Kajiwara et al., 2008; Stapleton and Dodder, 2008)). However, given the anaerobic conditions of the underground environment and the intense sunlight typical of tropical Asia, it appears likely that the most significant debromination occurs in the MSWDS. More studies are needed to quantify both the anaerobic and photolytic debromination of PBDEs in these sites.

#### **2.3.2.2. Temporal trend of PBDEs in the MSWDS**

The temporal trend of PBDEs indicated the reduction of BDE-209 over time, with a corresponding increase in the concentrations and/or emergence of the lower brominated PBDE congeners. This phenomenon was observed in the two MSWDS from the Philippines (Smokey Mountain, (PMS) and Payatas (PMP)) (Fig. 2.6). Leachate samples were collected from both MSWDS in 2002 (PMS02-1, PMP02-1,-2), and again in 2009 and 2010 (PMS09-1,-2 and PMP10-1,-2, respectively). Over the intervening period of 7 to 8 years there was a reduction in the concentrations of BDE-209 in both dumping sites, while the concentrations of BDE-202 increased substantially, from as low as non-detectable (ND) concentrations to as high as 72 pg/L in the PMS leachate and 7,700 pg/L in the PMP leachate (based on the data in the adsorbed phase; Table 2.4a). The results may indicate debromination of BDE-209 in the MSWDS. The low PBDE

concentrations in PMS (the lowest among all the sites examined) could possibly be associated with the site's closure in 1993, and the leaching out of the PBDEs over the intervening time.

### **2.3.3. Variability in PBDE concentrations among countries and MSWDS**

High concentrations of adsorbed PBDEs from tetra- to deca-BDE congeners were found in the leachate samples from Thailand, India, the Philippines, Malaysia and Indonesia (Table 2.4a, Fig. 2.7), which are more industrialized (Bożyk, 2006) and/or more populated (UNDESA, 2010) than the other Asian countries studied. Extremely high concentrations from mono- to deca-BDE congeners were obtained in Thailand, TB-2 (Table 2.4a). However, Cambodia and Vietnam, which are relatively less industrialized than the other five countries, also had high concentrations of PBDEs in the leachates (Fig. 2.7, Table 2.4a), almost comparable to those of India, Indonesia, the Philippines and Malaysia. The elevated PBDE concentrations in Vietnam may be correlated to its population (UNDESA, 2010), while those of Cambodia may be associated with the importation of e-waste. Among the tropical Asian countries investigated, Lao PDR had relatively lower PBDE concentrations in the leachates.

The cluster analysis (Fig. 2.3) also differentiated the tropical Asian countries according to the predominance of PBDE congeners in the leachates. India, Indonesia and Malaysia (Annex Figs. 2.2c, 2.2g) belong to Cluster 1, with a predominance of BDE-99 and BDE-47, indicating a greater influence of the technical penta-BDE products, or possibly the occurrence of debromination. Lao PDR, Vietnam and Thailand (Annex Figs. 2.2a, 2.2b, 2.2d) belong to Cluster 2, indicating a greater influence of the technical deca-BDE products. Cambodia and the Philippines (Annex Figs. 2.2b, 2.2e) exhibited variability in the PBDE congeners (some leachates under Cluster 1, others under Cluster 2). However, there is no available data on the direct importation of technical PBDE products by these Asian countries to corroborate with the PBDE profiles observed in their MSWDS. Some countries such as India, Malaysia, Thailand (APIC, 2012), and the Philippines have petrochemical industries which could possibly utilize technical PBDE products in the manufacture of polymers (OECD, 1994; BSEF, 2012). Among the tropical Asian countries studied, India is a producer of the technical deca-BDE product (<http://www.solarischemtech.com>). However, the

predominant congeners in the leachate sample were BDE-99 and BDE-47, which may be contributed by imported consumer products containing these penta-BDE congeners. In addition to the heterogeneity of the waste and the different composition of the flame retardants in consumer products, the occurrence of debromination may contribute to the variability of the PBDE congeners in the MSWDS.

#### **2.3.4. Tropical Asian MSWDS as potential sources of PBDEs in aquatic environments**

Table 2.5 shows a comparison of the PBDE congener concentrations recorded in this study with those found in the leachate samples from various locations around the world. The concentrations (in ng/L) of BDEs 33/28, 75, 47, 66, 85, 206, 207 and 209 in Thailand TB-2 were higher than those reported in Japan (Osako et al., 2004), South Africa (Odusanya et al., 2009; Daso, 2012), Canada (Danon-Schaffer, 2010) and the U.S. (Oliaei, 2002); and the difference for BDE-209 ranged from one to five orders of magnitude. Similarly, the concentrations of hexa-, hepta-, octa- and nona-BDEs, and BDE-209 in Thailand TB-2 were higher than those reported in Sweden (Öman and Junestedt, 2008). The upper range (UR) concentrations (in ng/L) of BDEs 47, 99, 153, 154 in the leachates from Cambodia, India (except BDEs 153, 154), the Philippines and Malaysia were higher than those in the leachates from Japan (Osako et al., 2004), South Africa (Odusanya et al., 2009) and northern Canada (Danon-Schaffer, 2010). The UR hexa- and hepta-BDE concentrations in the leachates from Cambodia, India (hepta only), the Philippines and Malaysia were higher than those in Sweden (Öman and Junestedt, 2008).

The concentrations (in ng/g dry weight) of PBDEs in the adsorbed phase of the leachate samples followed almost the same trend as the total PBDE (volume-based) concentrations (Annex Table 2.5). The BDE concentrations (specifically BDEs 47, 99, 100 and 154 in the Philippines and Malaysia; BDEs 206 and 209 in the Philippines; and BDE-206 in India) were higher than those in the landfill soil in Canada (Danon-Schaffer, 2010). The tetra- and hexa-BDEs in Cambodia, Thailand, the Philippines and Malaysia were also higher than those in the sediment of raw leachates from Sweden (Öman and Junestedt, 2008). In general, the concentrations of PBDEs in the leachates from the MSWDS in most of the tropical Asian countries included in this study were higher than

those reported in other countries. In particular, Thailand, Cambodia, India, the Philippines and Malaysia may be hotspots of PBDE contamination. The relatively higher population growth rates, rapid urbanization and greater prospects for industrialization in these tropical Asian countries will likely result in higher waste generation and leachate production in MSWDS that are often inadequate (i.e., mostly without leachate management system; Ngoc and Schnitzer, 2009); and this will result in increased transport of PBDEs to the environment.

Finally, the weight-based concentrations of some PBDE congeners in the leachates from Payatas, in the Philippines, were one to three orders of magnitude higher than the corresponding concentrations in the river sediments (Pasig River, where all samples were taken downstream from Payatas; Fig. 2.8). The results suggest that leachates from MSWDS may be potential sources of PBDEs, especially lower brominated congeners, in the aquatic environment.

## **2.4. Conclusion**

The results of the present study increased our knowledge on the fate of PBDEs in MSWDS, and the possible mechanisms for their environmental transport. While it is possible that deca-BDE in consumer products may be debrominated long before disposal in the MSWDS, some indicators considered in this study (e.g., methanogenic phase activity, anaerobic conditions, or the temporal reduction of BDE-209) would appear to support the hypothesis that debromination occurs in the MSWDS of tropical Asian countries. Environmental and socio-economic conditions that are characteristics of tropical Asian countries, such as the prevalent high ambient temperature, the accumulation of large volumes of degradable organic waste due to high population growth rates and the non-segregation of solid wastes, may induce debromination of deca-BDE in the MSWDS of tropical Asian countries. Moreover, the occurrence of PBDEs in the dissolved phase, possibly associated with the presence of DOM, may facilitate the transport of PBDEs from the dumping sites to the aquatic and terrestrial environments. The dumping sites of tropical Asian countries may thus be potential sources of PBDEs in the aquatic environment, and their possible role as amplifiers of the toxicity of PBDEs should not be ignored.

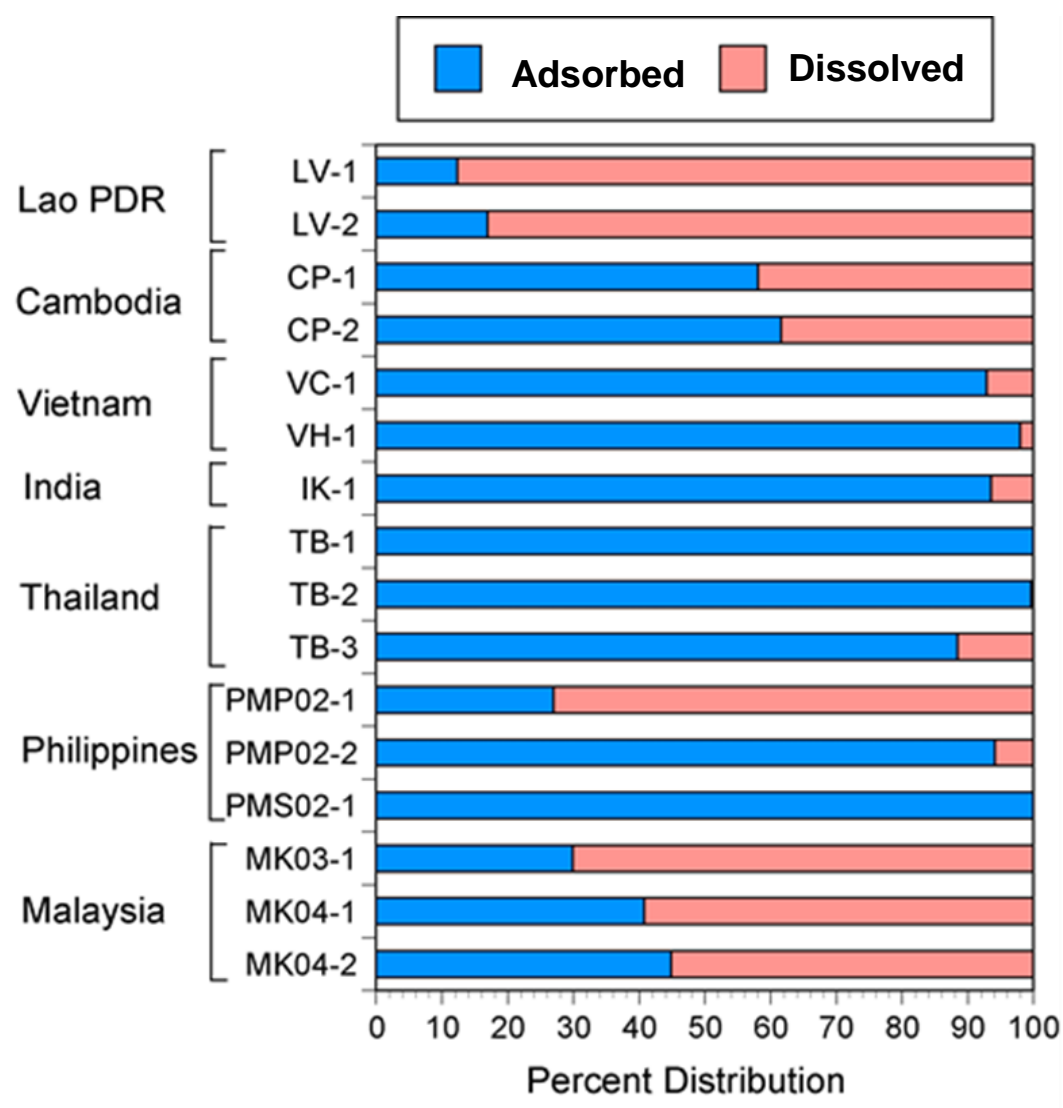


Fig. 2.1. Distribution of PBDEs in the adsorbed and dissolved phases of the leachate samples from tropical Asian countries.

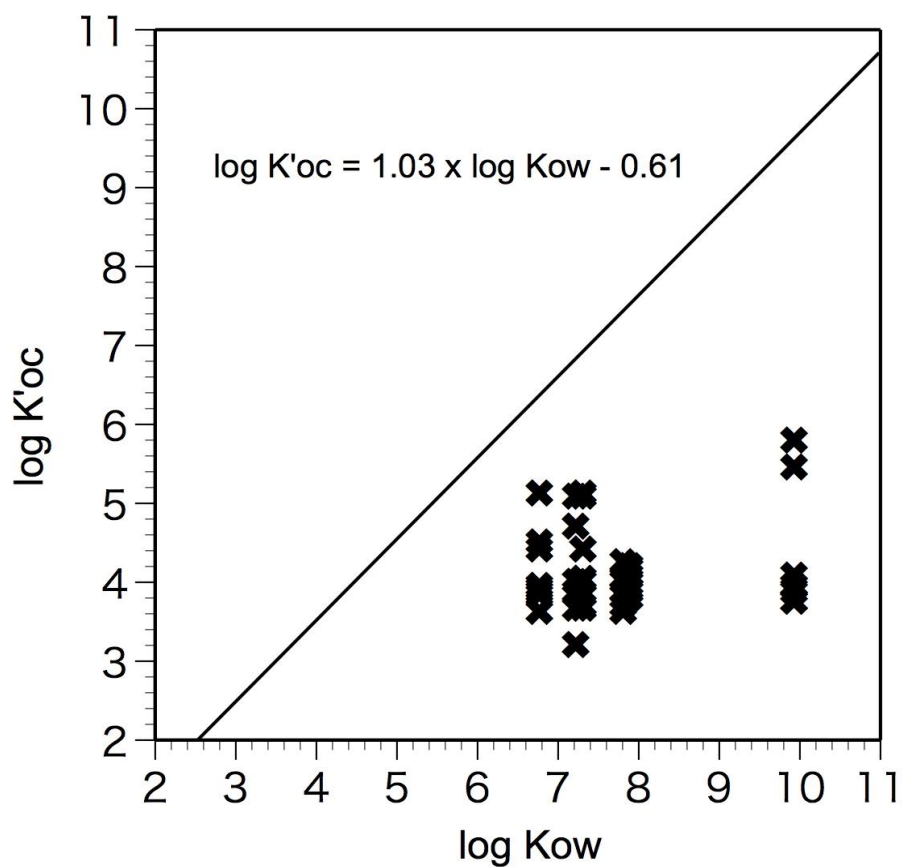


Fig. 2.2. Apparent organic-carbon normalized partition coefficients ( $K'_{oc}$ ) of PBDE congeners in the landfill leachates from tropical Asian countries compared to the corresponding octanol-water partition coefficients ( $K_{ow}$ ). Solid line relationship is based on equilibrium partitioning (Ref.: Seth et al., 1999).



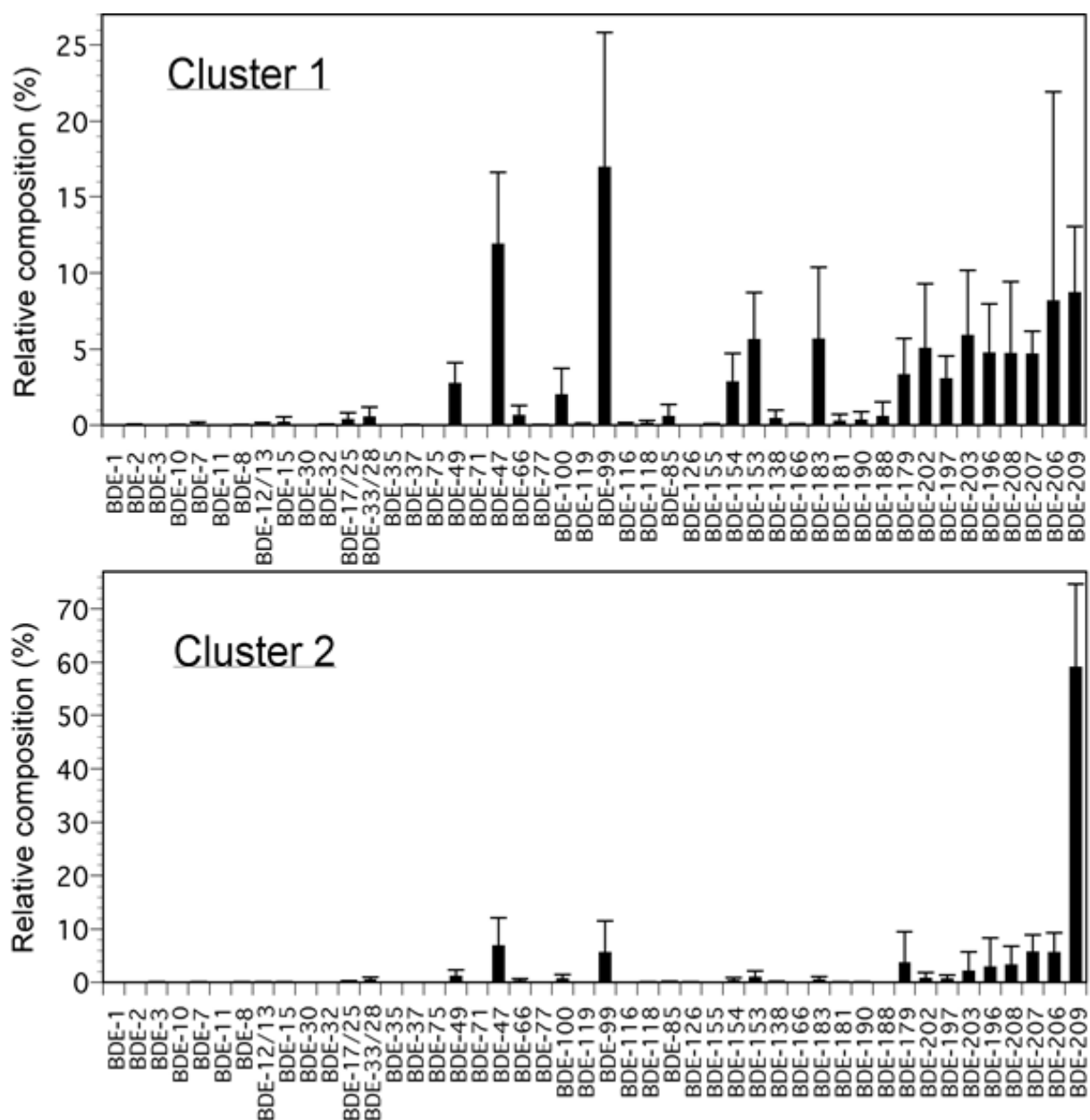


Fig. 2.3. Average congener profiles of the PBDEs in the adsorbed phase of landfill leachates, by clusters. Cluster 1 is consist of CP-1, IK-1, IJ-1, IJ-2, IJ-3, PMP02-1, PMP10-1, PMP10-2, MK03-1, MK04-1 and MK04-2; Cluster 2 is consist of LV-1, LV-2, LV-3, CP-2, VC-1, VH-1, TB-1, TB-2, TB-3, PMP02-2, PMS02-1 and PMS09-2. Error bar represents the standard deviation.

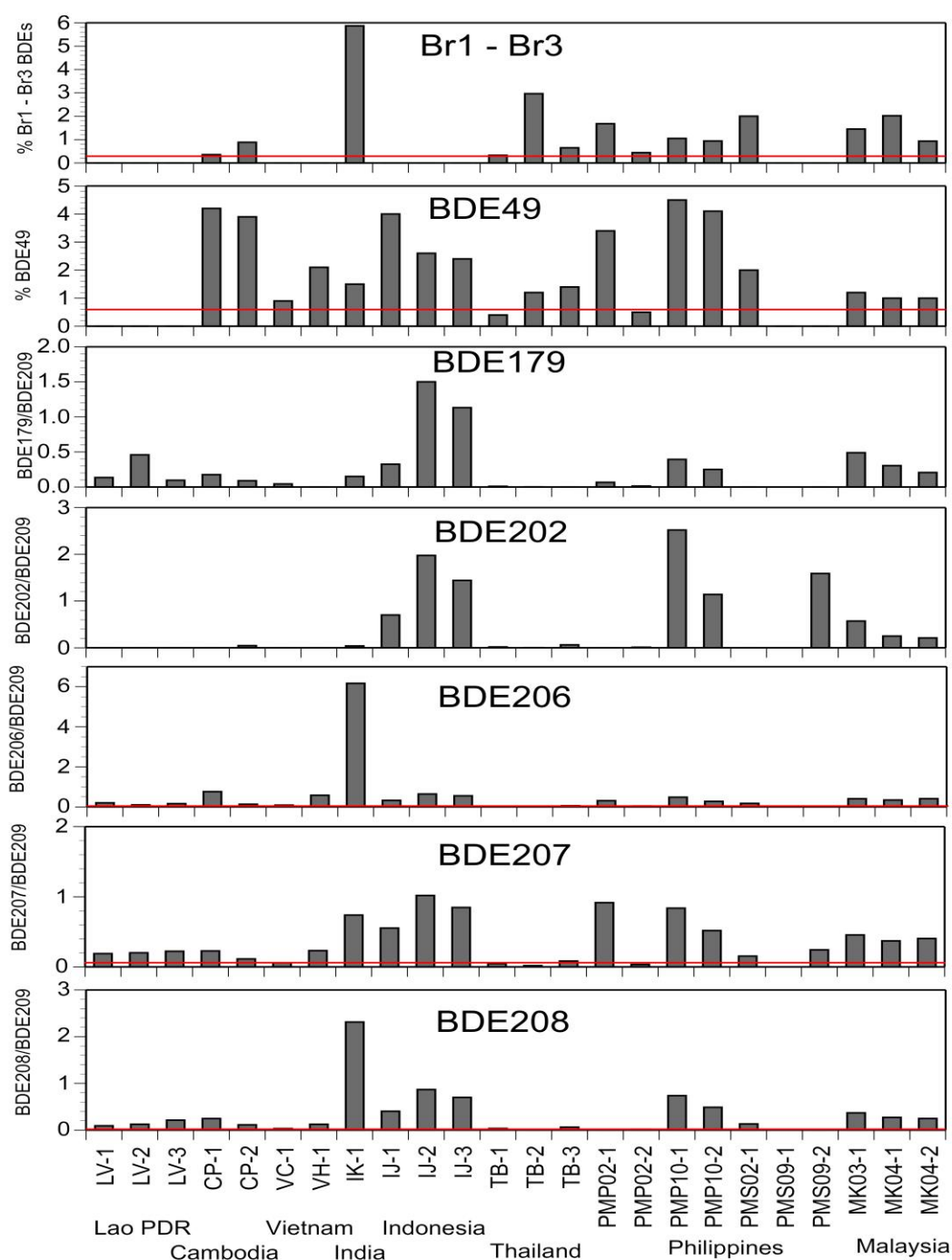


Fig. 2.4. Relative abundance of the non- or trace technical mixture component congeners in the adsorbed phase of landfill leachate samples from tropical Asian countries. Non-technical mixture component congeners: BDEs 179, 202; trace technical mixture component congeners: Br1-Br3 congeners, BDEs 49, 206, 207, 208. Red lines indicate the relative abundance of the congeners in the technical mixtures as reported by La Guardia et al. (2006). For BDEs 206, 207 and 208, their respective abundance in the technical deca-BDE mixture is indicated.

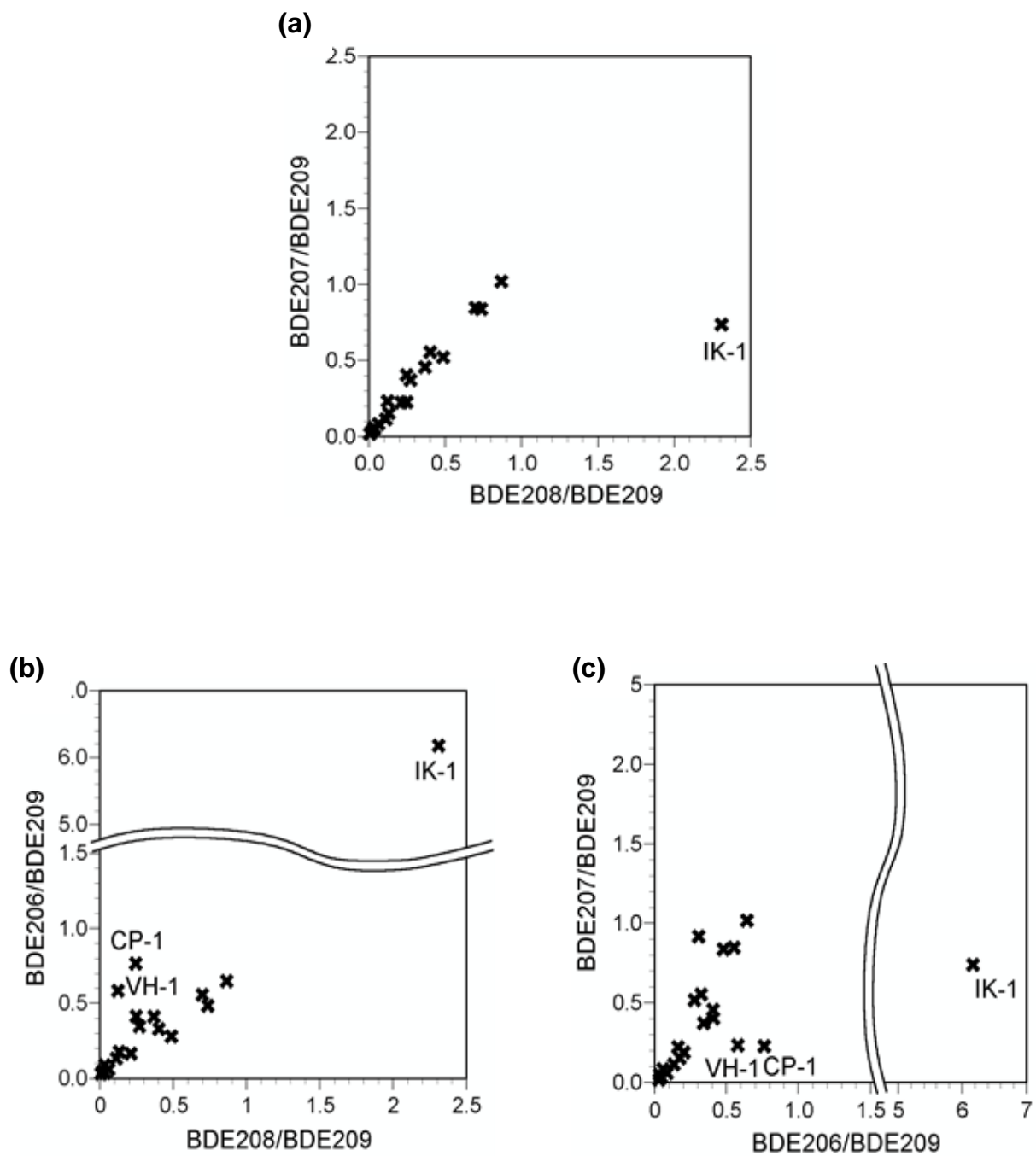


Fig. 2.5. (a) BDE208/BDE209 and BDE207/BDE209 ratios, (b) BDE208/BDE209 and BDE206/BDE209 ratios, and (c) BDE206/BDE209 and BDE207/BDE209 ratios in the landfill leachate samples from tropical Asian countries.

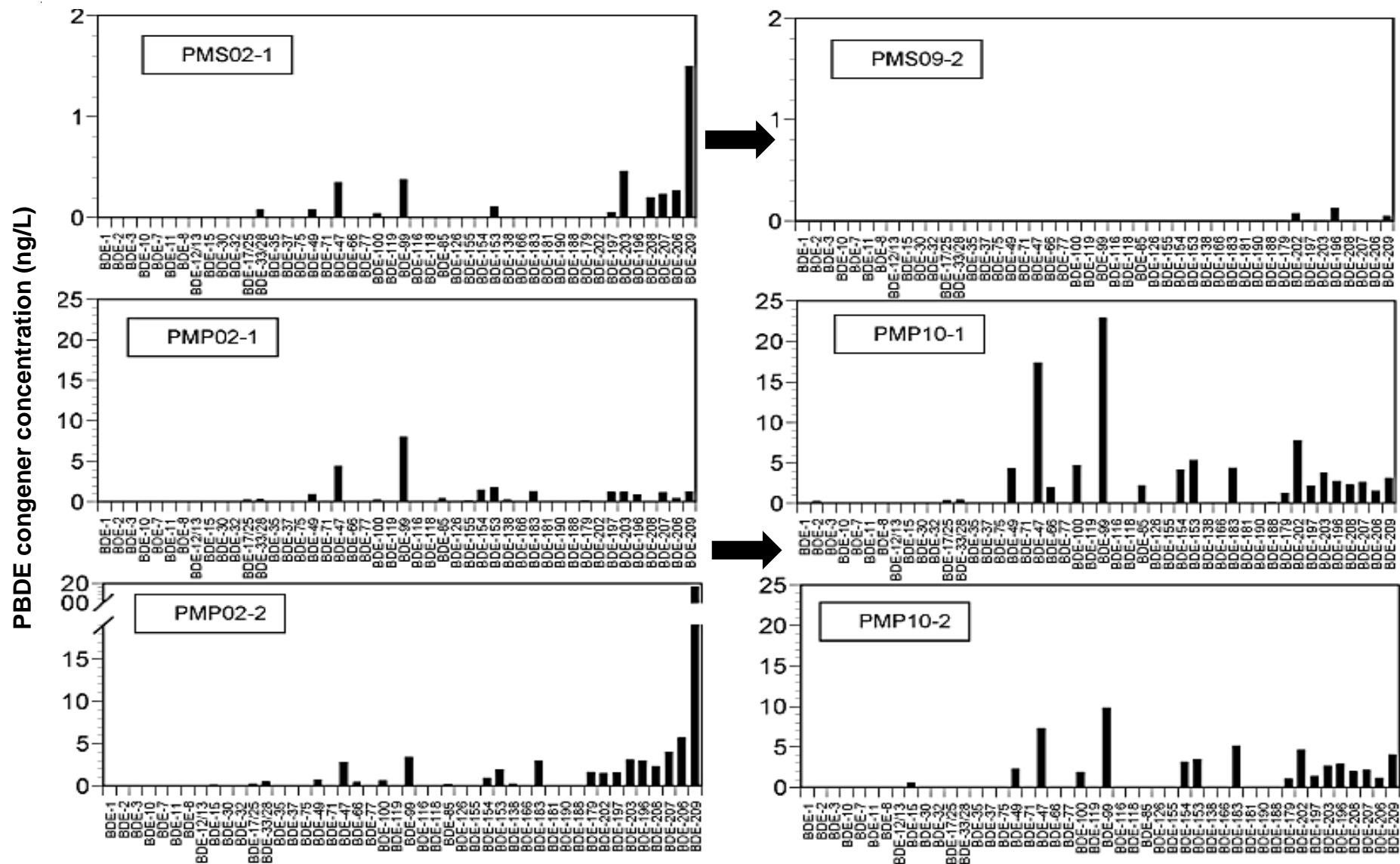


Fig. 2.6. Concentrations of PBDE congeners in the leachates from MSWDS in Manila, Philippines: Smokey Mt. in 2002 and 2009, and Payatas in 2002 and 2010.

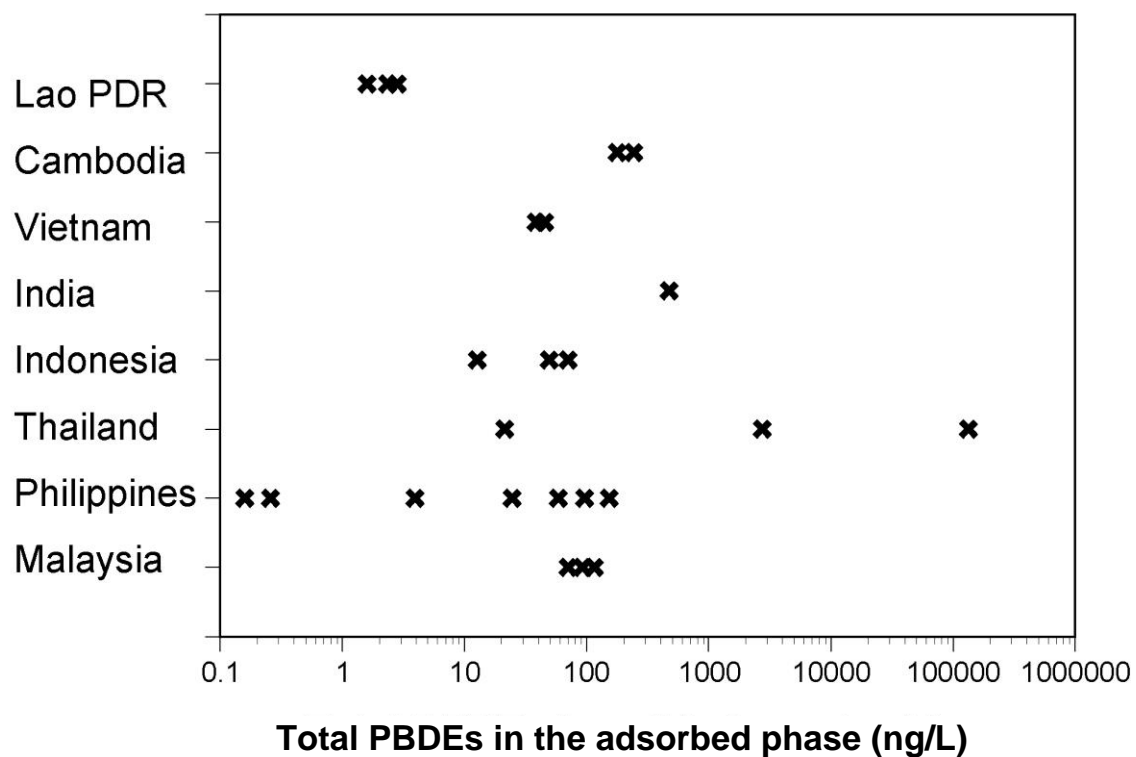


Fig. 2.7. Concentrations of total PBDEs in the adsorbed phase of landfill leachate samples from tropical Asian countries.

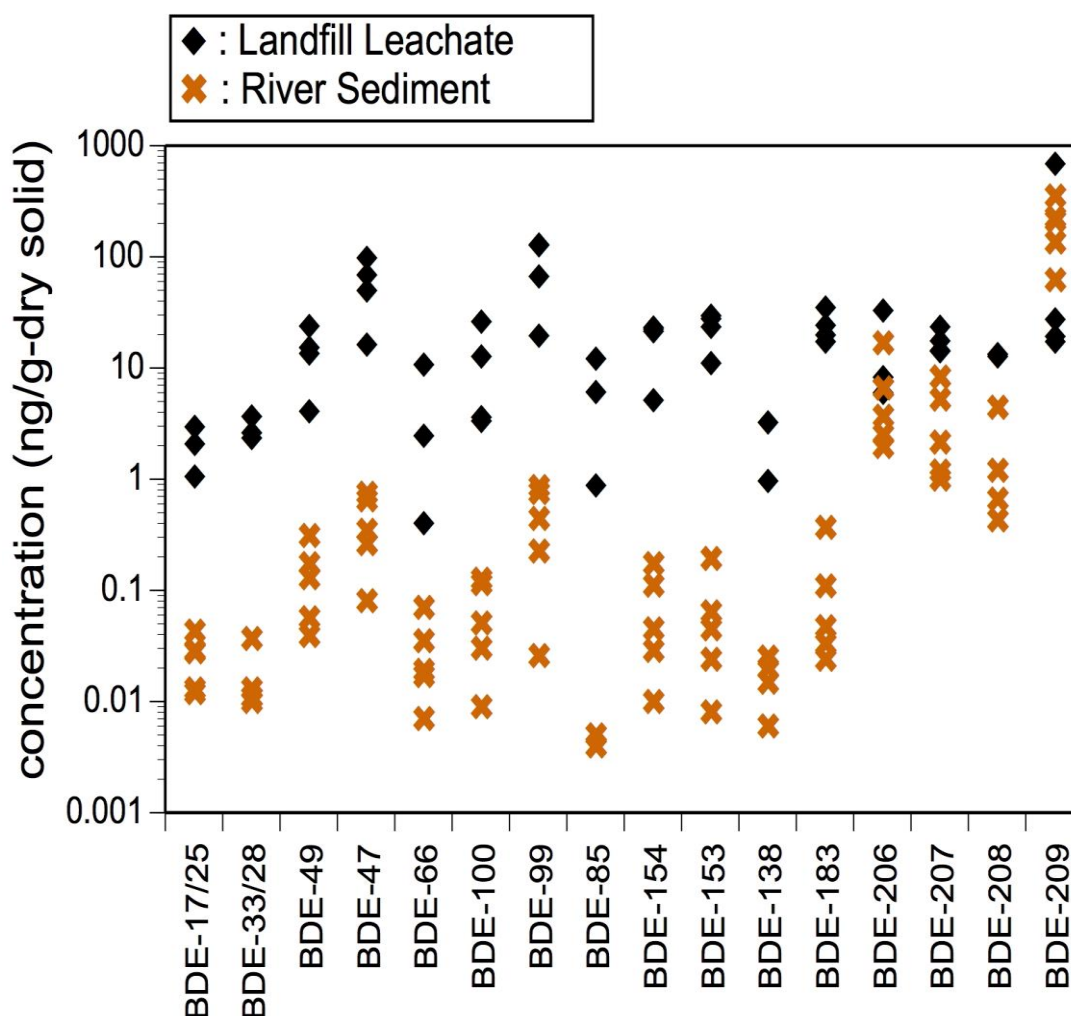


Fig. 2.8. Concentrations of PBDE congeners in the adsorbed phase of landfill leachates, and in downstream river sediments in Manila, Philippines. Leachate samples from an operational MSWDS: PMP02-1, PMP02-2, PMP09-1, PMP09-2. Sediment samples from the Pasig River: PR2, 3, 7, 8, 12 (information on sampling locations is available in Annex Table 2.1).

Table 2.1 Information on the selected MSWDS of tropical Asian countries and sampling conditions.

Country	City	Name of Dumping Site	Area	Start of Operation	Status <sup>a</sup>	Estimated Volume of Waste	Coordinates (deg. min. sec., deg. min. sec.)	Date of Sampling		No. of Samples	Sample Code	Type of Sampling
			(x 10 <sup>4</sup> m <sup>2</sup> )			(tons/day)		Dry Season	Wet Season	n		
Lao PDR	Vientiane	Km. 18 Xaythang District	60	1988	Operational	300	N 18 4 2, E 102 43 5	2005 Dec. 17 2005 Dec. 17 2005 Dec. 17		3	LV-1 LV-2 LV-3	Pool Pool Pool
Cambodia	Phnom Penh	Stung Mean Chey	12	1965	Operational	670	N 11 32 07, E 104 53 42		2004 Sep. 11 2004 Sep. 11	2	CP-1 CP-2	Stream Stream
Vietnam	Can Tho	Dong Thanh	5	1968	Operational	400	N 09 59 6, E 105 44 54		2004 May 18	1	VC-1	Stream
	Hanoi	Tay Mo	6	1997	Closed in 1999	750	N 21 01 09, E 105 45 1	2003 Dec. 22		1	VH-1	Stream
India	Kolkata	Dhapa	22	1981	Operational	3,500	N 22 32 38, E 88 25 17	2006 May 30		1	IK-1	Stream
Indonesia	Jakarta	Bantar Gebang	110	1989	Operational	6,000	N 06 20 59, E 106 59 45	2010 Sep. 30 2010 Sep. 30 2010 Sep. 30		3	IJ-1 IJ-2 IJ-3	Stream Stream Stream
Thailand	Bangkok	Kukot	6	1993	Closed in 2000	300	N 13 56 34, E 100 39 26		2003 May 20 2003 May 20 2003 May 20	3	TB-1 TB-2 TB-3	Pumping Pumping Pumping
Philippines	Metro Manila	Payatas	22	~ 1973	Operational	2,200	N 14 42 52, E 121 06 20		2002 Sep. 17 2002 Sep. 17	2	PMP02-1 PMP02-2	Stream Stream
								2010 Dec. 10 2010 Dec. 10 2011 Nov. 25 2011 Nov. 25 2011 Nov. 25		2 3	PMP10-1 PMP10-2 PMP11-1 PMP11-2 PMP11-3	Tank Tank Tank Tank Tank
	Metro Manila	Smokey Mountain	5	1974-76	Closed in 1993	300	N 14 37 50, E 120 57 38		2002 Sep. 17	1	PMS02-1	Pool
								2009 Dec. 14 2009 Dec. 14		2	PMS09-1 PMS09-2	Drippings Drippings
Malaysia	Kuala Lumpur	Tamang Beringin	32	1997	Operational	2,000	N 03 13 37, E 101 39 56		2003 Sep. 26	1	MK03-1	Stream
								2004 Jul. 21 2004 Jul. 21		2	MK04-1 MK04-2	Stream Stream

<sup>a</sup> At the time of sampling.

Table 2.2 Sample information on the leachate samples from the selected MSWDS of tropical Asian countries.

Country	Sample Code	Electrical Conductivity	pH	Leachate Temp.	Suspended Solids	POC <sup>a</sup>	f <sub>oc</sub> <sup>b</sup>	DOC <sup>c</sup>
		(mS/cm)		(°C)	(mg/L)	(mg/L)		(mg/L)
Lao PDR	LV-1	3.85	7.42	28.9	190	NA <sup>d</sup>	NA	NA
	LV-2	7.58	7.41	27.8	190	NA	NA	NA
	LV-3	3.00	7.57	24.0	110	NA	NA	NA
Cambodia	CP-1	25.0	8.25	33.8	1,490	184	0.124	NA
	CP-2	22.8	8.14	37.1	1,650	307	0.186	NA
Vietnam	VC-1	14.3	6.34	33.3	740	NA	NA	NA
	VH-1	10.1	8.25	17.7	1,950	159	0.082	NA
India	IK-1	26.3	6.01	35.2	6,010	NA	NA	NA
Indonesia	IJ-1	14.8	8.16	39.7	270	54	0.200	NA
	IJ-2	25.1	7.86	43.8	350	151	0.430	NA
	IJ-3	22.5	7.99	41.7	590	100	0.170	NA
Thailand	TB-1	7.93	6.83	37.2	61,600	1,900	0.031	NA
	TB-2	23.1	7.94	40.2	47,200	NA	NA	NA
	TB-3	12.8	7.79	41.1	180	28	0.156	NA
Philippines	PMP02-1	6.80	7.19	NA	62	20	0.317	NA
	PMP02-2	3.46	7.18	NA	170	17	0.099	NA
	PMP10-1	21.3	7.75	33.0	170	31	0.182	NA
	PMP10-2	13.7	8.34	34.5	140	30	0.215	NA
	PMP11-1	12.5	8.13	29.1	132	29	0.219	596
	PMP11-2	21.1	7.62	31.9	208	34	0.164	883
	PMP11-3	21.7	7.97	31.7	402	55	0.137	964
	PMS02-1	4.51	7.18	NA	78	15	0.187	NA
	PMS09-1	8.72	7.73	35.6	32	NA	NA	NA
	PMS09-2	7.70	8.16	31.2	48	NA	NA	NA
Malaysia	MK03-1	14.9	8.44	36.3	250	64	0.257	NA
	MK04-1	10.3	8.49	28.4	180	60	0.335	NA
	MK04-2	15.3	8.40	31.1	380	89	0.235	NA

<sup>a</sup>Particulate organic carbon. <sup>b</sup>fraction organic carbon. <sup>c</sup>Dissolved organic carbon. <sup>d</sup>Not Analyzed (samples were used up in the analysis of other compounds).



Table 2.3 Validation of the analytical method for extraction of adsorbed PBDEs in the leachate samples: recovery and reproducibility, and analysis of the standard reference material NIST SRM 1941b (Marine Sediment).

PBDEs	Recovery and reproducibility of the analytical method <sup>a</sup> (n=4)		Interlaboratory comparison of marine sediment NIST SRM 1941b <sup>b</sup>				This study			
	Mean % recovery	% RSD	Geometric mean	Exercise std. dev.	Range (mean $\pm$ std. dev.)		Mean conc. (n=3) (ng/g dry wt.)	Std. dev.	% RSD	% to geometric mean of the interlaboratory comparison
					Lower range	Upper range				
BDE-33/28	91 (BDE-28)	8	0.18	0.07	0.11	0.25	0.130	0.007	5.0	72
BDE-49			0.23	0.06	0.17	0.29	0.25	0.02	8.4	109
BDE-47	93	7	1.48	0.51	0.97	1.99	1.4	0.1	7.4	98
BDE-66			0.06	0.02	0.04	0.08	0.040	0.002	6.0	67
BDE-100			0.15	0.06	0.09	0.21	0.12	0.02	15	81
BDE-99	86	3	0.62	0.19	0.43	0.81	0.43	0.04	8.8	70
BDE-154	85	4	0.09	0.02	0.07	0.11	0.07	0.02	27	81
BDE-153	85	2	0.09	0.04	0.05	0.13	0.039	0.002	6.4	43
BDE-183	86	4	0.05	0.02	0.03	0.07	0.04	0.02	49	85
BDE-188	99	12								
BDE-179	87	13								
BDE-202	87	12								
BDE-208	107	15								
BDE-207	124	13								
BDE-209	93	10	24.1	14.1	10.0	38.2	17.4	0.09	0.50	72

<sup>a</sup>As described in Section 2.2.2: 1.5 g sediment spiked with 6, 250 pg of native mono- to hepta-BDE congeners, 10 pg of native octa- to nona-BDE congeners and 75,000 pg of native BDE-209. <sup>b</sup>Results of the interlaboratory comparison as summarized by Stapleton et al. (2007).

Table 2.4a Concentrations of adsorbed PBDEs in the leachate samples from tropical Asian countries.

PBDEs		Concentration (pg/L)													LOD (pg)				
		Lao PDR			Cambodia		Vietnam		India	Indonesia			Thailand			Batch No.			
		LV-1	LV-2	LV-3	CP-1	CP-2	VC-1	VH-1	IK-1	IJ-1	IJ-2	IJ-3	TB-1	TB-2	TB-3	2	3	4	5
Br1	BDE-1	ND <sup>a</sup>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	114,000	ND	5	300	300	700	
	BDE-2	ND	ND	ND	ND	212	ND	ND	ND	ND	ND	ND	9,520	21	7	90	200	60	
	BDE-3	ND	ND	ND	ND	ND	ND	ND	<LOD	ND	ND	ND	9,140	35,300	9	2	40	100	30
Br2	BDE-10	<LOD <sup>b</sup>	<LOD	ND	ND	ND	ND	<LOD	ND	ND	ND	ND	ND	<LOD	40	90	90	70	
	BDE-7	ND	ND	ND	ND	ND	ND	ND	2,600	ND	ND	ND	ND	332,000	<LOD	20	100	200	90
	BDE-11	ND	ND	ND	ND	ND	ND	ND	<LOD	ND	ND	ND	ND	ND	<LOD	20	400	80	90
	BDE-8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	397,000	<LOD	0.9	50	40	50	
	BDE-12/13	ND	ND	ND	ND	ND	ND	ND	2,080	ND	ND	ND	ND	331,000	<LOD	20	60	50	90
	BDE-15	ND	ND	ND	ND	ND	ND	ND	4,240	ND	<LOD	ND	ND	467,000	<LOD	20	90	60	50
Br3	BDE-30	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	<LOD	2	40	20	400	
	BDE-32	ND	ND	ND	ND	ND	ND	ND	675	ND	ND	ND	ND	62,900	7	0.7	20	20	200
	BDE-17/25	ND	ND	ND	ND	753	ND	ND	7,430	ND	ND	ND	ND	787,000	32	2	20	30	80
	BDE-33/28	ND	ND	ND	640	1,200	ND	ND	10,300	ND	ND	<LOD	ND	1,250,000	70	0.5	30	60	90
	BDE-35	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	<LOD	4	40	50	400
	BDE-37	ND	ND	ND	ND	ND	ND	ND	<LOD	ND	ND	ND	ND	157,300	<LOD	30	200	200	200
Br4	BDE-75	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	11,700	<LOD	3	10	10	70
	BDE-49	<LOD	ND	ND	7,590	9,640	390	812	6,830	468	1,270	1,690	11,300	1,530,000	290	2	20	30	200
	BDE-71	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	15	0.8	7	10	200
	BDE-47	391	151	<LOD	25,500	24,800	2,350	803	23,900	1,270	2,450	4,310	96,200	18,700,000	713	5	20	30	60
	BDE-66	ND	ND	ND	1,600	2,950	<LOD	ND	6,190	ND	ND	ND	ND	1,340,000	78	0.4	50	50	500
	BDE-77	ND	ND	ND	ND	ND	ND	ND	<LOD	ND	ND	ND	ND	ND	21	2	70	200	500
Br5	BDE-100	73	ND	ND	1,060	ND	<LOD	<LOD	457	<LOD	418	628	11,600	75,200	238	3	20	20	50
	BDE-119	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2	2	30	20	200
	BDE-99	351	<LOD	<LOD	44,300	40,700	1,570	<LOD	8,140	1,250	3,530	6,300	121,000	154,000	1,580	9	60	70	90
	BDE-116	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20	40	30	200
	BDE-118	ND	ND	ND	ND	ND	ND	ND	<LOD	ND	ND	ND	ND	248,000	<LOD	6	30	30	90
	BDE-85	ND	ND	ND	2,400	1,200	ND	ND	177	ND	ND	ND	ND	58,300	49	9	20	30	300
Br6	BDE-126	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	38	9	30	20	200
	BDE-155	ND	ND	ND	129	ND	ND	<LOD	ND	ND	ND	ND	ND	ND	13	1	20	20	200
	BDE-154	ND	ND	ND	3,890	4,100	ND	ND	<LOD	247	<LOD	1,450	12,800	74,500	231	0.9	40	20	80
	BDE-153	ND	ND	ND	14,700	8,270	ND	ND	<LOD	ND	2,360	3,470	10,800	416,000	304	2	200	30	200
	BDE-138	ND	ND	ND	393	972	ND	ND	ND	ND	<LOD	ND	ND	7,300	78	4	40	30	300
	BDE-166	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	<LOD	20	20	20	700
Br7	BDE-183	<LOD	ND	ND	2,110	3,220	<LOD	ND	<LOD	<LOD	6,740	9,350	ND	179,000	210	20	200	100	800
	BDE-181	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	82	9	30	30	1000
	BDE-190	ND	ND	ND	ND	ND	ND	ND	ND	ND	<LOD	ND	ND	ND	49	10	50	50	2000
	BDE-188	ND	ND	ND	ND	ND	ND	ND	ND	51	<LOD	176	ND	ND	ND	6	8	20	20
	BDE-179	137	356	72	5,340	8,300	1,420	ND	5,540	565	377	5,110	20,000	72,200	ND	5	2	10	20
	BDE-202	ND	ND	ND	ND	4,270	ND	ND	1,440	1,220	4,960	6,510	37,500	238,000	743	20	3	20	20
Br8	BDE-197	<LOD	<LOD	<LOD	1,680	2,410	<LOD	ND	3,150	551	2,500	3,170	35,600	266,000	472	20	20	30	20
	BDE-203	ND	ND	ND	ND	3,290	ND	ND	2,200	1,120	6,480	8,790	61,900	501,000	922	30	6	20	30
	BDE-196	<LOD	339	<LOD	ND	3,070	945	ND	5,390	1,060	5,020	5,950	61,400	503,000	802	3	20	50	30
Br9	BDE-208	<LOD	<LOD	160	7,450	10,400	1,090	1,030	84,900	702	2,180	3,150	73,400	789,000	747	30	6	30	30
	BDE-207	192	156	167	6,850	10,400	1,910	1,920	27,100	959	2,550	3,820	95,800	1,680,000	979	30	2	30	30
	BDE-206	207	<LOD	122	23,000	12,200	2,820	4,800	227,000	569	1,620	2,510	72,400	3,050,000	691	2	2	30	40
Br10	BDE-209	1,010	776	750	30,100	92,200	32,200	28,500	37,000	1,740	2,510	4,520	2,040,000	97,800,000	11,800	50	3	60	30
Batch number		4	4	4	3	3	4	4	3	5	5	5	3	3	2				
Vol. of sample (mL)		250	200	200	200	80	70	50	90	350	200	200	20	20	300				

<sup>a</sup>Not Detected by the instrumental analysis. <sup>b</sup>LOD (pg): Limit of Detection of BDE congeners (pg) = 3 x BDE congener concentration in the blank sample in pg. In units of pg/L: LOD<sub>sample</sub>, pg/L = 1000 x (LOD (pg) for corresponding batch / mL sample volume). To correlate individual samples to the corresponding LOD, batch number for each sample is indicated in the row of "Batch number". A batch of analysis is composed of 5-7 samples with one blank sample; blank values varied among the batches.

Table 2.4a Continuation

PBDEs		Concentration (pg/L)									LOD (pg)			
		Philippines							Malaysia			Batch No.		
		PMP02-1	PMP02-2	PMP10-1	PMP10-2	PMS02-1	PMS09-1	PMS09-2	MK03-1	MK04-1	MK04-2	Batch 1	Batch 2	Batch 5
Br1	BDE-1	ND <sup>a</sup>	ND	ND	ND	ND	ND	ND	58	42	ND	900	5	700
	BDE-2	ND	<LOD <sup>b</sup>	214	ND	ND	ND	ND	ND	17	ND	100	7	60
	BDE-3	ND	<LOD	ND	ND	ND	ND	ND	12	7	ND	70	2	30
Br2	BDE-10	ND	ND	ND	ND	ND	ND	ND	ND	111	<LOD	200	40	70
	BDE-7	<LOD	ND	ND	ND	ND	ND	ND	44	25	41	50	20	90
	BDE-11	ND	ND	ND	ND	ND	ND	ND	<LOD	14	ND	90	20	90
Br3	BDE-8	ND	ND	ND	ND	ND	ND	ND	39	74	16	20	0.9	50
	BDE-12/13	ND	<LOD	ND	ND	<LOD	ND	ND	36	78	30	80	20	90
	BDE-15	<LOD	54	ND	517	<LOD	ND	ND	62	58	81	30	20	50
Br4	BDE-30	ND	ND	ND	ND	ND	ND	ND	ND	6	ND	30	2	400
	BDE-32	ND	<LOD	ND	ND	ND	ND	ND	39	67	ND	9	0.7	200
	BDE-17/25	185	180	368	<LOD	<LOD	ND	ND	416	231	359	30	2	80
Br5	BDE-33/28	230	441	414	ND	74	ND	ND	535	644	459	30	0.5	90
	BDE-35	ND	<LOD	ND	ND	ND	ND	ND	21	38	30	70	4	400
	BDE-37	<LOD	<LOD	ND	ND	ND	ND	ND	75	27	69	100	30	200
Br6	BDE-75	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	5	3	70
	BDE-49	846	693	4,240	2,240	76	ND	ND	1,130	728	1,180	20	2	200
	BDE-71	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10	0.8	200
Br7	BDE-47	4,330	2,750	17,300	7,260	345	ND	ND	14,000	8,190	15,800	40	5	60
	BDE-66	25	415	1,910	<LOD	<LOD	ND	ND	630	898	598	20	0.4	500
	BDE-77	ND	ND	ND	ND	ND	ND	ND	ND	72	ND	20	2	500
Br8	BDE-100	210	607	4,650	1,860	39	ND	ND	3,440	1,940	4,360	5	3	50
	BDE-119	<LOD	ND	ND	ND	ND	ND	ND	ND	214	270	10	2	200
	BDE-99	7,940	3,320	22,800	9,820	375	ND	ND	18,200	13,300	23,900	40	9	90
Br9	BDE-116	ND	ND	ND	ND	ND	ND	ND	ND	365	ND	30	20	200
	BDE-118	ND	ND	<LOD	ND	ND	ND	ND	450	302	453	30	6	90
	BDE-85	380	148	2,150	<LOD	ND	ND	ND	ND	219	904	20	9	300
Br10	BDE-126	<LOD	<LOD	ND	ND	ND	ND	ND	ND	ND	ND	20	9	200
	BDE-155	41	ND	<LOD	ND	ND	ND	ND	63	129	26	30	1	200
	BDE-154	1,400	876	4,110	3,130	<LOD	ND	ND	2,990	2,330	2,720	90	0.9	80
Br1	BDE-153	1,750	1,870	5,270	3,410	109	ND	ND	8,970	5,260	8,710	80	2	200
	BDE-138	203	164	<LOD	ND	ND	ND	ND	1,090	860	1,450	70	4	300
	BDE-166	ND	ND	<LOD	ND	ND	ND	ND	172	ND	287	30	20	700
Br2	BDE-183	1,250	2,910	4,300	5,090	<LOD	ND	ND	5,000	3,460	4,850	600	20	800
	BDE-181	ND	ND	ND	ND	ND	ND	ND	1,160	82	1,450	200	9	1000
	BDE-190	ND	<LOD	ND	<LOD	ND	ND	ND	1,110	1,040	1,100	300	10	2000
Br3	BDE-188	ND	ND	78	<LOD	ND	ND	ND	2,920	665	1,570	20	6	20
	BDE-179	81	1,570	1,210	1,010	ND	ND	ND	2,780	2,470	2,800	20	5	20
	BDE-202	ND	1,430	7,700	4,570	ND	<LOD	72	3,250	2,030	2,860	20	20	20
Br4	BDE-197	1,120	1,530	2,070	1,340	49	<LOD	<LOD	2,650	2,170	2,840	50	20	20
	BDE-203	1,160	3,000	3,710	2,620	456	ND	ND	4,540	3,940	5,660	200	30	30
	BDE-196	830	2,940	2,720	2,820	ND	<LOD	123	3,500	2,910	4,150	30	3	30
Br5	BDE-208	ND	2,250	2,250	1,960	197	ND	ND	2,100	2,200	3,350	200	30	30
	BDE-207	1,100	3,960	2,560	2,080	228	<LOD	<LOD	2,600	3,000	5,500	200	30	30
	BDE-206	375	5,610	1,480	1,110	261	<LOD	ND	2,320	2,780	5,560	300	2	40
Br10	BDE-209	1,210	116,000	3,060	4,010	1,490	<LOD	45	5,690	8,100	13,500	400	50	30
Batch number		1	1	5	5	1	5	5	2	2	2			
Vol. of sample (mL)		1,000	700	250	250	1,000	575	583	450	1,000	500			

<sup>a</sup>Not Detected by the instrumental analysis. <sup>b</sup>LOD (pg): Limit of Detection of BDE congeners (pg) = 3 x BDE congener concentration in the blank sample in pg. In units of pg/L: LOD<sub>sample</sub>, pg/L = 1000 x (LOD (pg) for corresponding batch / mL sample volume). To correlate individual samples to the corresponding LOD, batch number for each sample is indicated in the row of "Batch number". A batch of analysis is composed of 5-7 samples with one blank sample; blank values varied among the batches.

Table 2.4b Concentrations of dissolved PBDEs in the leachate samples from tropical Asian countries.

PBDEs		Concentration (pg/L)															LOD (pg)		
		Lao PDR			Cambodia		Vietnam		India	Indonesia			Thailand			Batch No.			
		LV-1	LV-2	LV-3	CP-1	CP-2	VC-1	VH-1	IK-1	IJ-1	IJ-2	IJ-3	TB-1	TB-2	TB-3	2	3	4	
Br1	BDE-1	ND <sup>a</sup>	ND	NA <sup>b</sup>	ND	ND	ND	ND	ND	NA	NA	NA	ND	2,640	ND	280	400	600	
	BDE-2	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	ND	ND	50	200	300	
Br2	BDE-3	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	1,320	ND	60	80	200	
	BDE-10	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	ND	ND	70	50	20	
	BDE-7	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	9,460	ND	20	60	30	
	BDE-11	ND	ND	NA	ND	ND	ND	ND	7,140	NA	NA	NA	ND	ND	ND	200	60	30	
	BDE-8	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	6,870	ND	60	60	200	
	BDE-12/13	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	6,170	ND	60	100	200	
	BDE-15	ND	ND	NA	ND	<LOD <sup>c</sup>	ND	ND	ND	NA	NA	NA	ND	9,090	ND	300	90	300	
Br3	BDE-30	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	ND	ND	20	50	50	
	BDE-32	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	2,030	ND	20	30	30	
	BDE-17/25	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	25,300	ND	20	80	40	
	BDE-33/28	ND	ND	NA	<LOD	<LOD	ND	ND	17,600	NA	NA	NA	ND	33,500	ND	40	200	200	
Br4	BDE-35	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	ND	ND	70	200	200	
	BDE-37	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	3,810	ND	300	100	90	
	BDE-75	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	70	ND	4	8	9	
	BDE-49	ND	ND	NA	13,900	10,700	ND	ND	ND	NA	NA	NA	ND	38,800	ND	20	40	80	
	BDE-71	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	1,790	ND	20	30	30	
	BDE-47	ND	ND	NA	18,400	19,600	297	ND	7,460	NA	NA	NA	ND	100,000	853	20	30	20	
	BDE-66	5,619	ND	NA	<LOD	1,020	ND	ND	ND	NA	NA	NA	ND	41,400	ND	200	50	200	
	BDE-77	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	3,030	ND	90	40	80	
	BDE-100	ND	ND	NA	3,800	2,740	ND	ND	ND	NA	NA	NA	ND	ND	<LOD	6	20	7	
Br5	BDE-119	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	1,430	ND	20	20	20	
	BDE-99	<LOD	ND	NA	35,400	30,800	<LOD	ND	ND	NA	NA	NA	ND	48,400	468	40	60	50	
	BDE-116	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	ND	ND	70	200	200	
	BDE-118	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	ND	ND	70	63	60	
	BDE-85	2,710	ND	NA	778	<LOD	ND	ND	ND	NA	NA	NA	ND	8,330	ND	30	30	30	
	BDE-126	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	ND	ND	40	70	70	
	BDE-155	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	ND	ND	20	20	20	
	BDE-154	ND	ND	NA	5,230	2,580	ND	ND	ND	NA	NA	NA	ND	3,190	ND	30	20	40	
	BDE-153	ND	ND	NA	5,870	2,240	ND	ND	ND	NA	NA	NA	ND	12,800	ND	70	200	70	
Br6	BDE-138	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	1,420	ND	50	200	200	
	BDE-166	ND	<LOD	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	56	ND	20	20	20	
	BDE-183	ND	ND	NA	<LOD	1,370	ND	ND	ND	NA	NA	NA	ND	10,400	ND	60	200	70	
	BDE-181	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	ND	ND	30	60	60	
	BDE-190	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	ND	ND	60	600	1,000	
	BDE-188	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	ND	ND	9	7	10	
Br7	BDE-179	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	ND	ND	5	8	20	
	BDE-202	<LOD	<LOD	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	10,300	ND	20	30	7	
	BDE-197	ND	ND	NA	1,990	1,720	ND	ND	ND	NA	NA	NA	ND	7,600	184	8	40	20	
	BDE-203	4,360	3,440	NA	3,080	2,760	ND	ND	ND	NA	NA	NA	ND	15,100	ND	20	30	20	
Br8	BDE-196	4,190	2,440	NA	2,390	2,320	197	<LOD	ND	NA	NA	NA	<LOD	14,100	<LOD	50	20	30	
	BDE-208	ND	ND	NA	5,460	7,010	<LOD	<LOD	ND	NA	NA	NA	ND	13,000	208	30	30	50	
	BDE-207	<LOD	ND	NA	5,440	6,730	304	119	<LOD	NA	NA	NA	ND	16,700	278	30	20	30	
Br9	BDE-206	<LOD	2,890	NA	3,800	5,030	238	<LOD	<LOD	NA	NA	NA	ND	14,800	87	20	20	30	
	BDE-209	<LOD	<LOD	NA	23,500	56,100	2,360	636	ND	NA	NA	NA	ND	67,300	726	50	50	80	
Batch number		3	3		4	4	3	3	4				2	2	2				
Vol. of sample (mL)		20	20		50	50	100	120	20				200	125	150				

<sup>a</sup>Not Detected by the instrumental analysis. <sup>b</sup>Not Analyzed; all samples were used up in the analysis of other compounds. <sup>c</sup>LOD (pg): Limit of Detection of BDE congeners (pg) = 3 x BDE congener concentration in the blank sample in pg. In units of pg/L: LODsample, pg/L = 1000 x (LOD (pg) for corresponding batch / mL sample volume). To correlate individual samples to the corresponding LOD, batch number for each sample is indicated in the row of "Batch number". A batch of analysis is composed of 5-7 samples with one blank sample; blank values varied among the batches.

Table 2.4b Continuation

PBDEs		Concentration (pg/L)									LOD (pg)			
		Philippines							Malaysia		Batch No.			
		PMP02-1	PMP02-2	PMP10-1	PMP10-2	PMS02-1	PMS09-1	PMS09-2	MK03-1	MK04-1	MK04-2	1	2	4
Br1	BDE-1	ND <sup>a</sup>	ND	NA <sup>b</sup>	NA	ND	NA	NA	ND	ND	ND	900	280	600
	BDE-2	ND	ND	NA	NA	ND	NA	NA	ND	ND	ND	100	50	300
Br2	BDE-3	ND	ND	NA	NA	ND	NA	NA	ND	ND	ND	70	60	200
	BDE-10	ND	ND	NA	NA	ND	NA	NA	ND	ND	ND	200	70	20
	BDE-7	ND	ND	NA	NA	ND	NA	NA	ND	ND	ND	50	20	30
	BDE-11	ND	ND	NA	NA	ND	NA	NA	ND	ND	ND	90	200	30
	BDE-8	ND	ND	NA	NA	ND	NA	NA	ND	ND	ND	20	60	200
	BDE-12/13	ND	ND	NA	NA	ND	NA	NA	ND	ND	ND	80	60	200
	BDE-15	ND	ND	NA	NA	ND	NA	NA	ND	ND	ND	30	300	300
Br3	BDE-30	ND	ND	NA	NA	ND	NA	NA	ND	ND	ND	30	20	50
	BDE-32	ND	ND	NA	NA	ND	NA	NA	ND	ND	ND	9	20	30
	BDE-17/25	167	ND	NA	NA	ND	NA	NA	1,390	ND	911	30	20	40
	BDE-33/28	<LOD <sup>c</sup>	ND	NA	NA	ND	NA	NA	2,300	ND	ND	30	40	200
Br4	BDE-35	ND	ND	NA	NA	ND	NA	NA	ND	ND	ND	70	70	200
	BDE-37	ND	ND	NA	NA	ND	NA	NA	ND	ND	ND	100	300	90
	BDE-75	ND	ND	NA	NA	ND	NA	NA	ND	ND	ND	5	4	9
	BDE-49	2,500	ND	NA	NA	ND	NA	NA	6,530	1,250	3,510	20	20	80
	BDE-71	ND	ND	NA	NA	ND	NA	NA	ND	ND	ND	10	20	30
	BDE-47	8,770	1,290	NA	NA	ND	NA	NA	34,500	15,300	21,100	40	20	20
	BDE-66	<LOD	ND	NA	NA	ND	NA	NA	3,190	ND	2,970	20	200	200
	BDE-77	ND	ND	NA	NA	ND	NA	NA	ND	ND	ND	20	90	80
	BDE-100	2,500	304	NA	NA	ND	NA	NA	1,110	3,400	6,700	5	6	7
	BDE-119	ND	ND	NA	NA	ND	NA	NA	ND	ND	ND	10	20	20
Br5	BDE-99	16,200	1,500	NA	NA	ND	NA	NA	54,600	20,600	27,800	40	40	50
	BDE-116	ND	ND	NA	NA	ND	NA	NA	ND	ND	ND	30	70	200
	BDE-118	ND	ND	NA	NA	ND	NA	NA	<LOD	ND	ND	30	70	60
	BDE-85	532	ND	NA	NA	ND	NA	NA	2,970	<LOD	<LOD	20	30	30
	BDE-126	ND	ND	NA	NA	ND	NA	NA	10,300	ND	ND	20	40	70
	BDE-155	ND	ND	NA	NA	ND	NA	NA	389	ND	ND	30	20	20
	BDE-154	4,250	ND	NA	NA	ND	NA	NA	6,290	3,400	3,070	90	30	40
	BDE-153	5,700	ND	NA	NA	ND	NA	NA	22,900	10,300	13,500	80	70	70
Br6	BDE-138	<LOD	ND	NA	NA	ND	NA	NA	4,600	ND	ND	70	50	200
	BDE-166	ND	ND	NA	NA	ND	NA	NA	ND	ND	ND	30	20	20
	BDE-183	5,370	<LOD	NA	NA	ND	NA	NA	16,800	3,820	5,220	600	60	70
	BDE-181	ND	ND	NA	NA	ND	NA	NA	312	ND	ND	200	30	60
	BDE-190	ND	ND	NA	NA	ND	NA	NA	1,250	ND	ND	300	60	1,000
	BDE-188	ND	ND	NA	NA	ND	NA	NA	354	<LOD	<LOD	20	9	10
Br7	BDE-179	ND	ND	NA	NA	ND	NA	NA	ND	ND	ND	20	5	20
	BDE-202	ND	1,130	NA	NA	ND	NA	NA	ND	ND	ND	20	20	7
	BDE-197	4,600	1,140	NA	NA	ND	NA	NA	6,240	3,770	5,190	50	8	20
	BDE-203	3,080	2,570	NA	NA	ND	NA	NA	8,500	6,690	8,060	200	20	20
Br8	BDE-196	3,310	1,680	NA	NA	ND	NA	NA	7,880	5,030	6,240	30	50	30
	BDE-208	2,100	<LOD	NA	NA	ND	NA	NA	5,180	4,140	5,730	200	30	50
	BDE-207	2,500	<LOD	NA	NA	ND	NA	NA	6,990	6,240	8,650	200	30	30
	BDE-206	<LOD	<LOD	NA	NA	ND	NA	NA	4,410	3,950	6,010	300	20	30
Br10	BDE-209	5,070	<LOD	NA	NA	ND	NA	NA	16,600	15,100	17,700	400	50	80
Batch number		1	1			4			2	2	2			
Vol. of sample (mL)		130	120			200			100	30	35			

<sup>a</sup>Not Detected by the instrumental analysis. <sup>b</sup>Not Analyzed; all samples were used up in the analysis of other compounds. <sup>c</sup>LOD (pg): Limit of Detection of BDE congeners (pg) = 3 x BDE congener concentration in the blank sample in pg. In units of pg/L; LODsample, pg/L = 1000 x (LOD (pg) for corresponding batch / mL sample volume). To correlate individual samples to the corresponding LOD, batch number for each sample is indicated in the row of "Batch number". A batch of analysis is composed of 5-7 samples with one blank sample; blank values varied among the batches.

Table 2.4c Concentrations of  $\Sigma$ PBDEs<sub>Adsorbed+Dissolved</sub> in the leachate samples from tropical Asian countries.

PBDEs		Concentration (pg/L)													
		Lao PDR			Cambodia		Vietnam		India	Indonesia			Thailand		
		LV-1	LV-2	LV-3	CP-1	CP-2	VC-1	VH-1	IK-1	IJ-1	IJ-2	IJ-3	TB-1	TB-2	TB-3
Br1	BDE-1	ND <sup>a</sup>	ND	NA <sup>b</sup>	ND	ND	ND	ND	ND	NA	NA	NA	ND	117,000	ND
	BDE-2	ND	ND	NA	ND	212	ND	ND	ND	NA	NA	NA	ND	9,520	21
	BDE-3	ND	ND	NA	ND	ND	ND	ND	<LOD <sup>c</sup>	NA	NA	NA	9,140	36,600	9
Br2	BDE-10	<LOD	<LOD	NA	ND	ND	ND	<LOD	ND	NA	NA	NA	ND	ND	<LOD
	BDE-7	ND	ND	NA	ND	ND	ND	ND	2,600	NA	NA	NA	ND	341,000	<LOD
	BDE-11	ND	ND	NA	ND	ND	ND	ND	7,140	NA	NA	NA	ND	ND	<LOD
Br3	BDE-8	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	403,000	<LOD
	BDE-12/13	ND	ND	NA	ND	ND	ND	ND	2,080	NA	NA	NA	ND	337,000	<LOD
	BDE-15	ND	ND	NA	ND	<LOD	ND	ND	4,240	NA	NA	NA	ND	475,000	<LOD
	BDE-30	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	ND	<LOD
	BDE-32	ND	ND	NA	ND	ND	ND	ND	675	NA	NA	NA	ND	64,900	7
	BDE-17/25	ND	ND	NA	ND	753	ND	ND	7,430	NA	NA	NA	ND	812,000	32
	BDE-33/28	ND	ND	NA	640	1,200	ND	ND	27,900	NA	NA	NA	ND	1,280,000	70
	BDE-35	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	ND	<LOD
	BDE-37	ND	ND	NA	ND	ND	ND	ND	<LOD	NA	NA	NA	ND	161,000	<LOD
	BDE-75	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	11,800	<LOD
Br4	BDE-49	<LOD	ND	NA	21,500	20,300	390	812	6,830	NA	NA	NA	11,300	1,570,000	290
	BDE-71	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	1,790	15
	BDE-47	391	151	NA	43,900	44,400	2,650	803	31,400	NA	NA	NA	96,200	18,800,000	1,570
	BDE-66	5,619	ND	NA	1,600	3,970	<LOD	ND	6,190	NA	NA	NA	ND	1,380,000	78
	BDE-77	ND	ND	NA	ND	ND	ND	ND	<LOD	NA	NA	NA	ND	3,030	21
	BDE-100	73	ND	NA	4,860	2,740	<LOD	<LOD	457	NA	NA	NA	11,600	75,200	238
	BDE-119	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	1,430	2
Br5	BDE-99	351	<LOD	NA	79,700	71,500	1,570	<LOD	8,140	NA	NA	NA	121,000	1,590,000	2,050
	BDE-116	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	ND	ND
	BDE-118	ND	ND	NA	ND	ND	ND	ND	<LOD	NA	NA	NA	ND	248,000	<LOD
	BDE-85	2,710	ND	NA	3,100	1,200	ND	ND	177	NA	NA	NA	ND	66,600	49
	BDE-126	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	ND	38
	BDE-155	ND	ND	NA	129	ND	ND	<LOD	ND	NA	NA	NA	ND	ND	13
	BDE-154	ND	ND	NA	9,120	6,680	ND	ND	<LOD	NA	NA	NA	12,800	77,700	231
Br6	BDE-153	ND	ND	NA	20,600	10,500	ND	ND	<LOD	NA	NA	NA	10,800	429,000	304
	BDE-138	ND	ND	NA	393	972	ND	ND	ND	NA	NA	NA	ND	8,720	78
	BDE-166	ND	<LOD	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	56	<LOD
	BDE-183	<LOD	ND	NA	2,110	4,590	<LOD	ND	<LOD	NA	NA	NA	ND	189,000	210
	BDE-181	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	ND	82
	BDE-190	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	ND	49
	BDE-188	ND	ND	NA	ND	ND	ND	ND	ND	NA	NA	NA	ND	ND	ND
Br7	BDE-179	137	356	NA	5,340	8,300	1,420	ND	5,540	NA	NA	NA	20,000	72,200	ND
	BDE-202	<LOD	<LOD	NA	ND	4,280	ND	ND	1,440	NA	NA	NA	37,500	248,000	743
	BDE-197	<LOD	<LOD	NA	3,670	4,130	<LOD	ND	3,150	NA	NA	NA	35,600	274,000	656
	BDE-203	4,360	3,440	NA	3,080	6,050	ND	ND	2,190	NA	NA	NA	61,900	516,000	922
Br8	BDE-196	4,190	2,780	NA	2,390	5,400	1,140	<LOD	5,390	NA	NA	NA	61,400	517,000	802
	BDE-208	<LOD	<LOD	NA	12,900	17,400	1,090	1,030	84,900	NA	NA	NA	73,400	802,000	955
	BDE-207	192	156	NA	12,300	17,100	2,210	2,040	27,100	NA	NA	NA	95,800	1,700,000	1,260
	BDE-206	207	2,890	NA	26,800	17,200	3,060	4,800	227,000	NA	NA	NA	72,400	3,060,000	778
Br10	BDE-209	1,020	776	NA	53,600	148,000	34,600	29,100	37,000	NA	NA	NA	2,040,000	97,800,000	12,500
Total PBDEs		19,200	10,500		308,000	397,000	48,100	38,600	499,000				2,770,000	133,000,000	24,100

<sup>a</sup>Not Detected by the instrumental analysis. <sup>b</sup>Not Analyzed for dissolved PBDEs (samples were used up in earlier analysis of other compounds). <sup>c</sup>LOD: Limit of Detection of BDE congeners in the adsorbed or dissolved phases = 3 x BDE congener concentration in the blank sample in pg. In pg/L: LOD<sub>sample</sub>, pg/L = 1000 x (LOD (pg) for corresponding batch / mL sample volume). Data for LODs of the BDEs in the adsorbed and dissolved phases are found in Annex Tables 2.5a-5b,

Table 2.4c Continuation

PBDEs		Concentration (pg/L)									
		Philippines							Malaysia		
		PMP02-1	PMP02-2	PMP10-1	PMP10-2	PMS02-1	PMS09-1	PMS09-2	MK03-1	MK04-1	MK04-2
Br1	BDE-1	ND <sup>a</sup>	ND	NA <sup>b</sup>	NA	ND	NA	NA	58	42	ND
	BDE-2	ND	<LOD <sup>c</sup>	NA	NA	ND	NA	NA	ND	17	ND
	BDE-3	ND	<LOD	NA	NA	ND	NA	NA	12	7	ND
Br2	BDE-10	ND	ND	NA	NA	ND	NA	NA	ND	111	<LOD
	BDE-7	<LOD	ND	NA	NA	ND	NA	NA	44	25	41
	BDE-11	ND	ND	NA	NA	ND	NA	NA	<LOD	14	ND
	BDE-8	ND	ND	NA	NA	ND	NA	NA	39	74	16
	BDE-12/13	ND	<LOD	NA	NA	<LOD	NA	NA	36	78	30
	BDE-15	<LOD	54	NA	NA	<LOD	NA	NA	62	58	81
Br3	BDE-30	ND	ND	NA	NA	ND	NA	NA	ND	6	ND
	BDE-32	ND	<LOD	NA	NA	ND	NA	NA	39	67	ND
	BDE-17/25	352	180	NA	NA	<LOD	NA	NA	1,810	231	1,270
	BDE-33/28	230	441	NA	NA	74	NA	NA	2,830	644	459
	BDE-35	ND	<LOD	NA	NA	ND	NA	NA	21	38	30
	BDE-37	<LOD	<LOD	NA	NA	ND	NA	NA	75	27	69
Br4	BDE-75	ND	ND	NA	NA	ND	NA	NA	ND	ND	ND
	BDE-49	3,340	693	NA	NA	76	NA	NA	7,660	1,980	4,690
	BDE-71	ND	ND	NA	NA	ND	NA	NA	ND	ND	ND
	BDE-47	13,100	4,040	NA	NA	346	NA	NA	48,500	23,500	36,900
	BDE-66	25	415	NA	NA	<LOD	NA	NA	3,820	898	3,570
	BDE-77	ND	ND	NA	NA	ND	NA	NA	ND	72	ND
Br5	BDE-100	2,710	911	NA	NA	39	NA	NA	4,550	5,340	11,000
	BDE-119	<LOD	ND	NA	NA	ND	NA	NA	ND	214	270
	BDE-99	24,100	4,820	NA	NA	375	NA	NA	72,800	33,900	50,900
	BDE-116	ND	ND	NA	NA	ND	NA	NA	ND	365	ND
	BDE-118	ND	ND	NA	NA	ND	NA	NA	448	302	453
	BDE-85	912	148	NA	NA	ND	NA	NA	2,970	219	904
Br6	BDE-126	<LOD	<LOD	NA	NA	ND	NA	NA	1,030	ND	ND
	BDE-155	41	ND	NA	NA	ND	NA	NA	452	129	26
	BDE-154	5,650	880	NA	NA	<LOD	NA	NA	9,280	5,730	5,790
	BDE-153	7,450	1,870	NA	NA	109	NA	NA	31,900	15,600	22,200
	BDE-138	203	164	NA	NA	ND	NA	NA	5,690	860	1,450
	BDE-166	ND	ND	NA	NA	ND	NA	NA	172	ND	287
Br7	BDE-183	6,620	2,910	NA	NA	<LOD	NA	NA	21,800	7,270	10,100
	BDE-181	ND	ND	NA	NA	ND	NA	NA	1,470	82	1,450
	BDE-190	ND	<LOD	NA	NA	ND	NA	NA	2,360	1,040	1,100
	BDE-188	ND	ND	NA	NA	ND	NA	NA	3,280	665	1,570
	BDE-179	81	1,570	NA	NA	ND	NA	NA	2,780	2,470	2,800
	BDE-202	ND	2,560	NA	NA	ND	NA	NA	3,250	2,030	2,860
Br8	BDE-197	5,720	2,670	NA	NA	49	NA	NA	8,890	5,940	8,030
	BDE-203	4,240	5,570	NA	NA	456	NA	NA	13,000	10,600	13,700
	BDE-196	4,140	4,620	NA	NA	ND	NA	NA	11,400	7,940	10,400
Br9	BDE-208	2,100	2,250	NA	NA	197	NA	NA	7,280	6,340	9,080
	BDE-207	3,600	3,960	NA	NA	228	NA	NA	9,580	9,240	14,100
	BDE-206	375	5,610	NA	NA	261	NA	NA	6,730	6,730	11,600
Br10	BDE-209	6,280	116,000	NA	NA	1,490	NA	NA	22,300	23,200	31,200
Total PBDEs		91,300	162,000			3,700			308,000	174,000	258,000

<sup>a</sup>Not Detected by the instrumental analysis. <sup>b</sup>Not Analyzed for dissolved PBDEs (samples were used up in earlier analysis of other compounds). <sup>c</sup>LOD: Limit of Detection of BDE congeners in the adsorbed or dissolved phases = 3 x BDE congener concentration in the blank sample in pg. In pg/L: LOD<sub>sample</sub>, pg/L = 1000 x (LOD (pg) for corresponding batch / mL sample volume). Data for LODs of the BDEs in the adsorbed and dissolved phases are found in Annex Tables 2.5a-5b, respectively.

Table 2.5 Comparison of the PBDE concentrations in the leachate samples with concentrations reported for other countries.

Country	Sample	Concentration, ng/L											Reference
		BDE-33/28	BDE-75	BDE-47	BDE-66	BDE-77	tetra <sup>a</sup> -BDEs	BDE-85	BDE-99	BDE-100	BDE-119	penta <sup>b</sup> -BDEs	
Lao PDR	adsorbed+dissolved PBDEs	ND	ND	0.151-0.391	ND-5.62	ND	0.151-6.01	ND-2.71	<LOD-0.351	ND-0.073	ND	<LOD-3.13	This study
Cambodia	adsorbed+dissolved PBDEs	0.640-1.20	ND	43.9-44.4	1.60-3.97	ND	67.0-68.7	1.20-3.10	71.5-79.7	2.74-4.86	ND	75.4-87.7	This study
Vietnam	adsorbed+dissolved PBDEs	ND	ND	0.803-2.65	ND-<LOD	ND	1.62-3.04	ND	<LOD-157	<LOD	ND	<LOD-1.57	This study
India	adsorbed+dissolved PBDEs	27.9	ND	31.4	6.19	<LOD	44.4	0.177	8.14	0.457	ND	8.77	This study
Thailand (TB-1,-3)	adsorbed+dissolved PBDEs	ND-0.070	ND-<LOD	1.57-96.2	ND-0.078	ND-0.021	1.97-108	ND-0.049	2.05-121	0.238-11.6	ND-0.002	2.38-133	This study
Thailand (TB-2)	adsorbed+dissolved PBDEs	1,280	11.8	18,800	1,380	3,030	2,180	66.6	1,590	75.2	1.43	1,980	This study
Philippines (PMP-02)	adsorbed+dissolved PBDEs	0.230-0.441	ND	4.04-13.1	0.025-0.415	ND	5.15-16.5	0.148-0.912	4.82-24.1	0.911-2.71	ND-<LOD	5.88-27.7	This study
Philippines (PMS-02)	adsorbed+dissolved PBDEs	0.074	ND	0.346	<LOD	ND	0.422	ND	0.375	0.039	ND	0.414	This study
Malaysia	adsorbed+dissolved PBDEs	0.459-2.83	ND	23.5-48.5	0.898-3.82	ND-0.072	26.4-60.0	0.219-2.97	33.9-72.8	4.55-11.0	ND-0.270	40.3-81.8	This study
Reference values <sup>c</sup> :													
Japan	MSWLs raw leachates, overall	<0.008-0.97 (28)		<0.008-2.2		<0.008-<0.5		<0.008-1.8		<0.008-<0.5		Osako et al. (2004)	
South Africa, 2009	MSWLs raw leachates, total	0.1-3.3 (28)	0.74-7.43	1.469-9.793	ND-4.020	ND-4.257	ND-1.240		ND-5.191	ND-2.162	ND-5.392	Odusanya et al. (2009)	
South Africa, 2012	MSWLs raw leachates, total	ND-42.4 (28)		0.05-2,990				0.10-2,160		0.06-1,180		Daso et al. (2012)	
Canada, North	Landfills, raw leachates, total			BMDL <sup>d</sup> -6.199				BMDL-2.461		BMDL-2.587		Danon-Schaffier (2010)	
Canada, South	Urban landfills, raw leachates, total			BMDL-194				BMDL-500		BMDL-100		Danon-Schaffier (2010)	
U.S.A.	Landfill leachates (upper range <sup>e</sup> )			<5,000				<8,000		<2,000		Oliaei et al. (2002)	
Sweden <sup>f</sup>	Municipal landfills, raw leachates, total					8.5-7,100						1.7-7,000 Öman and Junestedt, 2008	

<sup>a</sup>tetra- BDEs =  $\Sigma$ BDEs 47, 49, 66, 71, 75, 77. <sup>b</sup>penta-BDEs =  $\Sigma$ BDEs 85, 99, 100, 116, 118, 119, 126. <sup>c</sup>Values converted to ng/L. <sup>d</sup>BMDL- Below method detection limit. <sup>e</sup>Estimated from the figure presented (Oliaei et al, 2002). <sup>f</sup>The BDE congeners for each homologue were not specified (Öman and Junestedt, 2008).



Table 2.5 Continuation

Country	Sample	BDE-153	BDE-154	hexa <sup>a</sup> -BDEs	BDE-183	hepta <sup>b</sup> -BDEs	octa <sup>c</sup> -BDEs	BDE-206	BDE-207	nona <sup>d</sup> -BDEs	BDE-209	Reference
Lao PDR	adsorbed+dissolved PBDEs	ND	ND	ND-<LOD	ND-<LOD	0.137-0.356	6.22-8.55	0.207-2.89	0.156-0.192	0.399-3.82	0.776-1.02	This study
Cambodia	adsorbed+dissolved PBDEs	10.5-20.6	6.68-9.12	18.2-30.2	2.11-4.59	7.45-12.9	9.14-19.9	17.2-26.8	12.3-17.1	51.7-52.0	53.6-148	This study
Vietnam	adsorbed+dissolved PBDEs	ND	ND	ND-<LOD	ND-<LOD	ND-1.42	<LOD-1.14	3.06-4.80	2.04-2.21	6.36-7.87	29.1-34.6	This study
India	adsorbed+dissolved PBDEs	<LOD	<LOD	<LOD	<LOD	5.5	12.2	227	27	339	37	This study
Thailand (TB-1,-3)	adsorbed+dissolved PBDEs	0.304-10.8	0.231-12.8	0.626-23.6	ND-0.210	0.341-20	3.12-196	0.778-72.4	1.26-95.8	2.99-242	12.5-2,040	This study
Thailand (TB-2)	adsorbed+dissolved PBDEs	429	77.7	515	189	261	1,560	3,060	1,700	5,560	97,800	This study
Philippines (PMP-02)	adsorbed+dissolved PBDEs	1.87-7.45	0.880-5.65	2.91-13.3	2.91-6.62	4.48-6.70	14.1-15.4	0.375-5.61	3.60-3.96	6.08-11.8	6.28-116	This study
Philippines (PMS-02)	adsorbed+dissolved PBDEs	0.109	<LOD	0.11	<LOD	<LOD	0.505	0.261	0.228	0.686	1.490	This study
Malaysia	adsorbed+dissolved PBDEs	15.6-31.9	5.73-9.28	22.3-47.5	7.27-21.8	11.5-31.7	26.5-36.5	6.73-11.6	6.34-9.08	22.3-34.8	22.3-31.2	This study
Reference values <sup>e</sup> :												
Japan	MSWLs raw leachates, overall	<0.008-<0.5	<0.008-1.2								<0.800-<50	Osako et al. (2004)
South Africa, 2009	MSWLs raw leachates, total	ND-0.875	ND-2.176		8.392-54.761							Odusanya et al. (2009)
South Africa, 2012	MSWLs raw leachates, total	ND-7,990	ND-713		ND-5,890						ND-6,380	Daso et al. (2012)
Canada, North	Landfills, raw leachates, total	BMDL <sup>f</sup> -3.846	BMDL-2.398		BMDL-28.429			ND-4.411	ND-7.310		ND-103.873	Danon-Schaffer (2010)
Canada, South	Urban landfills, raw leachates, total		BMDL-81.7						BMDL-21.3		BMDL-460	Danon-Schaffer (2010)
U.S.A.	Landfill leachates (upper range <sup>g</sup> )	<1,000	<1,000						<2,000			Oliaei et al. (2002)
Sweden <sup>h</sup>	Municipal landfills, raw leachates, total			<LOD-2		<LOD-5	<LOD-56			<LOD-1,100	<LOD-4,200	Öman and Junestedt, 2008

<sup>a</sup>hexa-BDEs =  $\Sigma$ BDEs 138, 153, 154, 155, 166. <sup>b</sup>hepta-BDEs =  $\Sigma$ BDEs 179, 181, 183, 188, 190. <sup>c</sup>octa-BDEs =  $\Sigma$ BDEs 196, 197, 202, 203. <sup>d</sup>nona-BDEs =  $\Sigma$ BDEs 206, 207, 208. <sup>e</sup>Values converted to ng/L. <sup>f</sup>BMDL- Below method detection limit. <sup>g</sup>Estimated from the figure presented (Oliaei et al, 2002). <sup>h</sup>The BDE congeners for each homologue were not specified (Öman and Junestedt, 2008).

## **Chapter 3**

### **Sedimentary PBDEs in Urban Areas of Tropical Asian Countries**

### 3.1. Introduction

Polybrominated diphenyl ethers (PBDEs) are one of the three major types of commercial brominated flame retardants (BFRs) that have been used in a wide range of industrial and consumer products since the 1970s (BSEF, 2012; de Wit, 2002; Stockholm Convention, 2009). They are estimated to constitute one third of the world's production of BFRs (Darnerud, 2003), at 67,000 metric tons/year (BSEF, 2012). Polymer-based products may contain as much as 30% PBDEs by weight (Hale et al., 2002) because of their inherent flammability (de Wit, 2002). However, the production of technical penta- and octa-BDE products has been halted (BSEF, 2012), and the tetra-, penta-, hexa- and hepta-BDEs have been classified as POPs by the Stockholm Convention in 2009 (Stockholm Convention, 2012) because of their toxicity to animals and humans (McDonald, 2002; Darnerud, 2003; Costa and Giordano, 2007; Ross et al., 2009), and their persistence in the environment (Ross et al., 2009; Stockholm Convention, 2009). Technical deca-BDE products are currently undergoing regulatory assessment in Europe (BSEF, 2013), presumably due to their potential to debrominate to more toxic congeners (Gerecke et al., 2005; He et al., 2006; Tokarz et al., 2008; Christiansson et al., 2009). However, the long historical usage of PBDEs in many consumer products, the majority of which are still in use, will ensure the proliferation of PBDEs in the environment for many years to come.

PBDEs are physically mixed into polymers; thus, they may leach out from the surfaces of plastics and textiles (de Wit, 2002), and would be distributed in various compartments of the environment including sediments. PBDEs are lipophilic (Rahman et al., 2001) and have low solubility in water (de Wit, 2002); therefore they are easily removed from the aqueous environment (Rahman et al., 2001). In particular, the high  $K_{ow}$  of BDE-209 ( $\log K_{ow} \sim 10$ ; Watanabe and Tatsukawa, 1990) would enable it to partition preferentially to the particles in water (Rahman et al., 2001; Hites, 2004; Ross et al., 2009), which would eventually sink as sediment (Hites, 2004). Thus, sediments can become reservoirs of PBDEs, especially BDE-209 (de Wit, 2002; Hites, 2004; Johannessen et al., 2008; Ross et al., 2009). Due to the continuing high-volume production and usage of technical deca-BDE products, many studies have observed the predominance of BDE-209

in sediments (Eljarrat et al., 2005; Moon et al., 2007; Tokarz et al., 2008; Toms et al. 2008; Chen et al., 2009), except in a few studies (Hale et al., 2003; Liu et al., 2005; Oros et al., 2005). The high levels of BDE-209 in sediments have become a concern because they may break down to lower brominated congeners (Tokarz et al., 2008; Ross et al., 2009). Deca-BDE has been found debrominated under natural sunlight (Stapleton and Dodder, 2008; Christiansson et al., 2009) and anaerobic microbial conditions (Gerecke et al., 2005; He et al., 2006; Robrock et al., 2008; Tokarz et al., 2008). As sediments are mostly anaerobic, debromination of BDE-209 would likely occur, although predicted at a slower rate due to its hydrophobicity (Tokarz et al., 2008). However, debromination of BDE-209 in sediments was not observed in some studies (Knoth et al., 2007; La Guardia et al., 2007; Johannessen et al., 2008). Given such contrasting observations on the behavior of PBDEs in sediments (i.e., predominance vs. non-predominance; debromination vs. no debromination), it may be inferred that the fate of PBDEs in the aquatic environment is not yet fully understood.

In 2001, the consumption of technical penta-, octa- and deca-PBDE products in Asia was 1.8%, 40% and 41% of the world's total production, respectively (Hites, 2004; BSEF, 2012). Most tropical Asian countries, such as India, Indonesia, Malaysia, the Philippines, Thailand and Vietnam have experienced unprecedented population and economic growths over the last decade (UNDESA, 2010; Worldbank, 2010). The combined population of these tropical Asian countries, including Lao PDR and Cambodia, has accounted for roughly 25% of the world's population since 2000 (UNDESA, 2010); thus it may be assumed that significant amounts of PBDE-laden goods may have been produced and consumed in the region. In addition, some of these countries may be recipients of imported surplus electronic goods from developed countries, which would eventually become e-waste. As a result, PBDEs may be present in various compartments of tropical Asian environments, including accumulation in sediments. However, data on sedimentary PBDEs in tropical Asian countries are limited to Hong Kong (Liu et al., 2005), Singapore (Wurl and Obbard, 2005), India (Binelli et al., 2007) and Indonesia (Ilyas et al., 2011).

The main objective of the study is to investigate the occurrence of PBDEs in surface sediment samples taken from urban areas of tropical Asian countries, including Lao PDR, Cambodia, Vietnam, India, Indonesia, Thailand, the Philippines and Malaysia. The profiles and concentration levels of the PBDE congeners were assessed in order to reveal the fate of PBDEs in tropical aquatic environments, particularly the debromination of BDE-209; and to evaluate the extent of PBDE contamination in tropical Asian countries. The spatial distribution of sedimentary PBDEs in a river system was also studied, to determine whether inland sources of PDBEs could impact coastal areas. Sediment samples from Japan were analyzed to benchmark the concentration levels of PBDEs in the sediments.

## **3.2. Materials and methods**

### **3.2.1. Sample collection**

Surface sediment samples were collected from canals or rivers ( $n = 3$  to  $6$ ) in the capital or major cities of tropical Asian countries: Vientiane (Lao PDR), Phnom Penh (Cambodia), Hanoi (Vietnam), Kolkata, Chennai and Mumbai (India), Jakarta (Indonesia), Bangkok (Thailand), Metro Manila (Philippines) and Kuala Lumpur (Malaysia) from 2000 to 2010. Marine sediments were collected in the Philippines ( $n = 2$  in 2002,  $n = 2$  in 2009; Manila Bay) and in Japan ( $n = 5$  in 2008; Tokyo Bay). Sampling information is found in Table 3.1.

Sediment samples were collected using an Ekman dredge. The top 2 cm sample was placed in a detergent- and solvent-rinsed stainless steel container with a Teflon-lined cover, using a stainless steel scoop. The samples were kept cold ( $\sim 4^{\circ}\text{C}$ ) during transport to the regional laboratory, packed in dry ice during transport to the laboratory of TUAT, and finally stored at  $-30^{\circ}\text{C}$  until further processing. Before analysis, the samples were freeze-dried.

### **3.2.2. Analytical method**

The method used for measuring PBDE levels in the sediment samples was described earlier in Chapter 2 section 2.2.2. Briefly, 1-2 g sediment samples were extracted with acetone/DCM (1:3

v/v) using an accelerated solvent extractor (ASE; Dionex-200). The extracts were spiked with surrogate standards (<sup>13</sup>C-labeled BDEs 3, 15, 28, 47, 99, 154, 153, 183, and f-BDE-208 (4'-fluoro-2,2',3,3',4,5,5',6,6'-nonabromo-diphenylether)). After the extracts were concentrated and solvent exchanged to hexane, they were subjected to initial clean-up in a 5% H<sub>2</sub>O-deactivated silica gel column where non- and slightly polar compounds including the PBDEs were eluted with hexane/DCM (3:1 v/v). The extracts were treated with activated Cu to remove elemental sulfur that may have been present in the sediment samples. The extracts were further cleaned up using a fully activated silica gel column. Alkane fractions were first eluted with 5 mL hexane, followed by elution of the PBDEs with 10 mL of hexane/DCM (3:1 v/v). The PBDE fractions were then concentrated to dryness and re-dissolved in 100 µL of isooctane containing <sup>13</sup>C-BDE-139 as an IIS. Nineteen mono- to hepta-BDE congeners (BDEs 3, 7, 15, 17, 28, 49, 71, 47, 66, 77, 100, 119, 99, 85, 126, 154, 153, 138, 183) in the extracts were analyzed using the GC/ MS (Thermo Electron Corporation Trace GC Ultra, Polaris Q MS with AS3000 Autosampler) in the selected reaction monitoring mode. The GC was equipped with a J&W Scientific DB-5 fused silica capillary column, 30 m x 0.25 mm i.d. x 0.25 µm film thickness. Nona-BDE congeners (BDEs 206, 207, 208) and BDE-209 in the extracts were quantified by GC with an ECD, using the Agilent Technologies 7890A GC System with ECD equipped with a shorter J&W Scientific DB-5 fused silica capillary column (15 m x 0.25 mm i.d. x 0.25 µm film thickness). Details of the instrumental conditions are found in Annex Table 3.1.

### **3.2.3. Quality assurance and quality control protocols**

A method blank (section 2.2.3) was included in every batch of 4-6 samples analyzed. The concentrations of PBDEs in the blank sample defined the LOD, taken as three times the concentration observed in the blank. Concentrations below the LODs were reported as <LOD. The final mono- to hepta-BDE concentrations in the sediment samples were obtained by correcting the results with the recoveries of the corresponding <sup>13</sup>C-labeled homolog PBDE surrogate standard,

while the nona-BDEs and BDE-209 were corrected with the recovery of the surrogate f-BDE-208. The median % recoveries of the surrogates in the sediment samples (n = 49) ranged from 56-93%.

The accuracy and precision of the method used for measuring the sedimentary PBDE levels were assessed earlier, based on the recoveries and RSD of the native PBDE congeners 28, 47, 99, 153, 154, 183, 179, 188, 202, 207, 208, 209 spiked into a sediment sample (n = 4), and on the results of the analysis of the SRM, marine sediment NIST SRM 1941b (n = 3). The mean % recoveries and % RSD ranged from 85-124% and 2-15%, respectively, for the native PBDE congeners; and 67-109% recovery (except BDE-153 at 43%) and 0.5-15 % RSD (except BDE-183 at 49%) for the SRM. The adequacy of our analytical method was indicated by the relatively good agreement of the results for the SRM with the mean values of the interlaboratory comparison exercise (Stapleton et al., 2007). The detailed QA/QC results is found in Chapter 2 section 2.2.3.

Debromination of BDE-209 during the analytical procedure was also verified, by subjecting a BDE-209 standard (n = 2) to the entire analytical method beginning from the accelerated solvent extraction. BDE-209 was not debrominated at any point in the analytical procedure, as indicated by the non-detection of nona- and octa-BDEs.

Because some sediment samples were stored in the freezer at -30°C for ~8 years until analysis, debromination of BDE-209 during storage was checked by comparing the concentrations of BDE-209 and the ratios of BDE206/209 and BDE207/209 in the NIST SRM 1941b marine sediment stored at -30°C, and analyzed in 2004 and 2012. The results of the statistical evaluation using T-test (Table 3.2) indicated that the concentration of BDE-209 did not decrease in 2012 relative to that in 2004, and that both results were not statistically different. Furthermore, there was no significant increase in the ratio of BDE207/209. The ratio of BDE206/209 did not also increase, although the results in 2004 and 2012 were statistically different (Table 3.2). These results confirmed that debromination of BDE-209 did not occur in the SRM while on storage for 8 years at -30°C.

Most of the samples in this study were analyzed in June to July 2009, i.e., a storage period of 1 to 7 years, except for the samples from Indonesia (n=3), that were stored for about 9 years. The

samples Philippines Manila Canals MC1, MC2, MC3 and MC6 that were obtained in 2010 were analyzed in 2011. From the results of the analysis of the SRM, we deduced that debromination of BDE-209 did not significantly occur in the sediment samples during storage at -30°C.

### **3.3. Results and discussion**

The concentrations of a total of 23 PBDE congeners were measured in 44 sediment samples collected from the selected tropical Asian countries, and in 5 sediment samples from Japan. PBDEs were detected at varying concentrations, ranging from non-detection (ND) for some PBDE congeners to a high concentration of 1,670 ng/g dry wt. (dw) for BDE-209 (Philippines MC3). The total PBDE concentrations in the sediment samples from the tropical Asian countries ranged from 0.83 (Lao PDR LVC1) to 3,140 ng/g dw (Philippines MC3), while the total PBDE concentrations in Japan (Tokyo Bay) ranged from 34.1 to 465 ng/g dw. The concentrations of the PBDE congeners in the sediment samples are summarized in Table 3.3.

#### **3.3.1. Congener profiles in the sediments from tropical Asian countries and Japan**

Among the PBDE congeners, BDE-209 was predominant in most of the samples (43 out of 49), ranging from 43 to 97% of the total PBDEs (Fig. 3.1). In particular, all the sediment samples from Lao PDR, Cambodia, Vietnam, India (Mumbai), Thailand, the Philippines and Malaysia exhibited the predominance of BDE-209 (Annex Figs. 3.1a-3.1c, 3.1f, 3.1h-3.1l). This pattern is consistent with previous reports from other areas worldwide (de Wit, 2002; Hites, 2004; Moon et al., 2007; Johannessen et al., 2008; Tokarz et al., 2008; Toms et al., 2008; Chen et al., 2009; Ilyas et al., 2011), and with the high  $K_{ow} = 9.97$  of BDE-209 (Watanabe and Tatsukawa, 1990), which would enable it to partition to particles in the water, and to the sediments (Rahman et al., 2001; Hites, 2004; Ross et al., 2009).

Nona-BDEs 206, 207, 208 were the next most abundant congeners after BDE-209, in most of the sediment samples. BDEs 47, 49, 99, 100, 153, 154, 183 at detectable concentrations, and traces of BDEs 3, 7, 15, 17, 28, 66, 71, 77, 85, 119, 126, 138, were also present (Fig. 3.1; Table



3.3). These PBDE congeners have been identified as components of the technical deca-, octa- and penta-BDE mixtures (La Guardia et al., 2006; Alaei et al., 2003), except BDEs 3, 7, 15 and 77. The PBDE congener profiles in the sediments indicated the higher importation of technical deca-BDE than octa- and penta-BDE products into Asia (Hites, 2004; BSEF, 2012).

### **3.3.2. Sedimentary PBDE levels in tropical Asian countries, in comparison with those in other countries**

The sediment samples from most of the urban areas of the tropical Asian countries studied showed similar or higher concentrations of PBDEs compared with those from various urban and/or highly industrialized locations around the world (Hale et al., 2002; Zheng et al., 2004; Eljarrat et al., 2005; Liu et al., 2005; Oros et al., 2005; Verslycke et al., 2005; Wurl and Obbard, 2005; Samara et al., 2006; Moon et al., 2007; Toms et al., 2008; Chen et al., 2009; Ilyas et al., 2011; Klosterhaus et al., 2012); specifically, BDE-209 and the lower brominated congeners BDEs 47, 99, 153 and 183 (Figs. 3.2a-3.2e). In particular, the sedimentary median concentrations (MCs) of BDE-209 in Malaysia, Cambodia, the Philippines and Thailand were higher than those reported for China (Chen et al., 2009), Hong Kong (Liu et al., 2005), Indonesia (Ilyas et al., 2011), South Korea (Moon et al., 2007), Australia (Toms et al., 2008), Spain (Eljarrat et al., 2005) and the USA (Klosterhaus et al., 2012). With respect to the lower brominated congeners, the MCs in the sediments from Cambodia were higher than most of the MCs cited in this study. Although the MCs of the lower brominated congeners in Lao PDR appeared to be the lowest among the tropical Asian countries studied, the concentration levels were mostly comparable to those reported for China (Zheng et al., 2004), Hong Kong (Liu et al., 2005), South Korea (Moon et al., 2007), Australia (Toms et al., 2008) and the USA (Klosterhaus et al., 2012).

### **3.3.3. Occurrence of PBDEs in the sediments from tropical Asian countries**

The total PBDE concentration profiles in the sediments from the eight tropical Asian countries and Japan are shown in Fig. 3.3. There were wide variations in the total PBDE

concentrations in the sediments, of about two orders of magnitude in most countries. This may be explained by point sources of PBDEs in the vicinity of the sampling sites, though specific sources were not identified for most of the locations. Relative to the sediment samples from Japan (with a total PBDE geometric mean concentration (GMC) of 100 ng/g dw), the lowest total PBDE GMC was obtained in Lao PDR (9.38 ng/g dw). Comparatively lower GMCs of total PBDEs were also found in Vietnam (34.2 ng/g dw), Indonesia (42.2 ng/g dw), Cambodia (58.4 ng/g dw) and India (67.3 ng/g dw), while comparatively higher GMCs of total PBDEs were obtained in Thailand (160 ng/g dw), the Philippines (178 ng/g dw) and Malaysia (275 ng/g dw).

Since PBDEs are used in the manufacture of consumer and industrial products, their consumption and occurrence in the environment may be correlated to the population and the GDP per capita of a country. The plot between the sedimentary PBDE levels and the urban population of the selected tropical Asian countries generally showed a significant correlation ( $R^2 = 0.78$ ; Fig. 3.4a), excluding the cities of Kuala Lumpur, Jakarta, Kolkata and Mumbai. Higher population may lead to higher consumption of consumer products that may contain PBDEs, and which may end up in the aquatic environments such as rivers and canals if not properly disposed. However, the relatively higher population in Jakarta, Kolkata and Mumbai did not correspond to higher PBDE concentrations in the riverine sediments; while the lower population in Kuala Lumpur corresponded to a higher mean sedimentary PBDE concentration. These results suggested the contribution of other factors in the distribution of PBDEs in the aquatic environment.

A significant correlation was also observed between the sedimentary PBDE levels and the GDP per capita of the selected tropical Asian countries ( $R^2 = 0.66$ ; Fig. 3.4b). High GDP per capita may translate into high purchasing power of the population for consumer goods that may contain PBDEs. In the case of Japan, the total PBDE GMC observed in the sediments was not proportional to its GDP per capita. Among other reasons, this may indicate that only a small fraction of PBDEs in consumer goods may have reached the environment i.e., in the sediments. Japan employs a system of stringent waste segregation, recycling and reuse of waste including plastic materials and

household appliances, and minimal landfilling of incineration residuals (Sakai, 1996), which may be effective in preventing the distribution of PBDE-containing waste into the environment.

Leachates from municipal solid waste dumping sites or landfills can be potential sources of PBDEs in sediments. PBDE concentrations in the leachates would likely have a positive correlation to sedimentary PBDE concentrations. This was evident in all the tropical Asian countries studied ( $R^2 = 0.66$ ; Fig. 3.5). Insufficient containment or treatment of leachates in landfills or dumping sites, including indiscriminate disposal of waste into waterways, may introduce PBDEs directly into the aquatic environment.

#### **3.3.4. Spatial distribution of sedimentary PBDEs in the Philippines**

The sedimentary concentrations of total PBDEs, BDE-209 and the sum of other PBDE congeners in the Pasig River (a major river system that bisects Metropolitan Manila, the national capital region of the Philippines, and drains into Manila Bay) were assessed, beginning upstream at location PR12, and continuing downstream through PR8, PR7, PR3 and PR2, to PR1 just before the river flows out to Manila Bay (locations MB1, MB4, MB17, MB18) (Fig. 3.6, Annex Fig. 3.2a). The concentrations of total PBDEs, BDE-209 and the other PBDE congeners in the river increased in the downstream direction, from the most inland location to the outflow, i.e., from PR12 through PR8, PR7 and PR2, except PR3 and PR1. PR3 is located near one of the river bends, and PR1 may be affected by the dynamics of freshwater and seawater mixing. Variability of PBDE concentrations in rivers may result from lesser accumulation of sediments at points where the water current is more rapid (Hites, 2004).

The concentrations of total PBDEs and BDE-209 in the canals or tributary rivers of the Pasig River, specifically at MC1, MC2, MC6 (Fig. 3.6, Annex Fig. 3.2a), were of about the same magnitude as those in the Pasig River, while the concentrations of the lower brominated congeners were higher in the canals than in the river (Fig. 3.6). The exceedingly high concentrations of total PBDEs, BDE-209 and the lower brominated congeners at MC3, (i.e., in Marikina River at three to four orders of magnitude higher than the farthest coastal location, MB18 (Fig. 3.6, Annex Fig. 3.2a)

may indicate point sources of PBDEs near MC3. Many manufacturing industries are located along the Marikina River, including a resin manufacturing plant. Some leachates from the Payatas dumping site, a major municipal solid waste dumping site in Metro Manila, may also flow into MC3 through the Calamiong Creek, which flows from the dumping site towards the Marikina River (Annex Fig. 3.2b). Deca-BDE in the environment is generally detected in sediments near to known point sources (Hardy, 2002). The PBDE concentrations were generally higher in the rivers than in the coastal areas. Among the four coastal locations, MB1 which is nearer to the mainland showed higher concentrations of PBDEs, which may indicate contamination from the Pasig River and its tributaries (Fig. 3.6), and suggesting that PBDEs from inland sources (e.g., rivers and canals) may impact coastal areas.

### **3.3.5. Indicators of debromination in the sediments from tropical Asian countries**

In general, the PBDE congener profiles in the sediment samples did not vary widely between countries (Annex Figs. 3.1a-3.1c, 3.1f, 3.1h-3.1l), except for India (Kolkata and Chennai) (Annex Figs. 3.1d-3.1e), Indonesia (Annex Fig. 3.1g) and Japan (Annex Fig. 3.1m), where some samples exhibited predominance of BDE-209, while other samples showed predominance of certain nona-BDEs such as 206, 207, 208 (Fig. 3.1). BDE-206 was dominant in India (Chennai INCH4, INCH9; Annex Fig. 3.1e) and Japan (Cn17; Annex Fig. 3.1m); BDE-207 in India (Kolkata KKSC4; Annex Fig. 3.1d); and BDE-208 in India (Kolkata KKSC2; Annex Fig. 3.1d) and Indonesia (J2; Annex Fig. 3.1g). The combined concentrations of nona-BDEs 206, 207, 208 in India (KKSC2, KKSC4, INCH4, INCH9), Indonesia (J2) and Japan (Cn17) represented 62-89% of the total PBDEs in the sediment samples (Fig. 3.1), which were higher than the reported proportions in the technical deca-BDE mixture (La Guardia et al., 2006). The concentration ratios of BDE206/209, BDE207/209 and BDE208/209 in the sediment samples also exceeded the reported ratios in the technical deca-BDE mixture (Fig. 3.7) by 2, 3 and 4 orders of magnitude, respectively. The nona-BDEs/BDE-209 ratios in other sediment samples also exceeded those in the technical deca-BDE mixture (Fig. 3.7). In most of the sediment samples except those with ND concentrations, the

BDE206/209, BDE207/209 and BDE208/209 ratios exceeded those in the technical deca-BDE mixture. This may indicate transformation of BDE-209 into nona-BDE congeners through debromination, which may occur during usage and disposal of consumer products, and after emission to the environment, including the riverine environments. Furthermore, the % concentrations of mono- to tri-BDEs and BDE-49 exceeded those in the technical deca-BDE mixture in a number of samples (Fig. 3.7). The congeners BDEs 3, 7, 15 and 77 detected in the sediment samples (Fig. 3.1, Table 3.3). which are not identified as components of the technical PBDE mixtures were possibly products of the debromination of higher brominated PBDE congeners.

In Chapter 2 section 2.3.2, the debromination of PBDEs in leachates of landfills or dumping sites was reported; although we also considered the occurrence of debromination before disposal in the dumping sites. If landfill leachates containing debrominated PBDEs would flow into canals and rivers, they could be the source of debrominated PBDEs to the sediments. To determine whether debromination occurred in the riverine environments, we compared the debromination indices (designated as the ratios of the concentrations of nona-BDEs to BDE-209, and % BDE-209) of the sediment samples with those of the leachate samples (Fig. 3.8). Debromination of BDE-209 may have occurred in the canals and rivers in India (KKSC2, KKSC4), Thailand (St.F, St.H) and the Philippines (MC3) as indicated by the higher nona-BDEs/BDE209 ratios in the sediments than in the leachates. Debromination has been reported to occur under anaerobic microbial conditions (Gerecke et al., 2005; He et al., 2006; Robrock et al., 2008; Tokarz et al., 2008); in particular, BDE-209 to BDE-206, 207, 208 in anaerobic sediment microcosms (Tokarz et al., 2008). Tokarz et al. (2008) observed that BDEs 206 and 207 were further degraded to BDEs 196, 197, 191, 184, 154, 128, 119, 99, 66, 47, 49, 28, 17; BDE-99 to BDE-66 and BDE-28; and BDE-47 to BDE-17. Because bottom sediments are normally more anaerobic than the water column, debromination probably occurred in the bottom sediments.

One of the techniques that would determine the anaerobic and redox conditions of sediments would be to utilize the isomer compositions of linear alkyl benzenes (LABs) in sediments. LABs

are ubiquitously observed in sediments from urban aquatic environments because of their persistence and hydrophobicity (Takada and Eganhouse, 1998). They are feedstock for the common anionic surfactants, linear alkylbenzene sulfonates (LAS), and are contained in significant amounts in synthetic detergents. LAB homologs consist of both internal (I) isomers (i.e., isomers in which the substitutional positions are near the center of the alkyl chain) and external (E) isomers (i.e., isomers in which the phenyl substitutional positions are near the terminal end of the alkyl chain and are more susceptible to aerobic microbial degradation). The concentration ratio of I to E isomers (I/E ratio) of sedimentary LABs would indicate the degree of aerobic biodegradation, and the redox conditions in the sediments (i.e., a low I/E ratio would mean anaerobic sedimentary conditions) (Takada and Ishiwatari, 1990; Isobe et al., 2004). Untreated sewage was found to have I/E ratios of around 0.7, whereas aerobically treated sewage (secondary effluents) had I/E ratios of around 3.5 (Takada and Eganhouse, 1998). LABs were measured in most of the sediment samples (Isobe et al., 2004), and the data are utilized in the present study. The bottom sediments from the selected tropical Asian countries generally showed lower I/E ratios ranging from 1.0 to 2.9 (Table 3.1), indicating anaerobic conditions probably due to larger inputs of organic matter from untreated wastewater. In particular, the I/E ratios in the sediment samples from India (KKSC2, KKSC4, INCH4, INCH9) and Indonesia (J2) were low at 1.0 to 1.6, indicating extreme anaerobic conditions. Correspondingly, debromination was evidently substantiated (i.e., % BDE-209 was less than 50%) in those sediment samples (Tables 3.1, 3.3). This may confirm the occurrence of debromination in anaerobic sediments from the selected tropical Asian countries. However, there were also samples with I/E ratios lower than 1.6 (i.e., extreme anaerobic conditions) that exhibited higher % BDE-209 (i.e., a condition of suppressed debromination), instead of lower % BDE-209 (i.e., to indicate a mediated or facilitated debromination) (Fig. 3.9). BDE-209 and LABs exhibit different structures; and therefore will follow different metabolic mechanisms. Some factors other than anaerobic conditions may have controlled the debromination of BDE-209 in those sediments; for example, the presence of specific microorganisms that would favor anaerobic debromination of PBDEs, as hinted by He et al. (2006). In addition, the greater availability of natural sunlight in shallower bodies of

water may induce photolytic debromination of BDE-209. Tropical Asian countries generally have intense and prolonged levels of solar radiation. Further studies would be needed to verify the occurrence of debromination in aquatic environments.

### **3.4. Conclusion**

The results of this study indicated widespread occurrence of PBDEs in the surface sediments from urban areas of the selected tropical Asian countries. BDE-209 was predominant in most of the sediment samples. The concentration levels of sedimentary BDE-209 in the tropical Asian countries studied (including countries with comparatively lower GDP per capita, such as Lao PDR and Cambodia) were higher than those in highly urbanized and industrialized countries. The debromination of BDE-209 to nona-BDE congeners in several anaerobic sediment samples was suggested. The amount of PBDEs in the aquatic environment (e.g., in the sediments in tropical Asian countries) may be correlated to the GDP per capita, and to the quantity of PBDEs contained in MSWDS. Without controlled use of PBDE-laden products, and improved management of PBDE-containing waste, tropical Asian countries may possibly have a significant contribution to the global distribution of PBDEs.

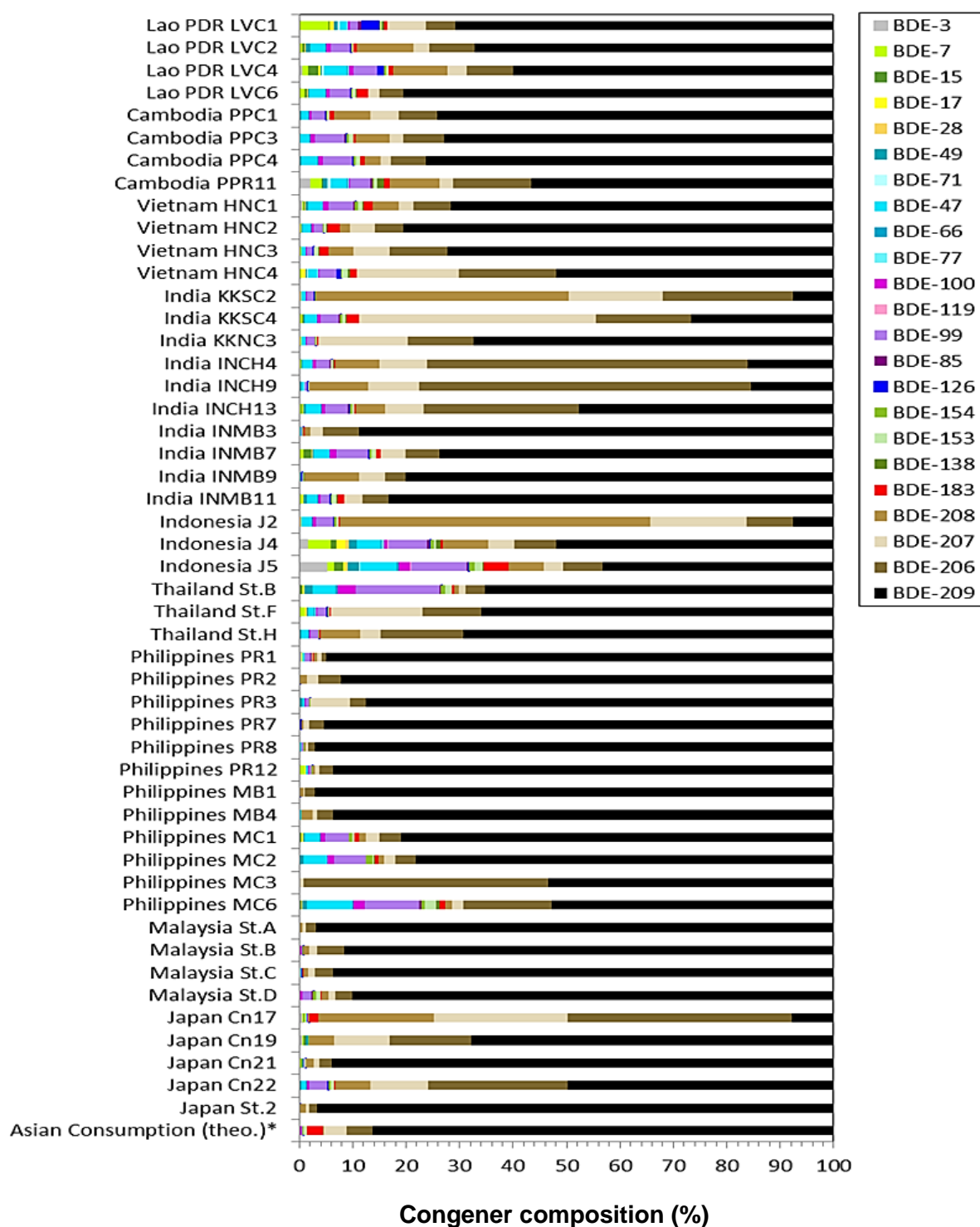


Fig. 3.1. Distribution of PBDE congeners in the sediments from urban cities of tropical Asian countries and from Japan. \*Estimated from the consumption pattern of the technical PBDE mixtures in Asia (BSEF, 2012) and the composition of the technical mixtures (La Guardia et. al., 2006).



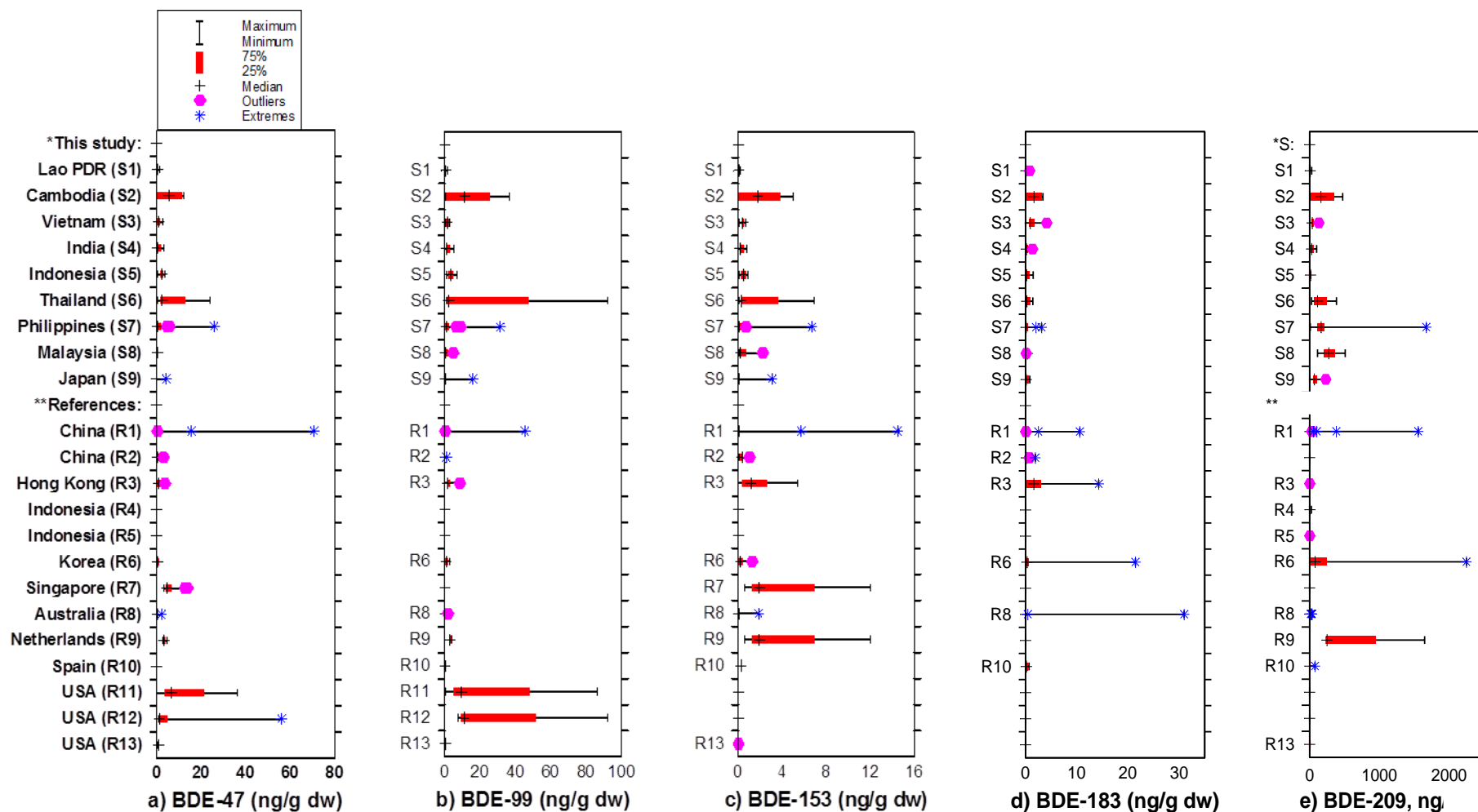


Fig. 3.2. Comparison of the concentrations of BDEs 47, 99, 153, 183 and 209 in the sediments from urban areas of tropical Asian countries and Japan, and with those from other locations around the world.

\*This study: Lao PDR (S1) to Japan (S9).

\*\*References: (R1) Beijiang River - Chen et al., 2009; (R2) Pearl River Delta - Zheng et al., 2004; (R3) Marine - Liu et al., 2005; (R4) Surabaya rivers, (R5) Surabaya coasts - Ilyas et al., 2011; (R6) Bays: Busan, Ulsan and Jinhae - Moon et al., 2007; (R7) Southeast and Northeast coasts - Wurl and Obbard, 2005; (R8) Industrial and urban - Toms et al., 2008; (R9) Scheldt Estuary - Verslycke et al., 2005; (R10) Coastal - Eljarrat et al., 2005; (R11) Polyurethane foam manufacturing facility - Hale et al., 2002; (R12) Niagara River - Samara et al., 2006; (R13) San Francisco Bay - Klosterhaus et al., 2012.

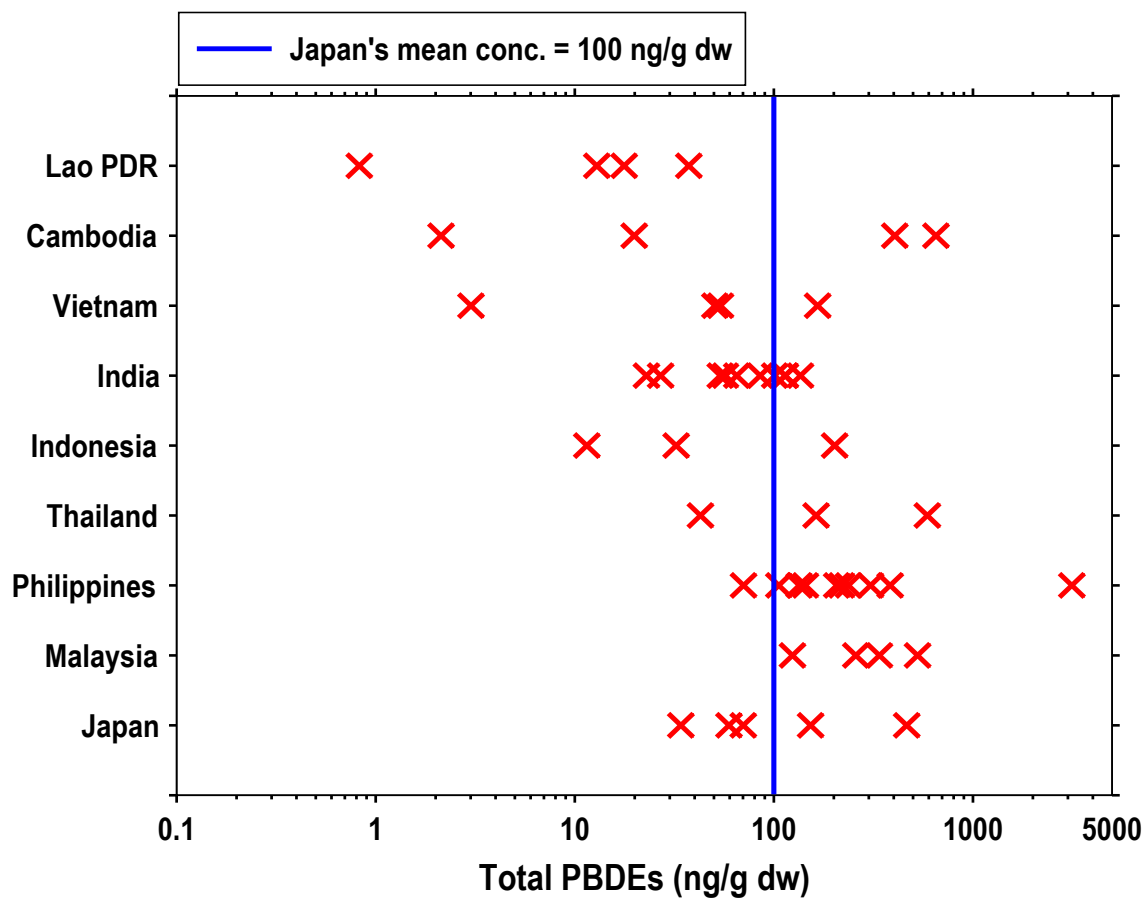


Fig. 3.3. Total PBDEs in the sediment samples from tropical Asian countries and from Japan.

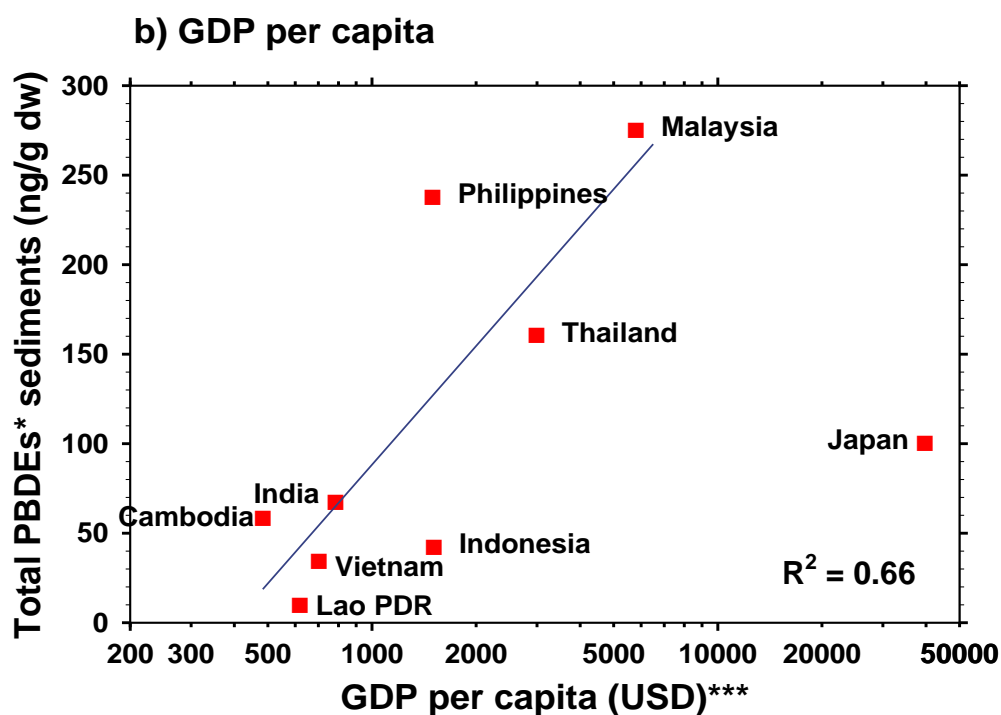
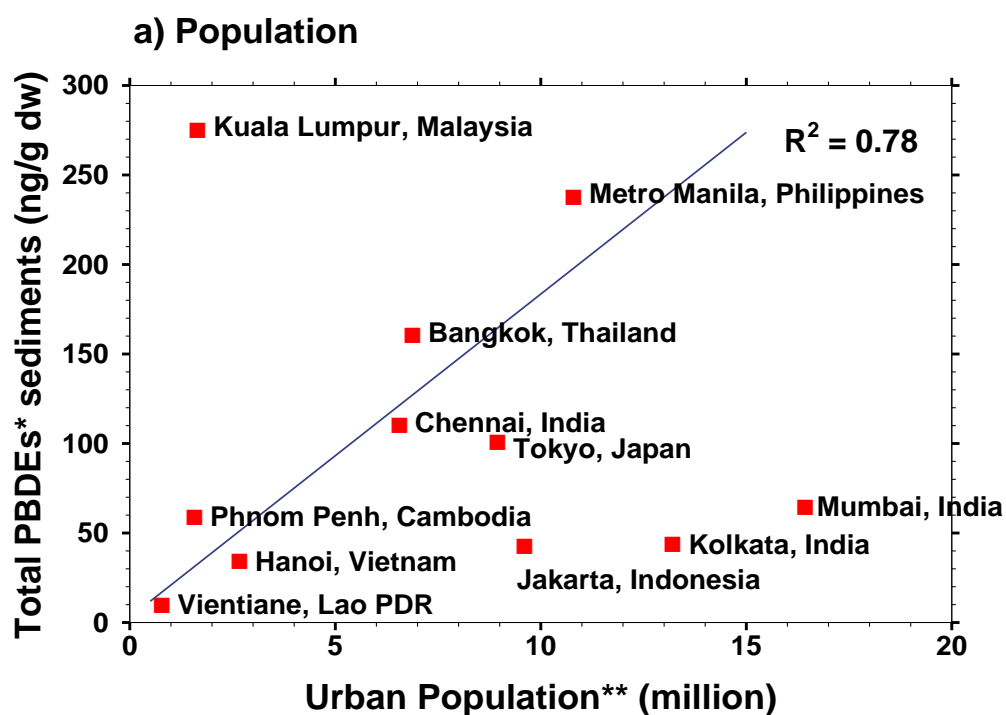


Fig. 3.4. Total PBDEs in sediments vs. (a) urban population, and (b) GDP per capita of the selected tropical Asian countries.

\*Geometric mean of all samples per country.

\*\*Based on available data (<http://www.unstats.un.org>).

\*\*\*Geometric mean in year 2000 and 2010 (World Bank, 2010).

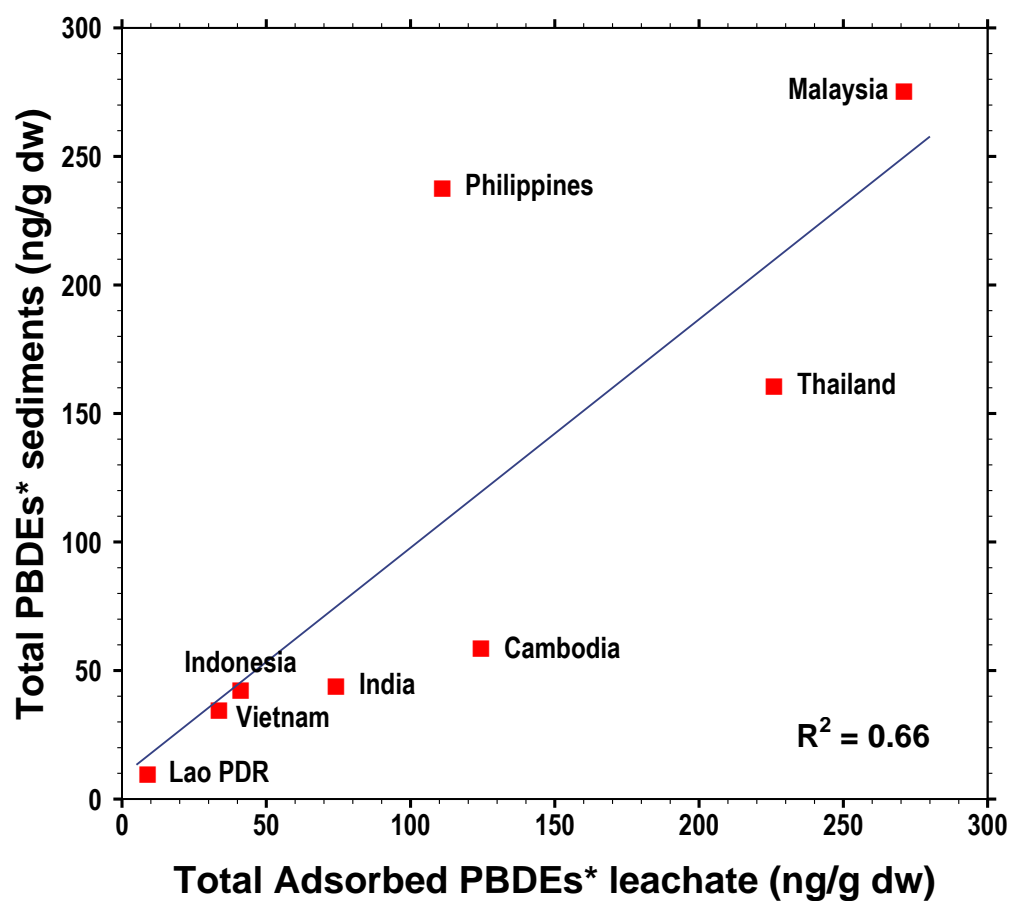


Fig. 3.5. Total PBDEs in sediments vs. total adsorbed PBDEs in the landfill leachates from the selected tropical Asian countries. Data of total adsorbed PBDEs in the landfill leachates is found in Chapter 2 Table 2.3a.

\*Geometric mean of all samples per country.

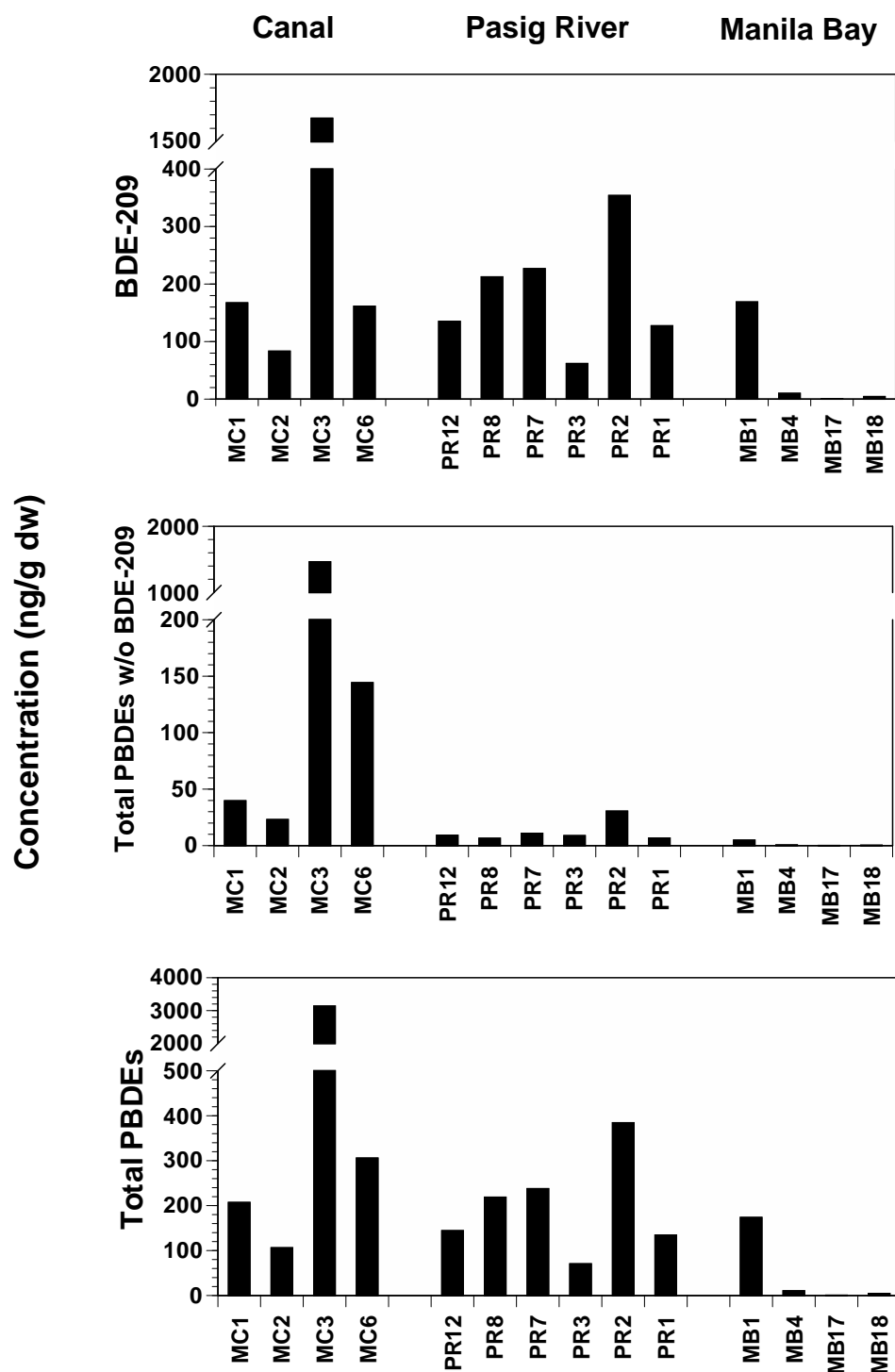


Fig. 3.6. Spatial distribution of sedimentary BDE-209, total PBDEs without BDE-209, and total PBDEs in the Philippines (Pasig River System and Manila Bay).

\*Manila Canals: MC 1, 2, 3, 6 are tributaries of the Pasig River.

\*\*Pasig River: upstream to downstream, PR 12, 8, 7, 3, 2, 1 flowing towards Manila Bay.

\*\*\*Manila Bay: near-shore to off-shore from the Pasig River, MB 1, 4, 17, 18.

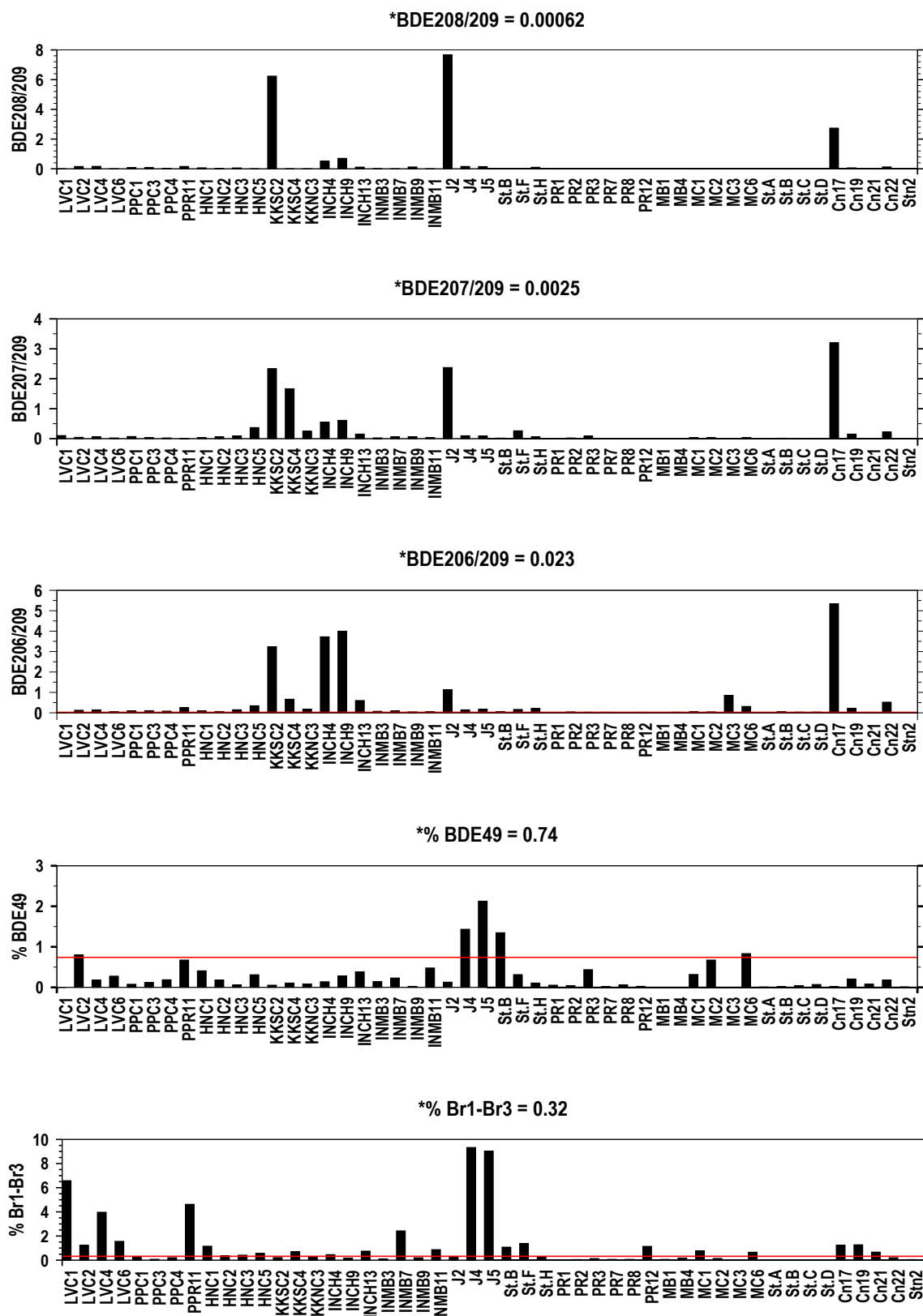


Fig. 3.7. Comparison of the concentration ratios of BDE208/209, BDE207/209 and BDE206/209, % BDE49 and % Br1-Br3 in the sediments from tropical Asian countries and from Japan, to the corresponding ratios and % in the technical deca-BDE mixture.

\* From the compositional analysis of the technical deca-BDE mixture (indicated by red lines; La Guardia et al., 2006).

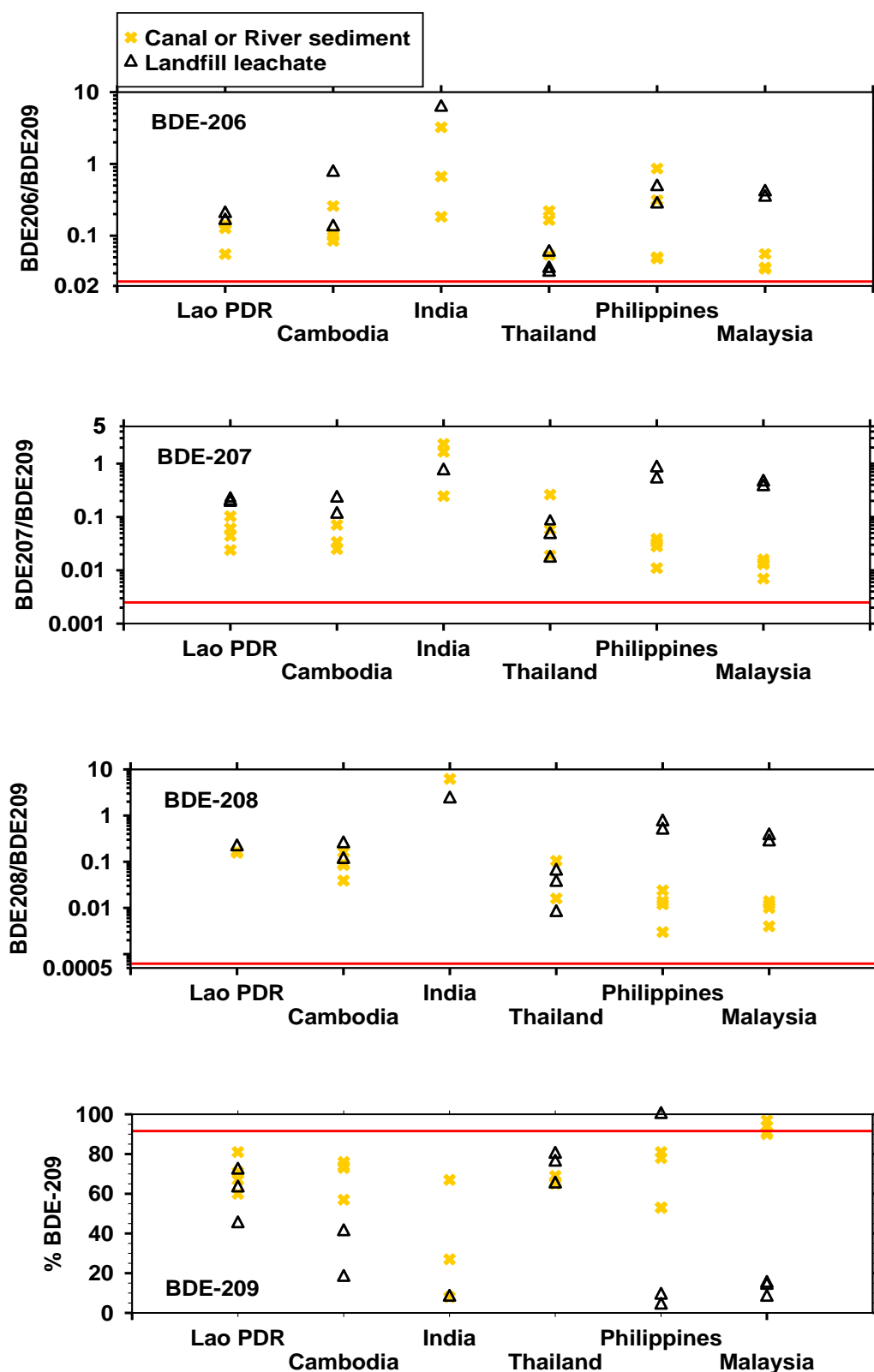


Fig. 3.8. Debromination indices of BDEs 206, 207, 208, 209 in the sediments and in the landfill leachate samples from Lao PDR, Cambodia, India, Thailand, the Philippines and Malaysia. Debromination index for each of the nona-BDEs is computed as the ratio of the concentrations of BDEs 206, 207, 208 to BDE-209 in the sample. The ratios of BDE206/209 (0.023), BDE207/209 (0.0025), BDE208/209 (0.00062) and the % BDE-209 (91.6) in the technical deca-BDE mixture (La Guardia et al., 2006) are indicated by red lines in the corresponding plots.

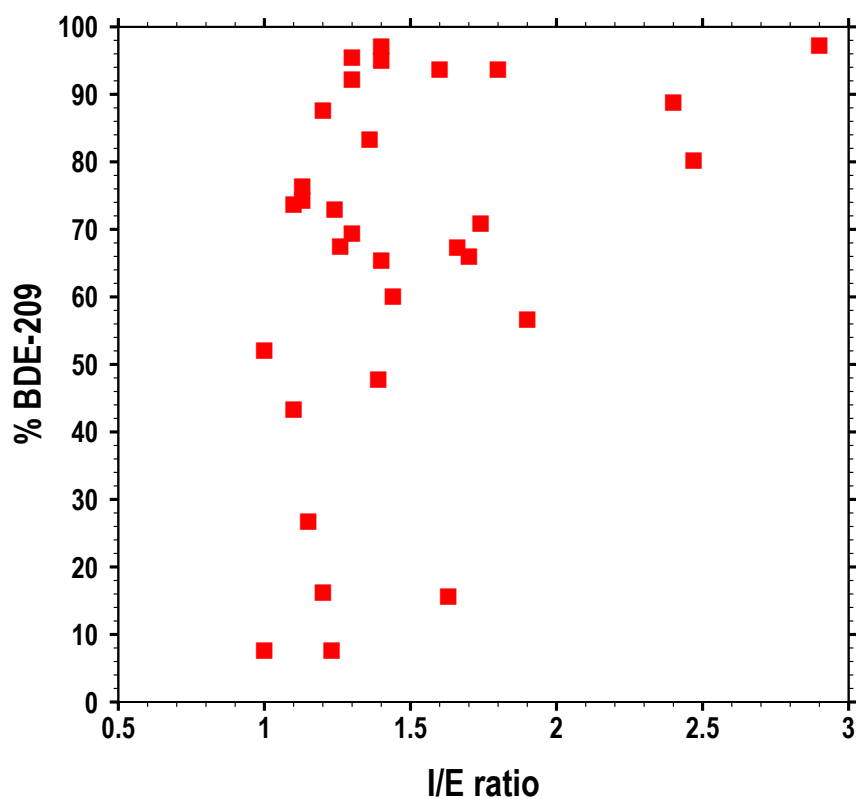


Fig. 3.9. I/E ratios vs. % BDE-209 in the sediment samples from tropical Asian countries. I/E ratio is the concentration ratio of the internal (I) isomers (i.e., isomers in which the substitutional positions are near the center of the alkyl chain) to the external (E) isomers (i.e., isomers in which the phenyl substitutional positions are near the terminal end of the alkyl chain) of linear alkyl benzenes in the sediments.



Table 3.1 Sample information on the sediment samples from tropical Asian countries.

Country	City Location	Water Body	Date of Sampling	Sample Code	Coordinates (deg. min. sec., deg. min. sec.)	Depth m	LAB <sup>a</sup> concentration (ng/g dw)	I/E Ratio <sup>b</sup>
Lao PDR	Vientiane	Canals	2005 December 16	LVC1	N 17 58 34.0, E 102 38 53.7	1	1,960	1.74
				LVC2	N 17 58 4.4, E 102 38 32.8	0.5	2,000	1.66
				LVC4	N 17 57 55.8, E 102 38 4.7	0.3	6,360	1.44
				LVC6	N 17 58 30.3, E 102 36 18.8	0.4	No data	No data
Cambodia	Phnom Penh	Canals	2004 September 11	PPC1	N 11 33 14.3, E 104 55 09.4	0.5	404	1.13
				PPC3	N 11 33 15.9, E 104 54 00.5	0.5	3,310	1.24
				PPC4	N 11 32 49.0, E 104 53 51.0	0.5	5,100	1.13
		Basac River		PPR11	N 11 30 10.6, E 104 56 27.9	10	14	1.90
Vietnam	Hanoi	Canals	2007 July 22	HNC1	N 20 58 28.7, E 105 51 51.8	1	No data	No data
				HNC2	N 20 59 45.9, E 105 51 43.9	1	No data	No data
				HNC3	N 21 0 26, E 105 51 39.1	1	No data	No data
				HNC5	N 20 58 33.9, E 105 51 55.4	1	No data	No data
India	Kolkata	Canals	2006 May 30	KKSC2	N 22 31 1.23, E 88 20 24.75	3	7,800	1.23
				KKSC4	N 22 32 7.2, E 88 23 48.5	2	8,920	1.15
	Chennai	Canal: Bakingham Adyar River	2006 May 29	KKNC3	N 22 36 10.9, E 88 25 0.1	2	8,410	1.26
			2007 December 8	INCH4	N 13 1 28.1, E 80 15 30.2	1	21,600	1.20
			2007 December 9	INCH9	N 13 0 47.0, E 80 15 32.6	2	13,900	1.63
	Mumbai	Canal: Malad Creek Canal: city sewage Canal: Malad Creek Mahim River	2007 December 11	INCH13	N 13 4 20.5, E 80 16 31.2	2	50,600	1.39
				INMB3	N 19 9 50.2, E 72 49 2.4	3	3,700	2.40
				INMB7	N 19 8 16.6, E 72 49 54.1	0.5	18,200	1.10
				INMB9	N 19 9 15.3, E 72 48 36.7	2	335	2.47
				INMB11	N 19 2 59.9, E 72 52 25.1	2	7,760	1.36
Indonesia	Jakarta	Canals	2000 September 28	J2	S 06 07 36.9, E 106 48 34.5	0.5	28,200	1.00 <sup>c</sup>
				J4	S 06 06 32.2, E 106 54 24.3	3	6,380	1.01
			2000 September 29	J5	S 06 07 03.9, E 106 47 02.9	3	34,000	1.07
Thailand	Bangkok	Canal: Samrong	2003 May 15	St.B	No GPS data	2	14,100	1.44
		Canal: Yai bridge	2003 May 17	St.F	No GPS data	2	1,340	1.67
		Canal: Banglumpoo		St.H	No GPS data	3	6,770	1.28

Table 3.1 Continuation

Country	City Location	Water Body	Date of Sampling	Sample Code	Coordinates (deg. min. sec., deg. min. sec.)	Depth m	LAB <sup>a</sup> concentration (ng/g dw)	I/E Ratio <sup>b</sup>
Philippines	Metro Manila	Pasig River	2002 September 11	PR1	N 14 35 31, E 120 56 51	5	1,370	1.43
				PR2	N 14 36 45, E 120 58 59	10	13,000	1.31
			2002 September 12	PR3	N 14 35 45, E 120 58 38	10	2,030	1.18
				PR7	N 14 36 46, E 121 0 8	5	8,500	1.27
				PR8	N 14 36 31, E 121 1 58	5	1,730	1.43
				PR12	N 14 33 30, E 121 4 2	2	514	1.55
		Manila Bay - 2 km away from the mouth of the Pasig River	2002 September 11	MB1	No GPS data	7	2,310	2.93
		Manila Bay - 8 km away from the mouth of the Pasig River		MB4	No GPS data	25	586	1.80
		Manila Bay - 20 km away from the mouth of the Pasig River	2009 December 16	MB17	N 14 36 21, E 120 45 4	21	No data	No data
		Manila Bay - 25 km away from the mouth of the Pasig River		MB18	N 14 35 54, E 120 41 44	22	No data	No data
	Metro Manila	Manila Canals: (Pasig River tributaries)	2010 December 12					
		Pateros/Taguig River		MC1	N 14 32 44.9, E 121 3 55.3	1	No data	No data
		Ilugin River		MC2	N 14 33 16.6, E 121 5 35.6	2	No data	No data
		Marikina River		MC3	N 14 33 58.4, E 121 4 30.5	3	No data	No data
		Canal: Estero de Binondo		MC6	N 14 35 48.7, E 120 58 29.1	6	No data	No data
Malaysia	Kuala Lumpur	Klang River	2004 July 20	St.A	N 03 02 46.9, E 101 26 49.1	7	No data	No data
				St.B	N 03 03 19.7, E 101 25 30.4	5	No data	No data
				St.C	N 03 02 44.0, E 101 24 31.7	5	No data	No data
				St.D	N 03 02 02.7, E 101 23 30.5	3	No data	No data
Japan	Tokyo	Tokyo Bay - sewage and urban run-off	2008 October 25	Cn17	N 35 38 29.1, E 139 44 54.1	4	15,100	3.91
		Tokyo Bay - moderately combined with sewer overflow		Cn19	N 35 37 43.1, E 139 44 54.1	5	34,800	3.36
		Tokyo Bay - moderately combined with sewer overflow		Cn21	N 35 35 43.0, E 139 44 51.0	6	1,580	3.13
		Tokyo Bay - sewage and urban run-off		Cn22	N 35 35 49.6, E 139 44 30.6	6	8,730	1.29
		Tokyo Bay - estuarine		Stn2	N 35 38 12.3, E 139 45 45.6	15	696	2.69

<sup>a</sup>Linear alkylbenzenes. <sup>b</sup>I/E ratio is the concentration ratio of the internal (I) isomers (i.e., isomers in which the substitutional positions are near the center of the alkyl chain) to the external (E) isomers (i.e., isomers in which the phenyl substitutional positions are near the terminal end of the alkyl chain) of linear alkylbenzenes in the sediments. <sup>c</sup>I/E ratios from 2000 to 2003 were taken from Isobe et al. (2004).

Table 3.2 Statistical evaluation of the concentrations of BDE-209 and the ratios of BDE 207/209 and BDE 206/209 in the NIST SRM 1941b marine sediment analyzed in 2004 and 2012.

Sample	BDE-209 (ng/g dw)		BDE 207/209 (%)		BDE 206/209 (%)	
	2004	2012	2004	2012	2004	2012
1	16.7	16.9	6.68	10.3	10.4	8.45
2	15.0	17.1	6.78	9.29	11.1	4.81
3	17.1	17.0	5.86	6.24	12.2	4.59
4	17.6		5.59		12.5	
T-Test: Two-Sample Assuming Equal Variances ( $\alpha = 0.05$ )						
	Variable 1	Variable 2	Variable 1	Variable 2	Variable 1	Variable 2
Mean	16.6	17.0	6.22	8.62	11.6	5.95
Variance	1.24	0.00734	0.352	4.53	0.889	4.69
Observations	4	3	4	3	4	3
Pooled Variance		0.749		2.02		2.41
df		5		5		5
t Stat		-0.654		-2.21		4.73
P(T<=t) one-tail		0.271		0.0392		0.00261
t Critical one-tail		2.02		2.02		2.02
P(T<=t) two-tail		0.542		0.0785		0.00521
t Critical two-tail		2.57		2.57		2.57
Interpretation		MNSD <sup>a</sup>		MNSD		MSD <sup>b</sup>

<sup>a</sup>Means are not statistically different.

<sup>b</sup>Means are statistically different.

Table 3.3 Sedimentary PBDEs in rivers, canals and coastal areas in urban cities of tropical Asian countries including Japan.

Country	Sample Code	PBDE Concentration (ng/g dw)									
		Br1 BDE-3	Br2 BDE-7 BDE-15		Br3 BDE-17 BDE-28		Br4 BDE-49 BDE-71 BDE-47 BDE-66 BDE-77				
Lao PDR	LVC1	<LOD <sup>a</sup>	0.049	<LOD	0.0058	<LOD	<LOD	<LOD	<LOD	<LOD	0.0016
	LVC2	0.026	0.082	0.071	0.018	0.021	0.142	<LOD	0.508	0.016	0.012
	LVC4	0.075	0.135	0.249	0.046	0.0059	0.024	0.071	0.529	0.047	0.023
Cambodia	LVC6	0.0083	0.403	0.116	0.0084	0.049	0.104	0.0024	1.08	0.120	0.010
	PPC1	0.0015	0.017	0.017	<LOD	0.0088	0.015	<LOD	0.267	0.030	<LOD
	PPC3	0.035	0.130	0.119	0.084	0.106	0.804	0.088	10.9	0.663	0.010
Vietnam	PPC4	0.124	0.139	0.049	0.122	0.423	0.761	0.024	12.0	0.929	0.104
	PPR11	0.046	0.046	0.0070	<LOD	<LOD	0.015	0.014	0.067	0.0060	<LOD
	HNC1	0.353	0.052	0.067	0.072	0.044	0.206	0.0037	1.43	0.019	0.023
India	HNC2	0.053	0.224	0.080	0.149	0.092	0.298	0.0058	2.58	0.232	0.133
	HNC3	0.050	0.121	0.029	0.004	0.019	0.032	0.011	0.359	0.043	0.0013
	HNC5	<LOD	<LOD	<LOD	0.017	<LOD	0.0094	0.0032	0.055	<LOD	0.0017
Indonesia	KKSC2	<LOD	0.077	0.030	0.010	<LOD	0.029	0.0046	0.442	0.017	0.0013
	KKSC4	<LOD	0.097	0.067	0.0020	0.026	0.029	<LOD	0.615	0.010	0.017
	KKNC3	<LOD	0.059	0.066	0.015	0.038	0.048	0.0094	0.445	0.014	0.0014
Thailand	INCH4	0.029	0.368	0.033	0.037	0.158	0.189	0.016	2.56	0.070	0.044
	INCH9	0.033	0.017	0.049	0.050	0.0056	0.239	0.0069	0.376	<LOD	0.012
	INCH13	0.294	0.237	0.099	0.207	0.024	0.439	0.090	3.10	0.226	0.013
Philippines	INMB3	0.022	0.029	0.036	0.019	0.0020	0.164	0.0036	0.123	<LOD	<LOD
	INMB7	0.183	0.335	1.03	0.009	0.023	0.151	<LOD	1.94	0.104	<LOD
	INMB9	0.0047	0.029	0.0090	<LOD	0.0027	0.0059	0.0048	<LOD	<LOD	0.010
Japan	INMB11	0.189	0.351	0.108	0.129	0.109	0.485	0.026	1.97	0.195	0.0043
	J2	0.119	0.121	0.127	0.041	0.232	0.260	0.025	3.83	0.217	0.023
	J4	0.184	0.487	0.130	0.198	0.075	0.165	0.012	0.497	0.027	0.045
Malaysia	J5	1.68	0.426	0.513	0.140	0.153	0.686	0.103	2.14	0.164	0.027
	St.B	0.875	0.342	2.01	1.45	1.68	7.95	1.09	23.8	2.66	0.042
	St.F	0.033	0.390	0.059	0.039	0.072	0.135	0.0090	0.472	0.0070	0.102
Philippines	St.H	0.118	0.094	0.071	0.014	0.080	0.176	0.014	2.15	0.177	0.043
	PR1	0.651	<LOD	0.010	0.014	0.020	0.072	<LOD	0.47	<LOD	ND <sup>b</sup>
	PR2	0.040	0.112	0.016	0.029	0.010	0.173	0.012	0.081	0.0068	0.016
Japan	PR3	0.017	0.0075	0.032	0.028	0.011	0.309	<LOD	0.348	0.035	<LOD
	PR7	0.0041	0.088	0.053	0.013	0.013	0.057	<LOD	0.262	0.019	0.0058
	PR8	0.038	0.0085	0.025	0.043	0.037	0.129	0.0018	0.743	0.017	<LOD
Philippines	PR12	0.225	1.28	0.126	0.012	0.011	0.039	0.012	0.650	0.070	0.019
	MB1	0.020	0.063	0.017	0.015	<LOD	<LOD	<LOD	0.014	0.011	<LOD
	MB4	0.0021	0.0078	0.0071	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Philippines	MB17	ND	<LOD	ND	ND	ND	ND	ND	0.0077	ND	ND
	MB18	<LOD	ND	ND	ND	ND	ND	ND	<LOD	ND	ND
	MC1	0.433	ND	0.527	0.213	0.444	0.659	ND	5.71	0.367	ND
Malaysia	MC2	0.058	ND	0.040	ND	0.056	0.715	0.042	4.60	0.124	ND
	MC3	ND	<LOD	<LOD	ND	0.040	0.105	<LOD	0.969	<LOD	ND
	MC6	ND	ND	1.33	ND	0.688	2.55	ND	25.8	0.768	ND
Japan	St.A	0.012	0.012	0.013	0.0063	0.012	0.057	<LOD	0.224	0.016	<LOD
	St.B	0.0028	<LOD	<LOD	<LOD	0.0033	0.030	<LOD	0.238	0.026	<LOD
	St.C	0.017	0.020	0.040	0.0075	0.034	0.136	0.0090	0.587	0.100	0.017
Japan	St.D	0.012	0.036	0.0076	0.023	0.018	0.184	0.011	0.383	0.030	0.011
	Cn17	0.218	0.040	0.119	0.010	0.036	0.0078	0.0017	0.072	0.019	0.0036
	Cn19	1.04	0.054	0.772	0.089	0.0022	0.318	0.014	0.089	0.019	0.041
Japan	Cn21	0.130	0.087	0.135	0.031	0.014	0.048	0.0093	0.042	0.0090	0.020
	Cn22	0.128	0.082	0.213	0.463	0.066	0.839	0.127	4.26	0.084	0.013
	Stn 2	0.019	0.0028	0.011	0.00085	0.0015	0.0092	<LOD	0.016	0.0022	<LOD
LODs, ng/g dw		0.003	0.002	0.002	0.003	0.002	0.009	0.006	0.02	0.007	0.0003
Lao PDR		0.0009	0.002	0.0008	0.002	0.007	0.002	0.007	0.02	0.004	0.004
Cambodia		0.05	0.02	0.007	0.002	0.007	0.0006	0.003	0.006	0.004	0.0004
Vietnam and India (Kolkata)		0.002	0.002	0.004	0.002	0.0008	0.005	0.003	0.02	0.007	0.004
India (Chennai and Mumbai)		0.01	0.007	0.006	0.003	0.004	0.003	0.00003	0.004	0.00007	0.0007
Indonesia		0.0003	0.009	0.007	0.006	0.01	0.006	0.009	0.02	0.007	0.009
Thailand and Malaysia		0.0008	0.002	0.001	0.001	0.00	0.002	0.000	0.00	0.030	0.020
Philippines (PR1)		0.02	0.002	0.006	0.002	0.003	0.002	0.0004	0.006	0.001	0.003
Philippines (PR2, 8)		0.00006	0.003	0.006	0.005	0.006	0.009	0.009	0.01	0.01	0.005
Philippines (PR3, 7, 12/MB1,4)		0.004	0.005	0.004	0.01	0.01	0.005	0.005	0.00	0.01	0.02
Philippines (MB17)		0.01	0.01	0.01	0.03	0.03	0.02	0.02	0.01	0.02	0.04
Philippines (MB18)		0.02	0.02	0.02	0.05	0.04	0.03	0.02	0.02	0.04	0.07
Philippines (MC1,2,3,6)		0.003	0.003	0.0008	0.0004	0.0008	0.003	0.003	0.006	0.002	0.0007
Japan											

<sup>a</sup>LOD (ng/g dw) : Limit of Detection of BDE congeners (ng/g dw) = (3 x BDE congener concentration in the blank sample (pg/μL) for corresponding batch x μL sample volume) / (1000 x dry wt. sample (g)). To correlate individual samples to the corresponding LOD, LOD is tabulated according to country (ies) included in the batch. A batch of analysis is composed of 4-6 samples with one blank sample; blank values varied among the batches.

<sup>b</sup>Not detected by the instrumental analysis.

Table 3.3 Continuation

Country	Sample Code	PBDE Concentration (ng/g dw)												
		Br5					Br6			Br7	Br9			Br10
		BDE-100	BDE-119	BDE-99	BDE-85	BDE-126	BDE-154	BDE-153	BDE-138	BDE-183	BDE-208	BDE-207	BDE-206	BDE-209
Lao PDR	LVC1	0.0052	ND <sup>a</sup>	0.013	0.0060	0.029	<LOD <sup>b</sup>	<LOD	0.0032	0.0060	ND	0.066	<LOD	0.643
	LVC2	0.139	0.018	0.644	0.014	0.0030	0.043	0.033	0.0019	0.110	1.86	0.526	1.51	11.9
	LVC4	0.095	<LOD	0.581	0.020	0.132	0.054	0.066	0.0051	0.111	1.29	0.469	1.12	7.72
	LVC6	0.232	0.018	1.37	0.101	0.0070	0.113	0.210	0.082	0.812	ND	0.729	1.67	30.1
Cambodia	PPC1	0.079	<LOD	0.535	0.022	<LOD	0.042	0.080	0.016	0.153	1.34	1.05	1.44	14.8
	PPC3	5.62	0.182	36.4	2.11	0.366	2.86	5.01	0.751	3.18	40.5	16.4	50.4	475
	PPC4	3.54	<LOD	22.0	0.761	0.311	1.67	3.50	0.175	3.41	12.0	7.80	26.2	309
	PPR11	<LOD	<LOD	0.082	0.012	ND	<LOD	<LOD	0.027	0.204	<LOD	0.325	1.26	2.13
Vietnam	HNC1	0.510	0.025	2.35	0.118	0.0069	0.266	0.416	0.089	0.914	2.49	1.38	3.51	36.3
	HNC2	0.564	0.0035	2.99	0.027	0.072	0.305	0.710	0.069	4.14	3.22	7.54	8.85	134
	HNC3	0.110	0.0028	0.598	0.039	0.018	0.057	0.387	0.188	0.931	2.46	3.66	5.82	38.9
	HNC5	0.010	0.00071	0.097	0.0026	0.021	0.0056	0.031	0.016	0.035	ND	0.584	0.548	1.58
India	KKSC2	0.166	0.0045	0.714	0.020	0.0030	0.081	0.043	0.0087	0.048	25.4	9.49	13.2	4.07
	KKSC4	0.153	0.0022	0.951	0.047	0.014	0.100	0.164	0.024	0.633	ND	12.0	4.80	7.20
	KKNC3	0.151	0.0074	0.821	0.011	0.0061	0.052	0.098	0.030	0.171	ND	9.48	7.06	38.5
	INCH4	0.719	0.033	3.63	0.208	0.060	<LOD	0.489	0.236	0.187	11.4	12.1	81.9	22.0
	INCH9	0.085	0.010	0.416	0.019	0.103	0.041	0.061	0.028	0.068	9.37	8.13	53.0	13.3
	INCH13	0.892	<LOD	4.86	0.269	0.086	0.409	0.479	0.015	0.257	6.26	8.43	33.0	54.6
	INMB3	0.060	<LOD	0.257	0.012	0.013	0.062	0.104	0.038	0.181	1.23	2.66	7.77	102
	INMB7	0.778	<LOD	3.82	0.072	0.126	0.274	0.472	0.092	0.490	ND	2.99	4.27	48.0
	INMB9	<LOD	<LOD	<LOD	0.0025	0.038	<LOD	<LOD	0.049	0.019	2.34	1.10	0.873	18.4
	INMB11	0.450	<LOD	1.72	0.126	0.083	0.331	0.735	0.182	1.37	ND	3.43	4.98	84.3
	J2	1.29	0.026	6.61	0.177	0.053	0.738	0.894	0.171	0.223	118	36.5	17.4	15.4
Indonesia	J4	0.083	0.024	0.818	0.075	0.010	0.075	0.043	0.096	0.045	0.970	0.582	0.886	5.98
	J5	0.653	0.041	3.36	0.151	0.026	0.351	0.477	0.056	1.50	2.12	1.20	2.36	13.9
	St.B	20.9	0.149	92.3	1.31	<LOD	4.89	6.95	0.704	1.43	6.12	7.38	20.7	385
Philippines	St.F	0.152	<LOD	0.694	0.045	<LOD	0.081	0.075	0.022	0.086	ND	7.39	4.67	28.2
	St.H	0.549	0.0094	2.31	0.056	<LOD	0.143	0.252	<LOD	0.270	11.9	6.51	25.0	113
	PR1	0.275	<LOD	1.41	0.100	<LOD	0.138	0.249	0.055	0.144	1.01	0.92	1.2	127
	PR2	0.0093	<LOD	0.026	<LOD	0.011	0.010	0.0083	<LOD	0.366	4.40	8.29	16.8	354
	PR3	0.115	<LOD	0.441	<LOD	<LOD	0.045	0.064	<LOD	0.047	ND	5.23	1.97	61.7
	PR7	0.051	<LOD	0.227	<LOD	<LOD	0.029	0.024	<LOD	0.024	1.20	2.15	6.58	227
	PR8	0.030	<LOD	0.851	<LOD	<LOD	0.173	0.192	0.025	0.109	0.427	1.00	2.53	212
	PR12	0.125	0.061	0.761	<LOD	<LOD	0.111	0.045	0.020	0.033	0.656	1.18	3.67	135
	MB1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1.04	0.610	3.04	169
	MB4	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.217	<LOD	0.311	9.74
	MB17	<LOD	ND	<LOD	ND	ND	ND	ND	ND	ND	ND	<LOD	ND	0.543
	MB18	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.104	0.124	4.16
	MC1	1.75	ND	8.91	0.045	ND	1.47	0.691	0.026	2.05	2.42	5.46	8.41	167
	MC2	1.30	ND	6.37	ND	ND	1.18	0.374	0.144	0.721	0.994	2.30	3.99	83.1
	MC3	0.177	ND	0.954	<LOD	ND	0.136	0.089	<LOD	0.155	5.50	18.1	1.440	1.670
	MC6	6.43	ND	31.2	1.069	ND	1.78	6.70	2.09	3.15	3.84	6.34	50.5	161
	St.A	0.061	<LOD	0.297	<LOD	<LOD	0.056	0.136	0.031	0.378	1.89	3.61	10.1	510
	St.B	0.064	<LOD	0.361	<LOD	<LOD	0.050	0.053	0.021	0.141	1.34	1.87	6.33	114
	St.C	0.176	<LOD	0.804	0.048	0.040	0.108	0.229	0.0087	0.354	3.25	4.24	11.0	318
	St.D	0.603	0.020	4.78	0.367	0.143	1.41	2.22	0.275	0.363	3.16	3.29	8.40	232
Japan	Cn17	0.014	0.0023	0.034	<LOD	0.0049	0.035	0.029	0.023	0.576	7.33	8.56	14.3	2.68
	Cn19	0.022	0.014	0.189	0.0069	0.0061	0.074	0.040	0.063	0.138	6.95	15.9	23.5	104
	Cn21	0.0053	0.0033	0.072	0.012	0.048	0.0064	0.014	0.020	0.053	0.916	0.575	1.43	55.8
	Cn22	2.87	0.039	16.0	0.272	0.046	1.92	3.053	0.358	0.840	29.9	50.9	121	232
	Stn 2	0.0012	<LOD	0.016	0.0017	<LOD	<LOD	0.0085	0.0023	0.044	0.796	0.428	1.03	67.8
LODs, ng/g dw														
Lao PDR		0.002	0.004	0.004	0.004	0.0009	0.005	0.005	0.001	0.001	0.02	0.05	0.1	0.5
Cambodia		0.02	0.02	0.03	0.005	0.04	0.007	0.03	0.006	0.02	0.06	0.07	0.09	0.6
Vietnam and India (Kolkata)		0.004	0.0003	0.008	0.0004	0.003	0.004	0.02	0.002	0.02	0.05	0.04	0.07	0.7
India (Chennai and Mumbai)		0.006	0.01	0.04	0.002	0.005	0.02	0.009	0.005	0.003	0.03	0.04	0.08	0.7
Indonesia		0.002	0.0005	0.005	0.002	0.002	0.002	0.006	0.003	0.005	0.3	0.3	0.4	3
Thailand and Malaysia		0.01	0.02	0.02	0.02	0.04	0.006	0.01	0.01	0.01	0.05	0.1	0.2	1
Philippines (PR1)		0.00	0.00	0.00	0.00	0.04	0.002	0.02	0.00	0.02	0.07	0.0002	0.002	0.4
Philippines (PR2, 8)		0.003	0.002	0.008	0.003	0.004	0.004	0.002	0.007	0.008	0.4	0.4	0.4	3
Philippines (PR3, 7, 12/MB1,4)		0.01	0.02	0.02	0.02	0.04	0.02	0.02	0.02	0.02	0.04	0.2	0.1	2
Philippines (MB17)		0.005	0.01	0.01	0.01	0.01	0.005	0.01	0.01	0.004	0.003	0.01	0.002	0.004
Philippines (MB18)		0.01	0.02	0.02	0.02	0.03	0.01	0.02	0.02	0.02	0.04	0.03	0.03	0.1
Philippines (MC1,2,3,6)		0.02	0.03	0.03	0.03	0.05	0.02	0.02	0.03	0.03	0.003	0.009	0.02	0.07
Japan		0.001	0.002	0.001	0.0008	0.0009	0.004	0.002	0.0009	0.006	0.2	0.1	0.2	0.8

<sup>a</sup>Not detected by the instrumental analysis <sup>b</sup>LOD (ng/g dw): Limit of Detection of BDE congeners (ng/g dw) = (3 x BDE congener concentration in the blank sample (pg/L) for corresponding batch x µL sample volume) / (1000 x dry wt. sample (g)). To correlate individual samples to the corresponding LOD, LOD is tabulated according to country(ies) included in the batch. A batch of analysis is composed of 4-6 samples with one blank sample; blank values varied among the batches.

**Chapter 4**

**Historical Occurrences of Polybrominated Diphenyl Ethers and  
Polychlorinated Biphenyls in Manila Bay, Philippines,  
and in the upper Gulf of Thailand**



#### 4.1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of brominated flame retardants that are used as additives in many polymers for the manufacture of consumer products such as EEE, textiles, upholsteries, and in many types of plastics to reduce their flammability (BSEF, 2012; de Wit, 2002). Three types of PBDEs, the penta-, octa-, and deca-BDEs have been manufactured since the 1970s (Hardy, 2002). However, the benefits derived from PBDEs are outweighed by their negative impacts on the environment and on humans and wildlife, due to their persistence, potential to bioaccumulate, toxicity, and their capacity for long-range environmental transport (Rahman et al., 2001; de Wit 2002; Ross et al., 2009; Stockholm Convention, 2012). In 2009, tetra-, penta-, hexa-, and hepta-BDEs were added to the list of POPs by the Stockholm Convention. Since PBDEs are not chemically bound to their matrix, they can leach out and be readily mobilized in the environment through runoff from domestic and industrial sources, as landfill leachates, and from atmospheric deposition (de Wit, 2002). PBDEs share similar chemical structures with polychlorinated biphenyls (PCBs), and are presumed to have similar toxicological and environmental properties (Hardy, 2002). PCBs were commercially produced earlier (from the 1930s until the 1970s) than PBDEs (1970s onwards). They were widely used in electrical equipment and in a variety of industrial and household products (Hardy, 2002), at an estimated total global usage of 1.2 metric tons (Johannessen et al., 2008). However, they were banned starting in the late 1970s to early 1980s (Johannessen et al., 2008). PCBs are also classified as POPs under the Stockholm Convention (2012).

PBDEs are hydrophobic, therefore, they can bind to the particulate matter in the aquatic environment (Rahman et al. 2001; Hites, 2004) and accumulate over time in sediments. PCBs also adsorb to sediments and organic matter, especially the higher chlorinated PCBs (Hardy, 2002). Both PBDEs and PCBs are detected in various environmental matrices, including tissues of wildlife and humans. Therefore, proper management of these contaminants, including formulation of strategies and action plans for containment, is necessary. This requires a historical knowledge of the levels of contamination in the environment as well as the sources, fate, and transport mechanisms.



Sediment cores have been used to estimate historical deposition and trends of persistent environmental contaminants, whereby the chronology of contamination is linked to the measurement of  $^{210}\text{Pb}$  or  $^{137}\text{Cs}$  activities in the sediment layers as a function of depth and time (Hites, 2004; Covaci et al., 2005; Stern et al., 2005; Kohler et al. 2008). The pioneering study by Hites et al. (1977) on the historical record of sedimentary polycyclic aromatic hydrocarbons ushered the use of sediment cores to trace the history of accumulation of many pollutants, including PCBs, organochlorine pesticides, dioxins, and furans (Covaci et al., 2005; Boonyatumanond et al., 2007; Zennegg et al., 2007; Kohler et al., 2008) in many aquatic ecosystems around the world. The historical accumulation of PBDEs in sediment cores in both freshwater and marine ecosystems has also been reported: first in the Baltic Sea (Nylund et al., 1992), and subsequently in other areas such as those in the Arctic (Stern et al., 2005; Evenset et al., 2007), Canada (Stern et al., 2005; Johannessen et al., 2008), Europe (Zegers et al., 2003; Guzzella et al., 2008; Kohler et al., 2008), the USA (Song et al., 2004; 2005a,b; Zhu and Hites, 2005), China (Chen et al., 2007), India (Binelli et al., 2007), Korea (Hong et al., 2010), and Japan (Minh et al., 2007). In those studies, the history of PBDE emissions was validated; concentrations and trends were correlated against the production and usage, and against the rate of urbanization and industrialization. Furthermore, the occurrence of congeners which are not contained in the technical products, and the unexpected concentrations of some congeners in the cores were attributed to the debromination of BDE-209 (Covaci et al., 2005; Stern et al., 2005). Yet very few studies on the historical occurrence, emissions, deposition and trends of PBDEs using sediment cores have been conducted in tropical Asian waters. Tropical Asian countries have experienced unprecedented economic and population growth in the last few decades, which are driving factors in the consumption of more PBDE-laden consumer goods. In addition, huge amounts of e-waste (e.g., 80% of e-waste from North America is exported to Asia; Wong et al., 2007), may have been exported to tropical Asian countries (Martin et al., 2004), and could be discharged into the environment during usage and disposal. Typical of most Asian countries, both the Philippines and Thailand have experienced rapid economic growth since the 1960s which was shortly interrupted by the Asian financial crisis in 1997 (Lloyd and

MacLaren, 2000; Burke and Ahmadi-Esfahani, 2006). Both countries have also experienced rapid population growth, urbanization, and industrialization in the last few decades. The megacities of Manila and Bangkok had populations of approximately 11.9 million (NSO, 2010) and 10.3 million (Ministry of Interior, 2013), respectively, in 2010. These factors may have likely contributed to the pollution in Manila Bay and the upper Gulf of Thailand, including inputs of PBDEs and PCBs. Varying historical usage of PBDEs and PCBs would likely be reflected in their vertical profiles in the sediment cores.

In this Chapter, the historical occurrence of PBDEs and PCBs in a typical tropical Asian environment is reported using sediment cores obtained from Manila Bay, Philippines, and the upper Gulf of Thailand. The main objective of this study is to understand the historical deposition of PBDEs by examining the vertical profiles of PBDE concentrations in the dated sediment cores. The historical trends of PBDE accumulation was assessed through comparison with the historical production of the technical PBDE products, and the historical trends of PCB deposition in Manila Bay and in the upper Gulf of Thailand. Furthermore, I investigated the debromination of BDE-209 in deeply buried sediments through detailed examination of the PBDE congeners in the cores.

## **4.2. Materials and methods**

### **4.2.1. Study areas**

Manila Bay and the upper Gulf of Thailand are typical tropical aquatic ecosystems in Southeast Asia. Manila Bay lies between latitudes 14°14'N and 14°50'N and longitudes 120°30'E and 121°00'E and covers 1800 km<sup>2</sup>. The upper Gulf of Thailand which is part of the larger Gulf of Thailand, is located between latitudes 12°60'N and 13°30'N and longitudes 100°00'E and 101°00'E and covers 10 000 km<sup>2</sup>. Both are important fishing grounds. However, Manila Bay serves as the ultimate sink for wastes generated in 26 river basins covering 17 000 km<sup>2</sup>, including heavily polluted rivers in Metro Manila and nearby provinces (EMB, 1991). Similarly, the upper Gulf of Thailand receives large amounts of sewage, runoff, and sediments, especially from the Chao Phraya River, which has a catchment area of 162 000 km<sup>2</sup> and flows through several cities, including

Bangkok (Boonyatumanond et al., 2007).

#### **4.2.2. Sampling**

##### **4.2.2.1. Sediment cores**

Sediment cores MB17 and MB18 were taken from Manila Bay in December 2009. Sediment core GT15 was taken from the upper Gulf of Thailand in June 2004 (Table 4.1). Both were collected with a gravity corer (Boonyatumanond et al., 2007) in an acrylic tube (11 cm i.d. × 100 cm length). Each core was sliced immediately on board at 2-cm intervals from the surface down to 20 cm, at 1-cm intervals down to 80 cm, and at 5-cm intervals down to the bottom. The outer 1-cm of each layer was trimmed to remove contamination. The samples were stored in pre-solvent-washed stainless steel containers with Teflon-lined covers, and transported cold (~4°C) to the local laboratory. The samples were packed with dry ice during transport to the laboratory of TUAT, and were stored at -30°C until further processing. Subsamples from each slice were used for the measurement of bulk density and water content. The remaining samples were freeze-dried and pulverized. Composite samples were formed by grouping and mixing equal portions of adjacent layers or slices (n = 3 to 15); and were used to measure the concentrations of PBDEs and PCBs (n = 12 composite samples for MB17 and MB18, n = 8 for GT15).

##### **4.2.2.2. Confirmatory samples for analysis of PCBs in Asian coastal waters: Plastic resin pellets and PUF disks in passive air sampler**

To examine the current emission of PCBs to the coastal environments in tropical Asia, two types of contemporary samples (i.e., plastic resin pellets and passive air samples) were collected from several locations in tropical Asian countries, including Manila Bay.

Plastic resin pellets are small granules, generally in the shape of a cylinder or disk with a diameter of a few millimeters. These plastic particles are the industrial feedstock of plastic products. They are unintentionally spilled into the environments and are brought to the oceans. Hydrophobic organic pollutants from the surrounding seawater such as PCBs are sorbed into and

concentrated in the pellets (Mato et al., 2001). Because of their persistence, these pellets are distributed on sandy beaches all over the world, and have been used as monitoring media (Ogata et al., 2009; Heskett et al., 2012; Mizukawa et al., 2013). Previous studies demonstrated that pellets reflect POPs levels in seawater (Ogata et al., 2009).

Plastic resin pellets were collected from 8 beaches of 4 Asian countries (i.e., the Philippines, Vietnam, Malaysia, and Japan; Annex Table 4.1). The pellet samples from the Philippines were collected in Manila Bay on the shoreline of Cavite City (14°27'53.6"N, 120°52'57.9"E) in December 2009, two days after the sampling of the sediment cores. All the collected pellet samples were wrapped immediately with aluminum foil, placed in a Ziploc bag, and sent to the laboratory of TUAT via air mail.

Polyurethane foam (PUF) disk passive air samplers (PAS) have been used in the atmospheric monitoring of POPs (e.g., Pozo et al. 2004; 2006). PAS were deployed at 6 locations in the same 4 Asian countries (Annex Table 4.2), twice during the dry season and the wet season for about 1 month. The sampling location of the PUF in Manila Bay was at the back of the Cavite City Hall (14°29'06"N, 120°54'46"E), and was closed to the sampling location of the pellets.

The sampling device (PUF and stainless steel housing) and the procedure used were according to Pozo et al., (2004). Before sampling, the PUF (14 cm diameter, 1.35 cm thick, 365 cm<sup>2</sup> surface area, 4.40 g mass, 207 cm<sup>3</sup> volume, 0.0213 g/cm<sup>3</sup> density) was rinsed successively with water, acetone, acetone/hexane (1:2 v/v), and DCM, oven-dried, wrapped with aluminum foil, and stored in Ziploc bag until deployment. To determine the air volume collected by the PAS, known amounts of PCB-30 were spiked as depuration standard to the PUF disk before deployment. All the PUF samples were wrapped with aluminum foil after retrieval, placed in a Ziploc bag, and sent to the laboratory of TUAT via air mail.

### **4.2.3. Analytical methods**

#### **4.2.3.1. Bulk density, water content, and organic carbon**

A 2-cm<sup>3</sup> wet subsample of each layer was weighed before and after drying at 105°C to

obtain the dry bulk density (dry-g/cm<sup>3</sup>) and the water content (%). The organic carbon (OC) content of each layer in GT15 was measured previously with a CN analyzer (Boonyatumanond et al., 2007). The OC contents of MB17 and MB18 were measured from subsamples of the composites by the Philippine Bureau of Soils and Water Management using the Walkley–Black extraction procedure and spectrophotometry (Schumacher, 2002).

#### **4.2.3.2. Sedimentation geochronology measurements**

The sedimentation geochronology of the samples was determined from <sup>137</sup>Cs and <sup>210</sup>Pb radioisotopes by gamma-ray spectrometry (i.e., Ortec GXP25P for GT15; Ortec GWL-120120 for MB17 and MB18). GT15 was dated from the <sup>137</sup>Cs activity of each layer of freeze-dried core samples since the <sup>210</sup>Pb activity was too low for quantitative discussion, and was confirmed by molecular markers (Boonyatumanond et al., 2007). MB17 and MB18 were dated from the <sup>210</sup>Pb activity measured in subsamples of the composites since the <sup>137</sup>Cs activity was too low for quantitative evaluation.

#### **4.2.3.3. PBDEs and PCBs**

PBDEs were measured using the procedure described in Chapters 2 and 3 sections 2.2.2 and 3.2.2, respectively. PCBs were also measured from the same sediment core extracts used for the analysis of PBDEs. Briefly, 2–3 g of composite samples was extracted in an accelerated solvent extractor (Dionex ASE-200) with acetone/DCM (1:3 v/v). The extracts were spiked with <sup>13</sup>C-labeled PBDEs 3, 15, 28, 47, 99, 154, 153, 183, and f-BDE-208 (4'-fluoro-2,2',3,3',4,5,5',6,6'-nonabromo-diphenylether), and with <sup>13</sup>C-labeled PCBs 28, 52, 101, 153, 138, 180, and 209 as surrogate standards. The extracts were cleaned up through a 5% H<sub>2</sub>O-deactivated silica gel column to remove polar components, treated with activated Cu to remove elemental sulfur, and further cleaned up using a fully activated silica gel column. After elution of the alkane fractions, PBDEs and PCBs were eluted together with hexane/DCM (3:1 v/v) as the second fraction.

The evaporated extract was redissolved in 100 µL of isooctane containing <sup>13</sup>C-BDE-139 as

an IIS. Thirty six mono- to hepta-BDEs (1, 2, 3, 7, 8, 10, 11, 12/13, 15, 17/25, 30, 32, 33/28, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 116, 118, 119, 126, 138, 153, 154, 155, 166, 181, 183, 190) were analyzed in the extracts by GC/MS (Thermo Electron Corporation Trace GC Ultra, Polaris Q MS with AS3000 Autosampler) in the selected reaction monitoring mode, using a J&W Scientific DB-5 fused silica capillary column (30 m  $\times$  0.25 mm i.d.  $\times$  0.25  $\mu$ m film thickness). Nine hepta- to deca-BDEs (188, 196, 197, 202, 203, 206, 207, 208, 209) were quantified on an Agilent Technologies 7890A GC System and 7683 Series Injector with  $\mu$ ECD system, equipped with a shorter DB-5 column (15 m  $\times$  0.25 mm i.d.  $\times$  0.25  $\mu$ m film thickness). Detailed instrumental conditions are described in Chapters 2 and 3 sections 2.2.2 and 3.2.2, respectively.

After the analysis of PBDEs, the extracts were evaporated to dryness under a stream of nitrogen gas and redissolved in appropriate volumes of the PCBs IIS containing  $^{13}\text{C}$ -CBs 32, 141, and 208. Thirty eight di- to deca-PCB congeners (CBs 8, 18, 28, 44, 49, 52, 66, 74, 87, 99, 101, 105, 110, 118, 128, 138, 146, 149, 151, 153, 156, 157, 158, 167, 170, 172, 177, 178, 180, 183, 187, 189, 194, 195, 199, 196/203, 206, 209) were analyzed using the same GC/MS system, except that the instrumental conditions were similar to those described by Hirai et al. (2011).

Basically, a similar analytical procedure was used for the analysis of PCBs in the plastic resin pellets and in the PUF disk, except in the extraction steps. The pellets were soaked in hexane (Ogata et al., 2009), while the PUF disk was extracted by pressurized fluid extraction with DCM at 50°C (Dionex ASE-300).

#### **4.2.4. Quality assurance and quality control protocols**

PBDE and PCB concentrations in the core samples were recovery-corrected with the corresponding  $^{13}\text{C}$ -labeled homologue surrogate standards (except for the di- and octa-CBs, which were corrected with the tri- and hepta-  $^{13}\text{C}$ -labeled CBs, respectively), while BDEs 188, 196, 197, 202, 203, 206, 207, 208, and 209 were corrected with the surrogate f-BDE-208. Details of the accuracy and precision of the analytical method for measuring PBDEs in sediments (i.e., recoveries and RSD of native PBDE congeners spiked into a sediment sample (n = 4) and in the SRM: NIST

SRM 1941b marine sediment (n = 3)) is found in Chapter 2 section 2.2.3. In summary, the RSD of individual congeners was <15% and the recoveries of the PBDE standards spiked after extraction were >85%. The analytical results of the NIST SRM sample were within the range of 43% to 109% of the certified values. The results of a confirmatory test (n = 2) indicated that BDE-209 was not extensively debrominated (only <22%) during the analytical procedure starting from the accelerated solvent extraction until the GC/MS analysis of the extracts (Chapter 2 section 2.2.3). The results of the NIST SRM marine sediment analyzed in 2004 and in 2012 (Chapter 3 section 3.2.3) also gave assurance that debromination of BDE-209 did not occur in the sediment core samples while on storage at -30°C for 1.5 years (Philippines MB17, MB18) and 7 years (Thailand GT15). The accuracy and precision of our analytical method for measuring PCBs in sediments were reported earlier by Boonyatumanond et al. (2007).

A method blank (section 2.2.3) was analyzed for every batch of 8 samples. The concentrations of PBDEs and PCBs in the blank sample defined the LOD, taken as 3× the concentration in the blank sample. To examine the vertical profiles of the PBDEs and PCBs in the core samples, concentrations below the LODs were included.

#### 4.2.5. Air Volumes Derived from Depuration Compounds

To calculate the air concentrations in the PUF, air volumes were derived based on the fraction of depuration compounds (PCB-30) retained by the PUF disk (Annex Table 4.2) using equation (1) according to Pozo et al. (2004).

$$K_A = -\ln(C_t/C_0)\delta_{\text{FILM}}K_{\text{PUF-A}}\rho/t \quad (1)$$

where  $K_A$  is the mass transfer coefficient (cm/day);  $C_t/C_0$  is the recovery of the depuration compound (PCB-30) initially spiked to the PUF disks (listed in Annex Table 4.2);  $\delta_{\text{FILM}}$  is the thickness of the PUF (0.0135 m);  $K_{\text{PUF-A}}$  is the PUF-air partition coefficient;  $\rho$  is the density of PUF (0.0213 g/cm<sup>3</sup>); and  $t$  is the exposure time in days.  $K_{\text{PUF-A}}$  was approximated using the octanol-air partition coefficient ( $K_{\text{oa}}$ ) according to Santiago and Cayetano (2011), and corrected for air temperature (average during the deployment period) according to Chen et al. (2003). Sampling

rate ( $R$ ,  $\text{cm}^3/\text{day}$ ) was calculated as follow:

$$R = A_{\text{puf}} K_A \quad (2)$$

where  $A_{\text{puf}}$  is the surface area of PUF ( $0.0365 \text{ cm}^2$ ). The sampling rates,  $R$  and air volumes are listed in Annex Table 4.2.

### 4.3. Results and Discussion

To reconstruct the historical deposition of PBDEs and PCBs in Manila Bay, the sediment accumulation rates of  $0.38 \text{ g cm}^{-2} \text{ yr}^{-1}$  in MB17 and  $0.35 \text{ g cm}^{-2} \text{ yr}^{-1}$  in MB18 (or sedimentation velocities of  $\sim 1.74$  and  $1.16 \text{ cm yr}^{-1}$ , respectively) were estimated from the slope of excess  $^{210}\text{Pb}$  plotted against mass depth ( $\text{g/cm}^2$ ) (Annex Fig. 4.1; Annex Table 4.3.). The values were comparable to those reported by Sta. Maria et al. (2009). For GT15, the sediment accumulation rate of  $0.46 \text{ g cm}^{-2} \text{ yr}^{-1}$  was estimated from  $^{137}\text{Cs}$  (Boonyatumanond et al., 2007). Together with the bulk density data, specific depth intervals were correlated with the age or year of deposition starting from the time of sampling. Thus, the  $\sim 1\text{-m}$  sediment cores covered 60 to almost 80 years i.e., 1931–2009 (MB17); 1940–2009 (MB18); 1940–2000 (GT15), which also roughly covered the commercial production of PBDEs in the 1970s and PCBs in the 1930s.

The vertical profiles of the water and the OC contents of the cores (i.e., slightly but smoothly decreasing from the surface to the bottom (Annex Figs. 4.2, 4.3)), suggested that the sediment core samples were largely undisturbed, and may serve as reliable references for the reconstruction of the history of PBDE and PCB deposition.

#### 4.3.1. Occurrences of PBDEs and PCBs in the sediment cores

Total PBDEs and total PCBs were generally detected at higher concentrations in the upper layers, and at lower concentrations in the bottom layers of the sediment core samples (Tables 4.2–4.5, Figs. 4.1, 4.2). PBDEs appeared first in the 1970s in MB18 (Fig. 4.1), consistent with the start of their commercial production then. PBDEs also occurred first in layers corresponding to the 1970s in the cores from the Pearl River Estuary, China (Chen et al., 2007), Lake Erie, USA (Zhu



and Hites, 2005), and Greifensee, Switzerland (Kohler et al., 2008). Conversely, PBDEs were detected at layers corresponding to the time before their commercial production in MB17 and GT15. The same trend also occurred in Lake Superior (Song et al., 2004), Lake Michigan (Zhu and Hites, 2005), and Tokyo Bay (Minh et al., 2007).

The concentrations of total PBDEs in the three cores exhibited a trend of faster increase in layers corresponding to the mid-1980s until the mid-1990s, followed by a decrease until the early 2000s, and again an increase toward the upper layers or in recent years (Figs. 4.1, 4.2). This trend may have corresponded to the economic condition in the Asian region, i.e., its rapid economic growth until the mid-1990s, which was interrupted by the Asian financial crisis in 1997–1999 and the economic recovery since 2000 (Lloyd and MacLaren, 2000; Burke and Ahmadi-Esfahani, 2006). Consumption of PBDEs may be driven by economic factors, e.g., the GDP per capita of a country may translate into high purchasing power for consumer goods laden with PBDEs which may end up in the coastal environment (Chapter 3, section 3.33).

The PCBs in the three cores also increased over time, although earlier than the PBDEs, showing a trend of rapid increase (i.e., from the 1980s (MB17), 1960s (MB18), and 1940s (GT15), generally followed by a decrease, and again an increase in recent years (Figs. 4.1, 4.2). The earlier usage of PCBs than of PBDEs in the Philippines and Thailand was consistent with the historical usage of PCBs worldwide (Johannessen et al., 2008). Based on official record, the use of PCBs in Thailand started in 1955 (Boonyatumanond et al., 2007). Detection of PCBs in layers corresponding to earlier than 1955 (including also the presence of PBDEs in the bottom layers of the cores, corresponding to periods earlier than the 1970s; Figs. 4.1, 4.2) would suggest a downward migration of sediment particles through the pore water, or vertical mixing of the sediments possibly through bioturbation (Boonyatumanond et al., 2007). Bioturbation has been defined as the process of sediment mixing through animal activities (Nickell et al, 2003), and it can affect the biogeochemical cycling and redistribution of pollutants (Goldhaber et al., 1977; Benninger et al., 1979; Nickell et al, 2003). The presence of fragmented clam shells especially in cores MB17 and MB18 may suggest the occurrence of bioturbation. Bioturbation due to deep burrowing animals

such as crustaceans, bivalves and worms have been observed (Benninger et al., 1979; Nickell et al., 2003), and at depths from 70 to 110 cm (Benninger et al., 1979). Estimating the rates of bioturbation can be complicated as this involves the abundance, distribution, behavior and activity of the benthic biological community including their responses to environmental changes (Nickell et al., 2003). A bioturbation rate of 1-3% of the maximum mixing rate for the top 2-3 cm was estimated for the top layer to ~ 10 cm in a sediment core from Long Island Sound (Benninger et al., 1979). In this study, the bioturbation rates in the cores were not assessed. The effects of bioturbation may have a negligible effect on the vertical profiles of the PBDEs and PCBs in these particular cores. The PBDE and PCB profiles in the cores matched with important events that were associated to the commercial production and usage of both compounds.

The increasing concentrations of PCBs toward the upper layers of the three cores (Figs. 4.1, 4.2) were in contrast to the decreasing or leveling of trends observed in other areas, such as in Masan Bay, Korea (Hong et al., 2010), Lake Maggiore, Italy (Guzzella et al., 2008), the Norwegian Arctic (Evenset et al., 2007), the Strait of Georgia, Canada (Johannessen et al., 2008), and the Great Lakes, USA (Song et al., 2004, 2005a,b). There may be current inputs of PCBs to Manila Bay and to the upper Gulf of Thailand (Boonyatumanond et al.; 2007). The current inputs of PCBs to Manila Bay would be consistent with the 6 to 70 times higher concentrations of PCBs in the plastic resin pellets (which reflect PCBs in seawater) collected from Manila Bay, than those from surrounding Asian countries (i.e., Malaysia and Vietnam) (Fig 4.3.). The study by Santiago and Rivas (2012) in 2009 also reported the detection of PCBs in the waters of Manila Bay (6.1-9.8 ng/L); and in two water bodies that contribute runoff water to the bay, the Pasig River (0.9-32.8 ng/L) and Laguna Lake (3.0-10.9 ng/L), at concentrations higher than those reported for the coast of Hong Kong; the Pearl River Delta, Chao Phraya and Mekong Rivers; and in the Venice Lagoon respectively (Santiago and Rivas, 2012).

Current inputs of PCBs to the catchment of Manila Bay were further confirmed by the detection of PCBs in air. The average PCB concentration detected in the passive air samples from the Manila Bay area was about 4 to 86 times higher than those obtained in Malaysia, Vietnam and

Japan (Fig. 4.3). This is consistent with the study on Global Atmospheric Passive Sampling (GAPS) conducted in December 2004 to March 2005 (Pozo et al., 2006), where the PCB air concentration in Metropolitan Manila (Quezon City) was the highest among the 41 global sampling sites. Some of the PCBs in the air may have reached the waters of Manila Bay through atmospheric deposition and surface runoff, and may have eventually settled as sediments. The ongoing inputs of PCBs in Manila Bay could be due to a less effective regulation, inadequate management of PCB stockpiles including insufficient control of illegal recycling activities, e.g. retro filling of old transformers that may have caused leakage into the environment. Two power plants were once located near the banks of the Pasig River, and two more near the lakeshore of Laguna Lake (one is still operational), which may be possible emission sources of PCBs. In a similar situation, PCBs were still discharged in the estuarine and near-shore environment of the Danshui River in Taiwan (Hung et al., 2006); ongoing inputs of PCBs from the shipping industry were considered in the detection of PCB residues in coastal sediment samples in Kaohsiung, Taiwan (Jiang et al., 2011).

Inventories for BDE-209 in Manila Bay and in the upper Gulf of Thailand ( $8.5\text{--}22\text{ ng/cm}^2$ ) were lower than those in the Pearl River Estuary (Chen et al., 2007), Tokyo Bay (Minh et al., 2007), and in Lakes Erie, Michigan, and Ontario (Song et al., 2005a,b; Zhu and Hites, 2005) ( $38\text{--}1700\text{ ng/cm}^2$ ), and comparable to those in Greifensee (Kohler et al., 2008), Lake Superior (Song et al., 2004) and Lake Huron (Song et al., 2005a) (Table 4.6). The inventories for  $\Sigma\text{PCBs}$  ( $47\text{--}92\text{ ng/cm}^2$ ) were also lower than those in Lakes Erie and Ontario ( $169\text{--}263\text{ ng/cm}^2$ ; Table 4.6). However, the doubling times for BDE-209 ( $\sim 6$  years) were comparable to those in the Pearl River Estuary (2.6–6.4 years; Chen et al., 2007) and in Lakes Erie and Michigan (5.3–7.5 years; Zhu and Hites, 2005), but faster than those in Greifensee (9 years; Kohler et al., 2008) and the Norwegian Arctic (15 years; Evenset et al., 2007) (Table 4.6).

#### **4.3.2. PBDE congener profiles in the sediment cores**

BDE-209 was predominant, especially on the surface layers (Fig. 4.4; Tables 4.2a, 4.2b, 4.3). Other dominant congeners were the octa-BDEs 196, 197 (in MB18) and 202, nona-BDEs 206

and 207, penta BDE-99, and tetra BDE-47. BDEs 1, 2, 3, 7, 8, 10, 11, 12/13, 15, 85, 100, 119, 138, 153, 154, 155, 166, 181, 183, 188, 190, 197, and 208 were sporadically detected, but BDEs 17/25, 30, 32, 33/28, 35, 37, 49, 71, 75, 116, 118, 126, and 203 were not detected (Fig. 4.5, Tables 4.2a, 4.2b, 4.3). The dominant congeners are components of the technical deca- and penta-PBDE products, except BDE-202. The concentrations of the congeners associated with the technical deca-BDE products (BDEs 209, 207, 206, 197, 196) were higher than those of BDEs-99 and 47 in the sediment cores, suggesting higher consumption of the technical deca- than the penta-BDE products in the Philippines and Thailand. The detection of BDE-183 in GT15 (Fig. 4.5, Table 4.3) would suggest consumption of technical octa-BDE products in Thailand. Although BDE-183 was not detected in MB17 or MB18, the presence of BDEs 196 and 197 may indicate consumption of technical octa-BDE products in the Philippines. Records on the importation of technical PBDE products in the Philippines and Thailand are not available; however, the consumption of technical deca-, octa-, and penta-BDE products in Asia was estimated at 23 000, 1500, and 150 tons, respectively, in 2001 (Hites, 2004). The distribution pattern of the PBDE congeners in the core samples was consistent with the importation of PBDEs in Asia. The same profiles were also found in the landfill leachates and sediments from rivers and canals (including surface sediments in Manila Bay) in the Philippines and in Thailand (Chapters 2 and 3 sections 2.3.2.1, 3.3.1, respectively).

The concentrations of BDE-209 generally increased toward the surface (Figs.4.6, 4.7; ~2009 in the Philippines), which would indicate increased consumption of technical deca-BDE products in recent years, presumably since only the technical deca-BDE products remain on the market. The predominance of BDE-209 and its increasing concentration toward the surface of the cores were also observed in cores from other Asian countries (Pearl River Estuary, China (Chen et al., 2007); Tokyo Bay, Japan (Minh et al., 2007); Masan Bay, Korea (Hong et al., 2010)), the Great Lakes, USA (Song et al., 2004; 2005a,b; Zhu and Hites, 2005), and in Europe, Lake Maggiore (Guzzella et al., 2008) and Greifensee (Kohler et al., 2008).

The concentrations of BDE-47 (ranging from ND to 13 pg/g dw; Figs.4.6-4.7, Tables 4.2a,

4.2b, 4.3) were lower than those in the Bay of Bengal, India (35–8832 pg/g dw; Binelli et al., 2007), Lake Maggiore (ND to 1300 pg/g dw; Guzzella et al., 2008), Greifensee (210–740 pg/g dw; Kohler et al., 2008), and the Norwegian Arctic (>50–<500 pg/g dw; Evenset et al., 2007). The vertical profiles of BDEs 47 and 99 in MB17 and MB18 (Fig. 4.6) indicated an earlier consumption of technical penta-BDE products than of deca-BDE products in the 1970s, peak consumption in the mid-1980s to 1990, and a generally decreasing trend in recent years (which appeared to coincide with the early production (Zegers et al., 2003), the phase-out in 1998 (Ross et al., 2009), the ban of the technical penta-BDE products in 2004 (BSEF, 2012), and possibly with the regulatory action of the Stockholm Convention in 2009 (2012)).

There were differences in the congeners and concentration profiles in MB17 and MB18. BDEs 47 and 99 were more detected in MB17 than in MB18 (Fig. 4.6). BDE-202 was detected at higher concentrations and in more layers in MB18; octa-BDE 197 was detected only in MB18 (Fig. 4.6, Tables 4.2a-4.2b). Other factors may have affected the distribution of PBDEs in Manila Bay, e.g., hydrological characteristics. Diffusion by water currents may influence the accumulation of sediments (de las Alas and Sodusta, 1985). However, the water current at locations MB17 and MB18 may be similar (de las Alas and Sodusta, 1985), as also suggested by the comparable sedimentation rates of 0.38 and 0.35 g cm<sup>-2</sup>yr<sup>-1</sup> in MB17 and MB18, respectively. A more important factor may be the proximity to possible point sources of PBDEs near MB18. The presence of an oil refinery and polymer industries along the coast of the province of Bataan may have resulted in higher PBDE concentrations in MB18.

#### **4.3.3. Debromination of BDE-209 in the sediment cores**

The vertical profiles of the concentration ratios of BDE202/209 in the cores (Fig. 4.8) generally increased downward, which may indicate debromination of BDE-209. BDE-202 was proposed as a debromination marker (Gerecke et al., 2005; Tokarz et al., 2008). Kohler et al. (2008) reported the formation of BDE-202 through anaerobic microbial transformation of BDE-208 in sewage sludge, and ascribed the detection of BDE-202 in the cores from Greifensee taken at a depth

of 31 m to debromination of deca-BDEs. The cores from the Philippines and Thailand were anoxic, as suggested by the formation of copper sulfide during sulfur treatment of the extracts, which may have favored anaerobic debromination in the cores.

The values of % BDE-209 in the cores (Fig. 4.8) also decreased downward, with a corresponding increase in the proportions of nona-BDEs 206 and 207 (Fig. 4.9), suggesting the transformation of BDE-209 to BDEs 206 and 207, especially in the bottom layers. The concentration ratios BDEs 206/209, 207/209 (Fig. 4.9) and 196/209, and the % Br1–Br3 BDE congeners (Fig. 4.10) exceeded the reported ratios in the technical deca-BDE mixture (La Guardia et al., 2006); and may indicate debromination of BDE-209 or of other higher-brominated congeners. Debromination of BDE-209 to BDEs 206, 207, and 208 in anaerobic sediment microcosms has been reported, where BDE-206 and 207 were further degraded to BDEs 196, 197, and other lower-brominated congeners (Tokarz et al., 2008).

These BDE-209 debromination profiles are similar to those that are observed for the leachate samples (Chapter 2 section 2.3.2.1). As inland sources of PBDEs can affect coastal areas (Chapter 3 section 3.3.4), PBDE congeners resulting from the debromination of BDE-209 in dumping sites or landfills and rivers may find their way to coastal areas over time and become part of the sediment core. Most of the debromination indices (i.e., BDE-202/209, 206/209, and 207/209) in the Philippine and Thailand sediment cores were higher than those in the corresponding landfill leachates and even in the river sediments (Fig. 4.11), suggesting that debromination may be more significant in the cores. Longer residence of BDE-209 (~20 years), especially from the more anaerobic middle to the bottom layers, may have favored the debromination. The BDE-202/209, 206/209, and 207/209 ratios (Figs. 4.8, 4.9) increased and % BDE-209 (Fig. 4.8) decreased with increasing depth (i.e., residence time) in the cores.

#### **4.4. Conclusion**

Dated sediment core samples were able to capture the historical deposition of PBDEs and PCBs in Manila Bay and in the upper Gulf of Thailand, reflecting important events and factors that

influenced the usage of both compounds. Deca-BDE was likely debrominated, especially in the bottom layers of the cores, and may provide the source of lower brominated but more toxic congeners. Ongoing PCB pollution was evident in the increasing surficial concentrations in the cores, especially in Manila Bay; and was corroborated by the relatively high concentrations of PCBs detected in beached plastic resin pellets and in ambient air from the Manila Bay area. Thus, the cores were able to provide information on the status of PBDE and PCB contamination in the Philippines and Thailand. Sediment cores may be used to predict future trends on the accumulation of PBDEs and PCBs in tropical Asian environments, and may provide the basis for the formulation of policies and strategies toward the appropriate management and containment of these compounds.

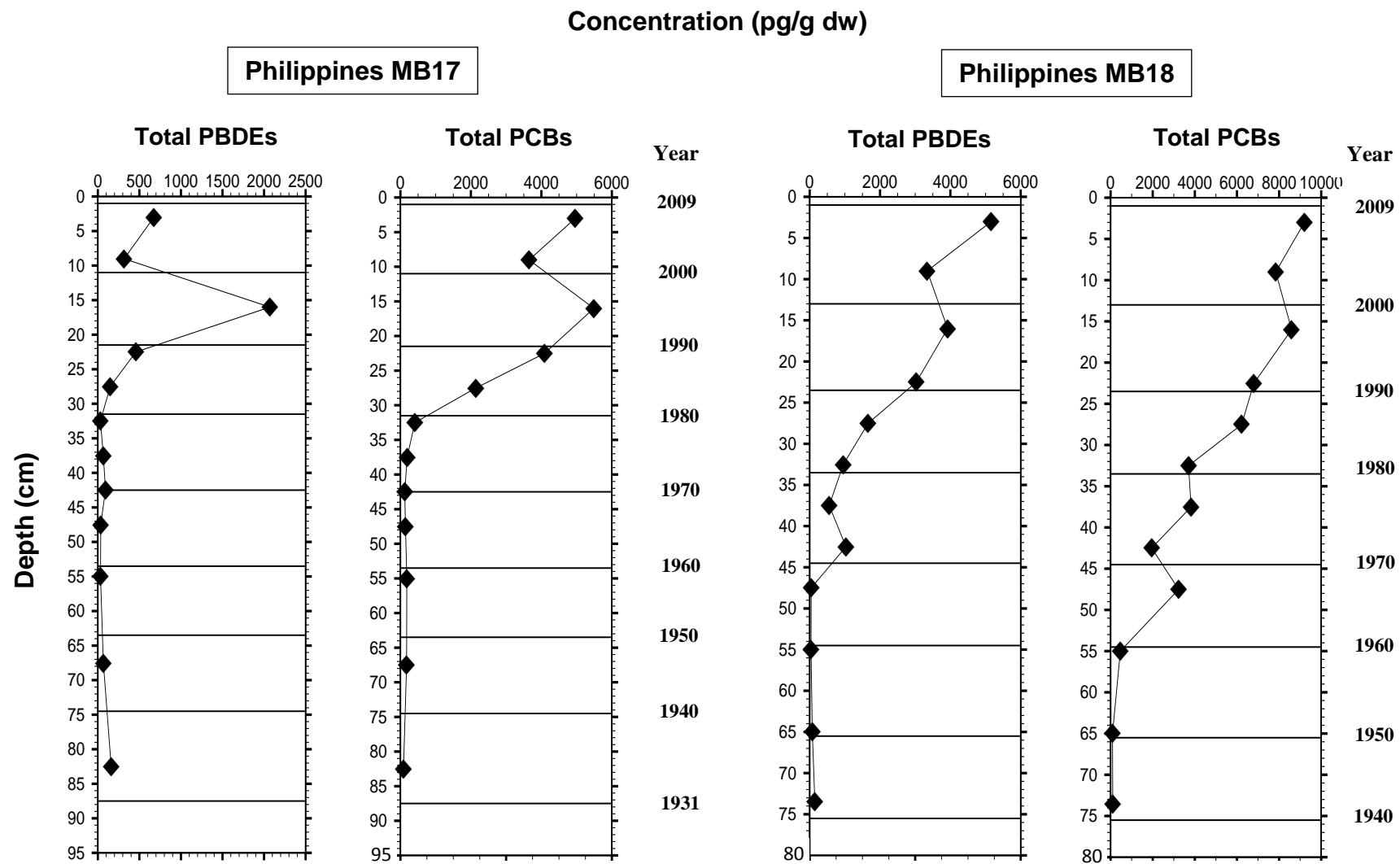


Fig. 4.1. Vertical profiles of total PBDEs and PCBs in the sediment core samples from the Philippines.



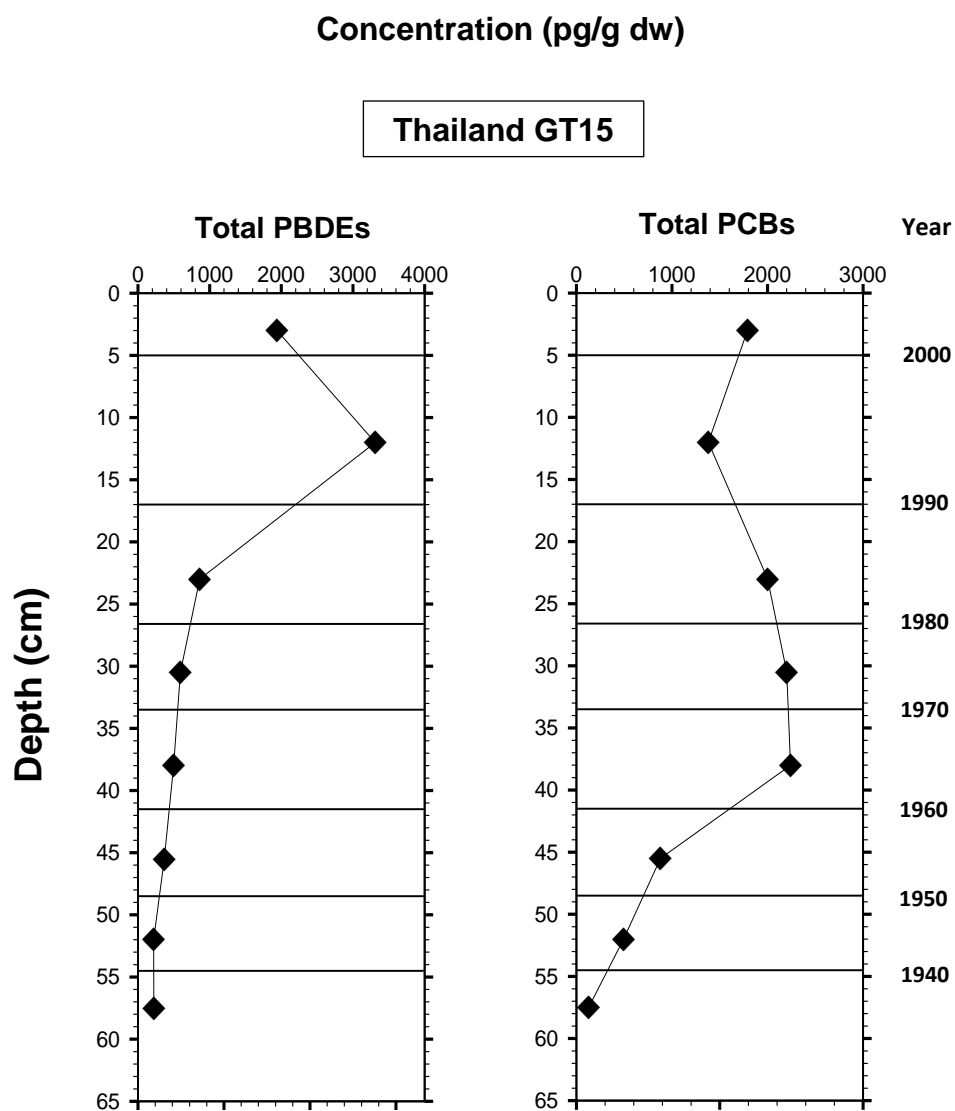


Fig. 4.2. Vertical profiles of the total PBDEs and PCBs in the sediment core sample from Thailand.

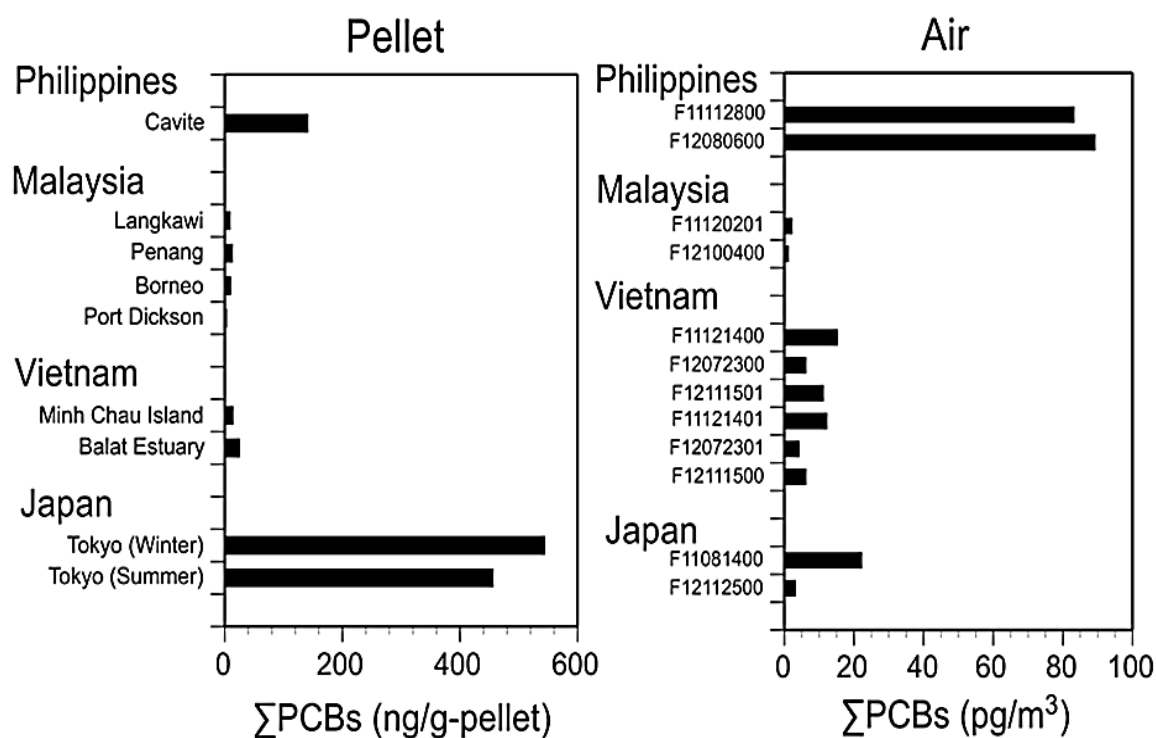


Fig. 4.3. Concentrations of PCBs in beached plastic resin pellets and in air from the Philippines (Cavite in Manila Bay area), Malaysia, Vietnam and Japan.  $\Sigma$ PCBs is the sum of the concentrations of CBs 66, 101, 105, 110, 118, 128, 138, 149, 153, 170, 180, 187 and 206. PCBs in air were obtained by passive air sampling using PUF disks.

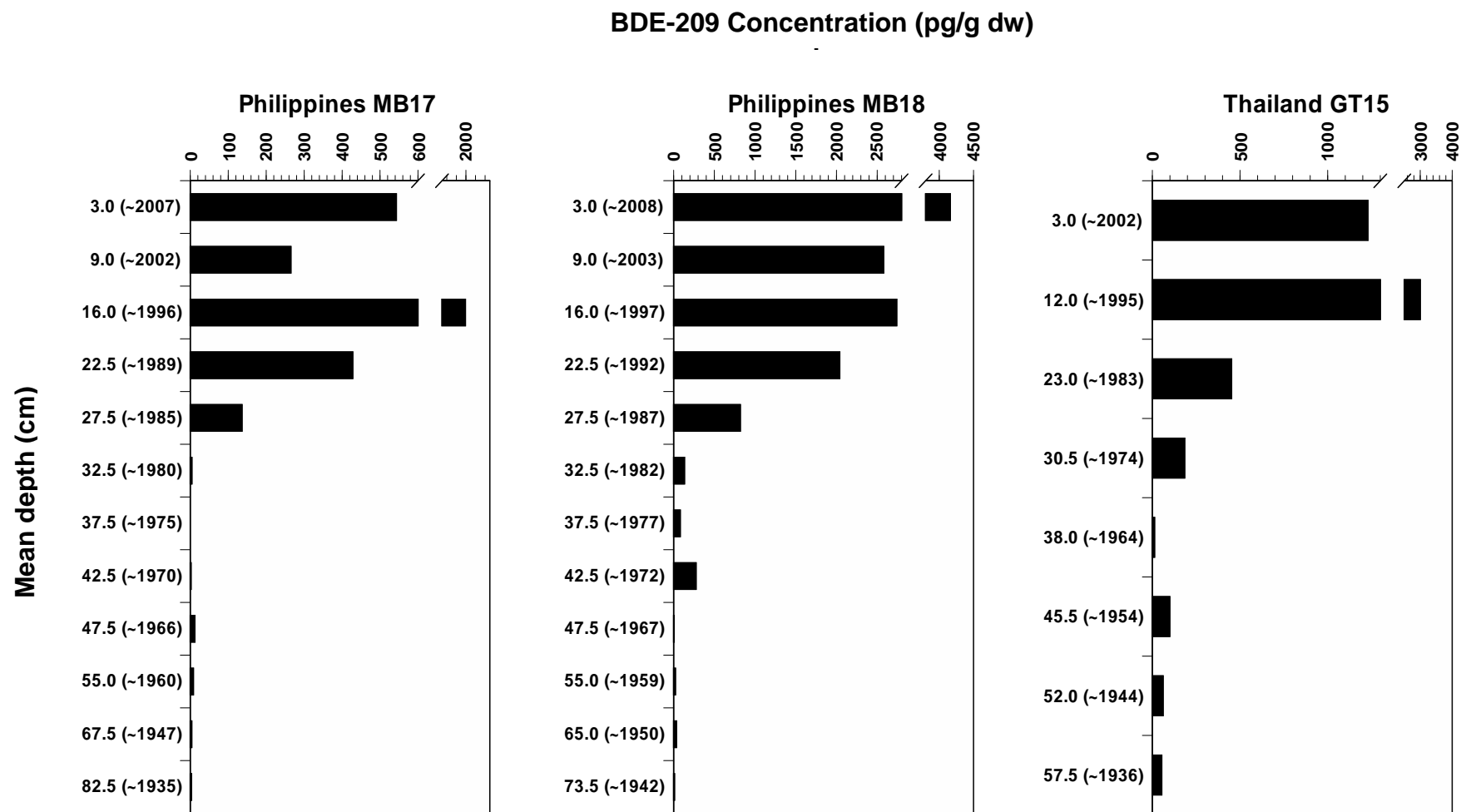


Fig. 4.4. Concentrations of BDE-209 in the sediment core samples from the Philippines and Thailand as a function of depth and year of deposition.

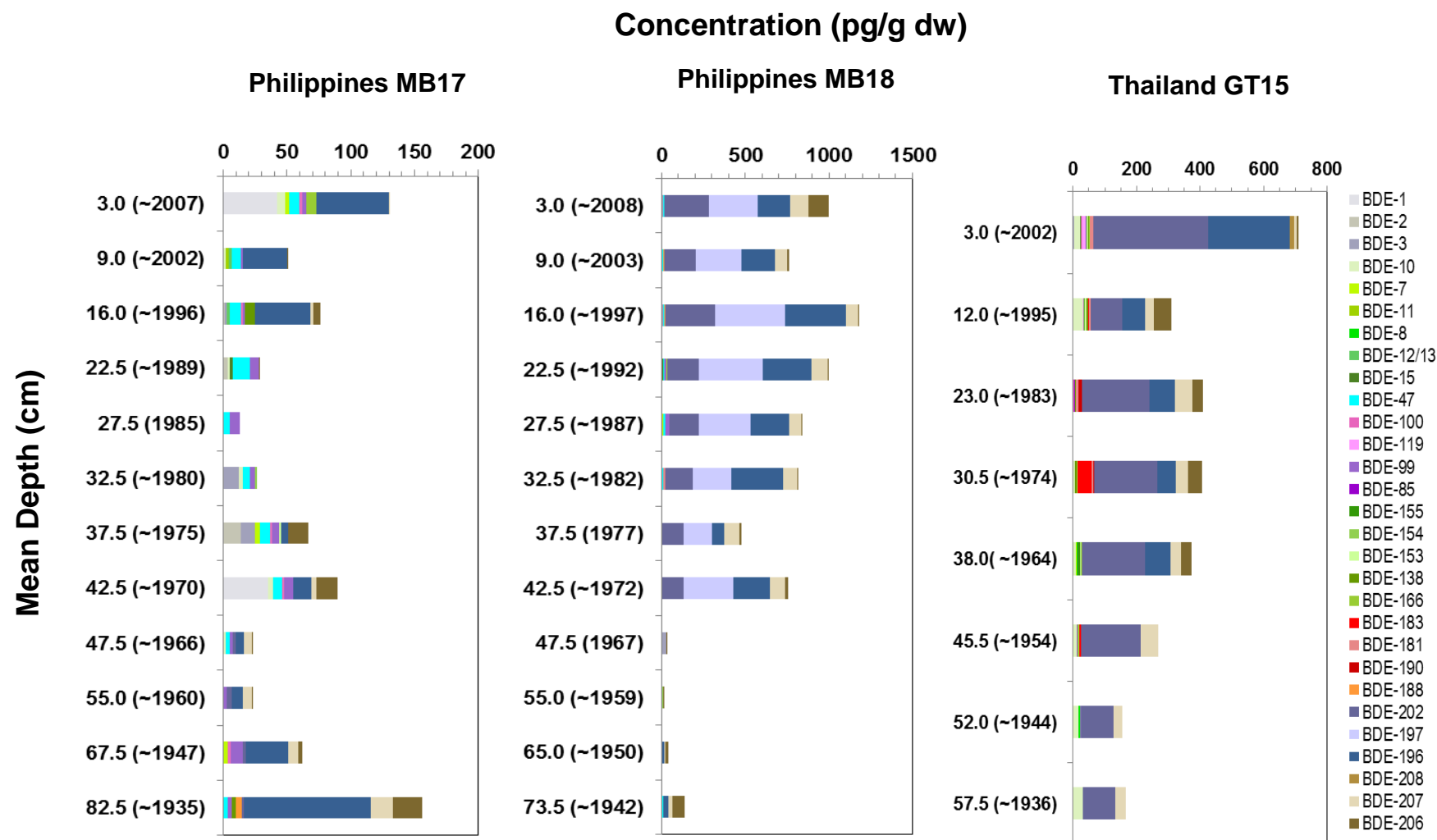


Fig. 4.5. Concentrations of detectable PBDE congeners in the sediment core samples from the Philippines and Thailand as a function of depth and year of deposition. BDEs 30, 32, 17/25, 33/28, 35, 37, 75, 49, 71, 116, 118, 126 and 203 were not detected in the sediment core samples

## Concentration (pg/g dw)

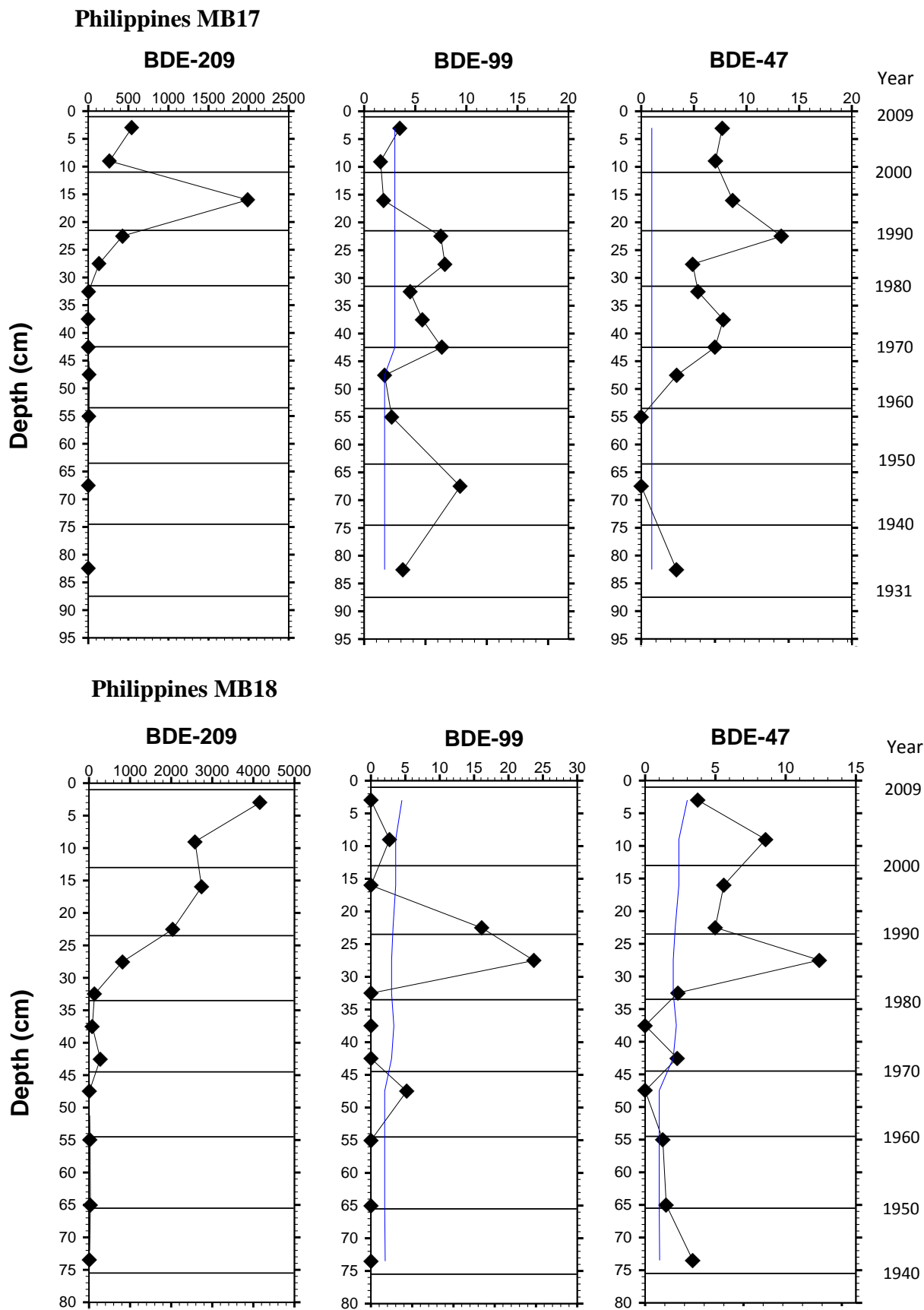


Fig. 4.6. Vertical profiles of BDEs 209, 99 and 47 in the sediment cores from the Philippines. Blue or vertical lines without symbols indicate the corresponding PBDE concentrations in the blank sample.

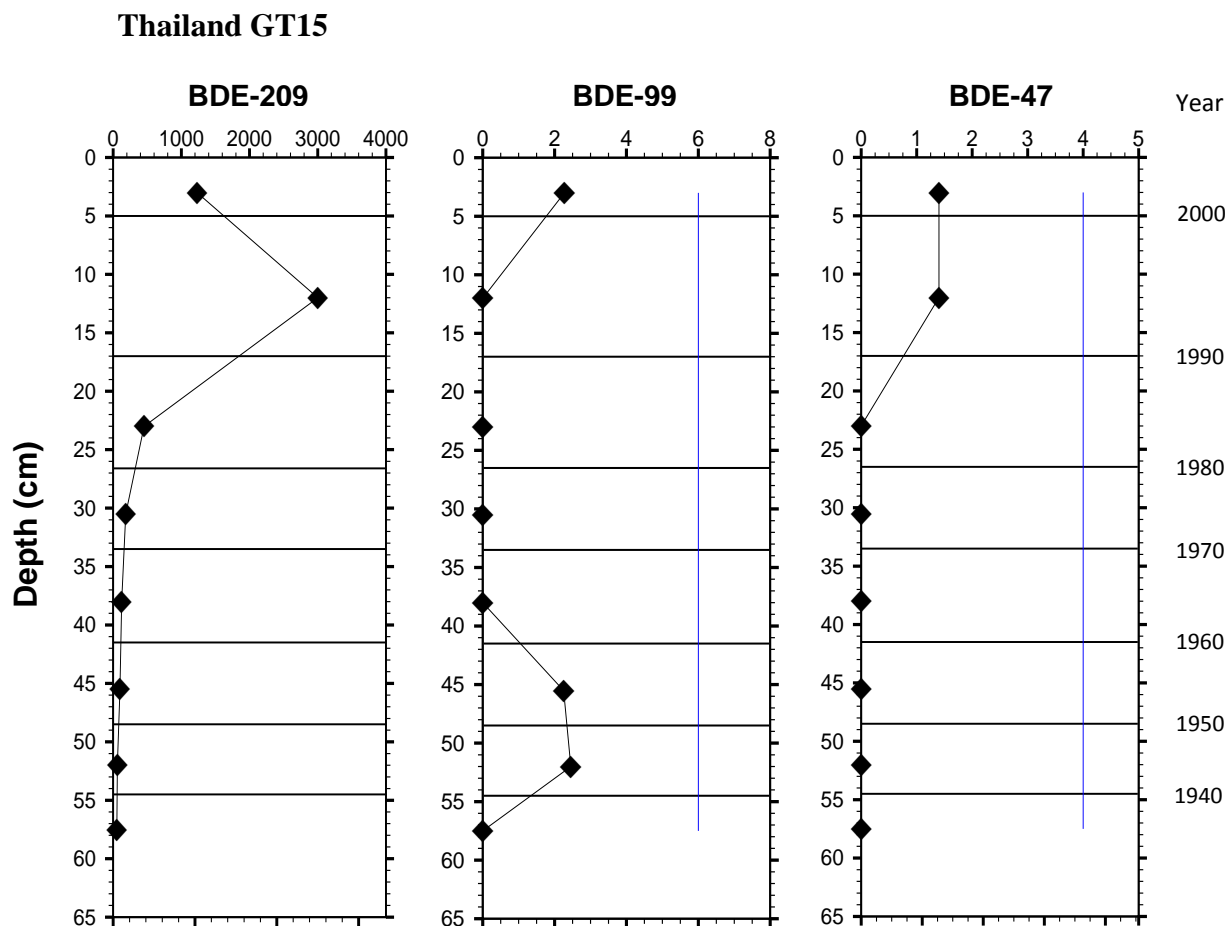


Fig. 4.7. Vertical profiles of BDEs 209, 99 and 47 in the sediment core sample from Thailand. Blue lines or vertical lines without symbols indicate the corresponding PBDE concentrations in the blank sample.

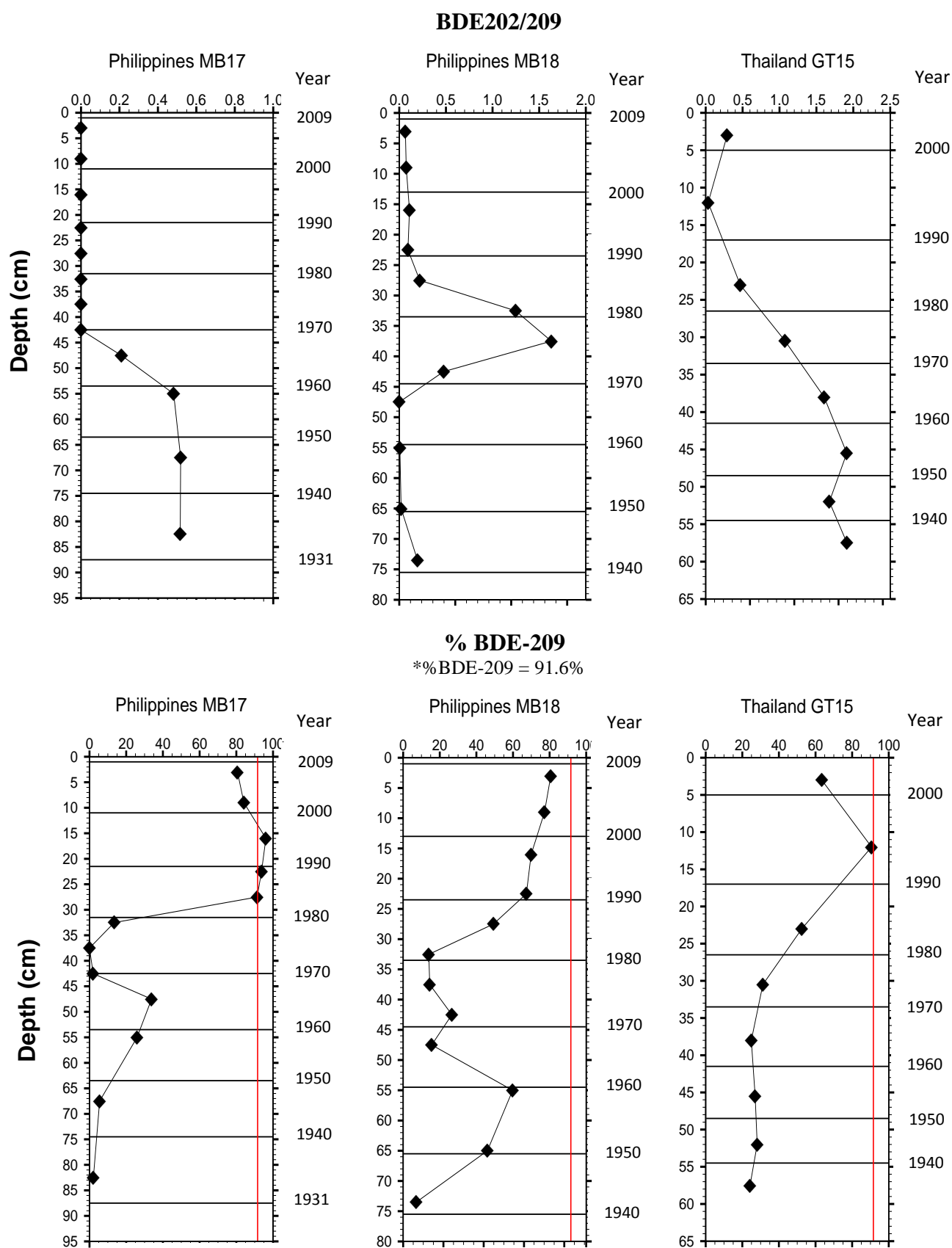


Fig. 4.8. Vertical profiles of the concentration ratios of BDE202/209 and % BDE-209 in the sediment cores from the Philippines and Thailand. \*From the compositional analysis of the technical deca-BDE mixture (indicated by the red or vertical lines without symbols; La Guardia et al., 2006).

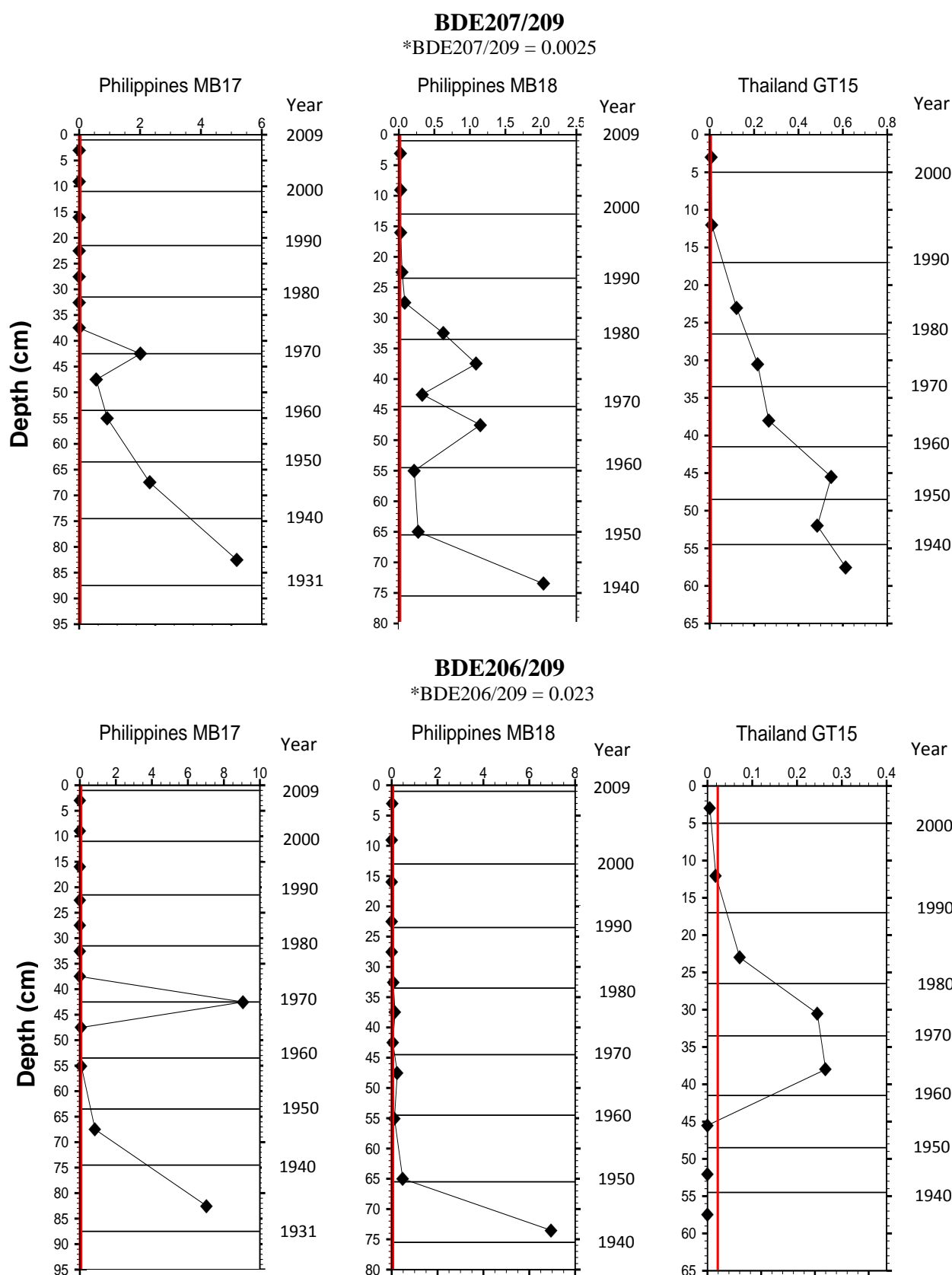


Fig. 4.9. Comparison of the concentration ratios of BDE207/209 and BDE206/209 in the sediment cores from the Philippines and Thailand. \*From the compositional analysis of the technical deca-BDE mixture (indicated by the red or vertical lines without symbols; La Guardia et al., 2006).



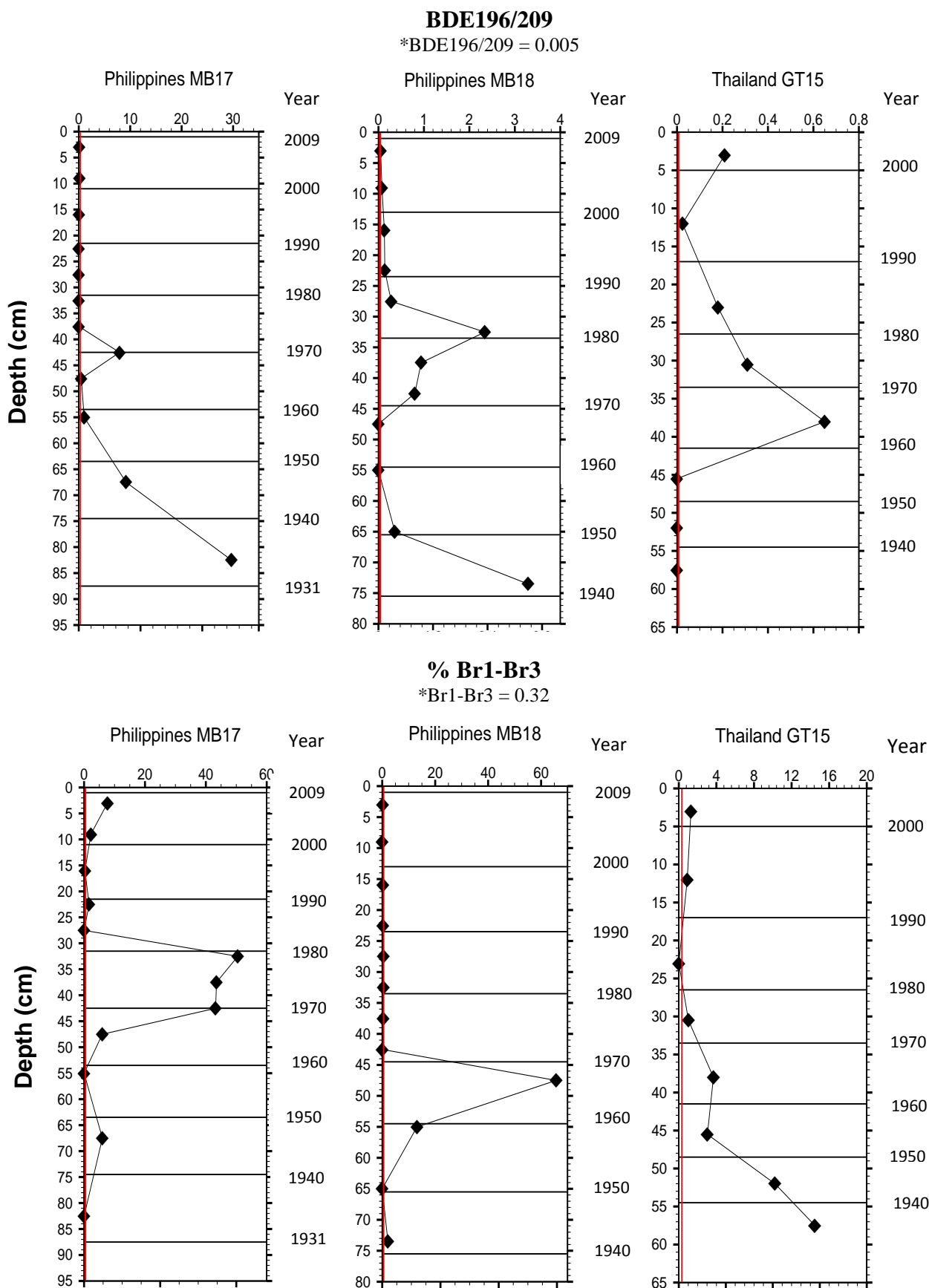


Fig. 4.10. Comparison of the concentration ratios of BDE196/209 and % Br1-Br3 in the sediment core samples from the Philippines and Thailand. %Br1-Br3 includes BDEs 3, 7, 15. \*From the compositional analysis of the technical deca-BDE mixture (indicated by red lines; La Guardia et al., 2006).

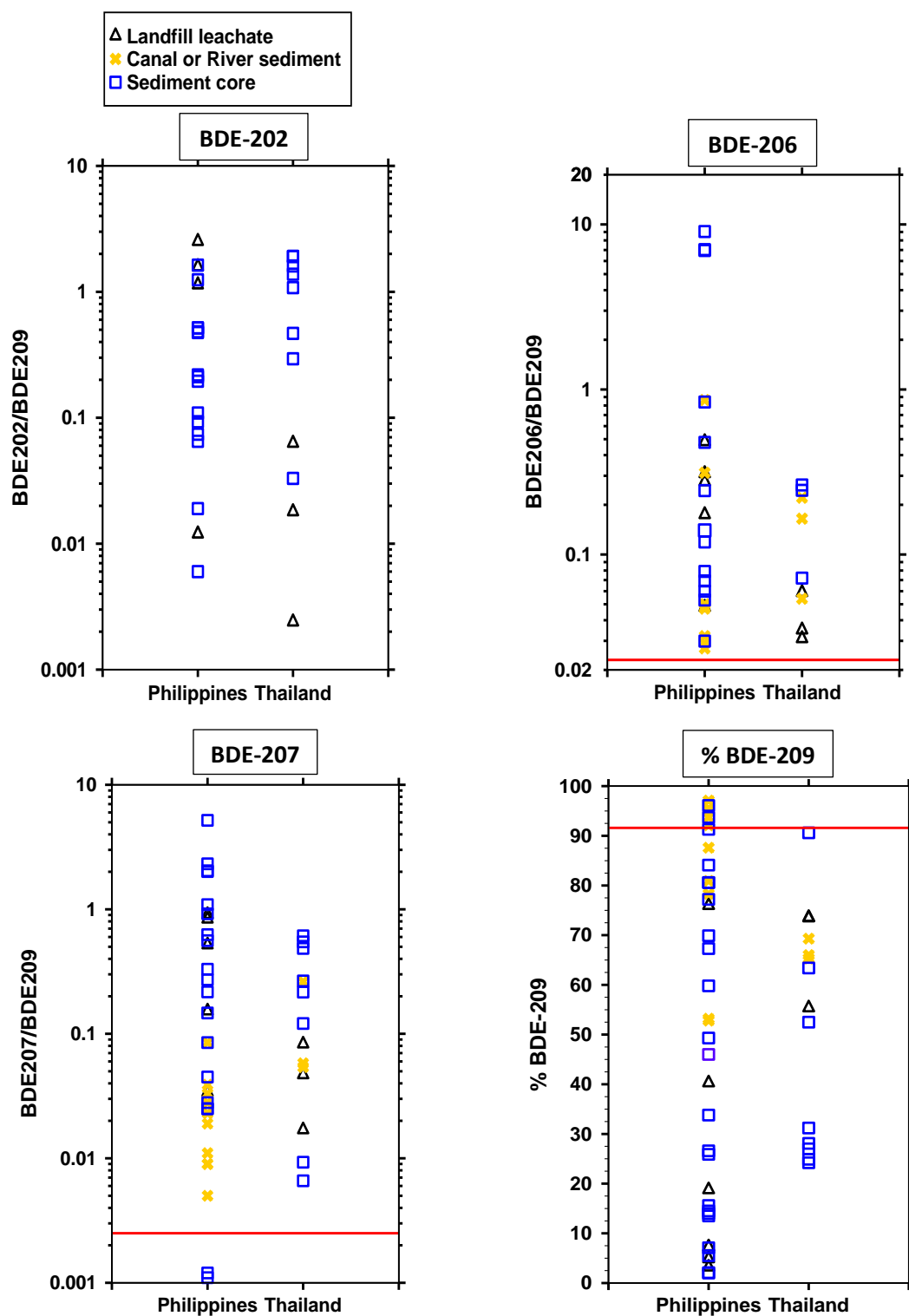


Fig. 4.11. Debromination indices of BDEs 202, 206, 207, 209 in the landfill leachates, river sediments, and in the sediment core samples from the Philippines and Thailand. The ratios of BDE206/209 (0.023), BDE207/209 (0.0025) and the % BDE-209 (91.6) in the technical deca-BDE mixture (La Guardia et al., 2006) are indicated by the horizontal red lines in the corresponding plots. BDE-202 was not detected in the technical octa- and deca-BDE mixtures (Kohler et al., 2008).

Table 4.1 Sampling information for the sediment cores from the Philippines and Thailand.

Country	Location	Code	Coordinates	Date of sampling	Water depth	Core length
			(deg. min. sec., deg. min. sec.)		m	cm
Philippines	Manila Bay	MB17	N 14 36 21, E 120 45 4	2009 December 16	21	90
	Manila Bay	MB18	N 14 35 54, E 120 41 44	2009 December 16	22	78
Thailand	Upper Gulf of Thailand	GT15	N 13 21 86, E 100 34 60	2004 June 10	13.8	60

Table 4.2 Concentrations of PBDEs in the sediment core samples from the Philippines.

## 4.2a. MB 17

PBDEs		Concentration, pg/g dry wt.												LOD, pg	
Composite No.		1	2	3	4	5	6	7	8	9	10	11	12	Batch 3	Batch 4
Mean Depth, cm		3	9	16	22.5	27.5	32.5	37.5	42.5	47.5	55	67.5	82.5		
~ Year of sedimentation		~2007	~2002	~1996	~1989	~1985	~1980	~1975	~1970	~1966	~1960	~1947	~1935		
Br1	BDE-1	42.0	ND <sup>a</sup>	ND	ND	ND	ND	ND	34.9	ND	ND	ND	ND	70	70
	BDE-2	ND	ND	1.5 <sup>b</sup>	3.5	ND	ND	14.1	ND	ND	ND	ND	ND	8	9
	BDE-3	ND	ND	1.2	ND	ND	12.2	11.1	ND	ND	ND	ND	ND	6	8
Br2	BDE-10	6.89	2.0	ND	1.7	ND	3.1	ND	4.4	2.1	ND	ND	ND	20	20
	BDE-7	2.9	ND	ND	ND	ND	ND	3.8	ND	ND	ND	3.98	ND	10	10
	BDE-11	ND	2.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10	9
	BDE-8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10	9
	BDE-12/13	ND	2.7	2.7	ND	ND	ND	ND	ND	ND	ND	ND	ND	20	10
	BDE-15	ND	ND	ND	2.2	ND	ND	ND	ND	ND	ND	ND	ND	20	7
	BDE-30	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20	20
Br3	BDE-32	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	30	20
	BDE-17/25	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	30	20
	BDE-33/28	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20	20
	BDE-35	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	40	40
	BDE-37	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	40	30
	BDE-75	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	9	7
	BDE-49	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20	9
Br4	BDE-71	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20	10
	BDE-47	7.69	7.04	8.68	13.3	4.88	5.40	7.79	7.00	3.38	ND	ND	3.34	8	7
	BDE-66	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20	20
	BDE-77	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	30	30
	BDE-100	2.4	ND	1.2	ND	ND	ND	1.3	1.3	ND	ND	2.2	ND	20	10
	BDE-119	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20	20
	BDE-99	3.5	1.6	1.9	7.5	7.9	4.5	5.7	7.6	2.0	2.7	9.35	3.8	20	20
Br5	BDE-116	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	200	40
	BDE-118	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	40	20
	BDE-85	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	30	20
	BDE-126	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20	20
	BDE-155	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	7	8
	BDE-154	ND	ND	ND	ND	ND	1.0	ND	ND	ND	ND	ND	ND	6	10
	BDE-153	ND	ND	ND	ND	ND	ND	1.9	ND	ND	ND	ND	ND	10	10
Br6	BDE-138	ND	ND	7.6	ND	ND	ND	ND	ND	ND	ND	ND	2.7	20	20
	BDE-166	7.7	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	8	9
	BDE-183	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	8	8
	BDE-181	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	9	10
	BDE-190	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	9	10
	BDE-188	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	4.7	20	5
	BDE-202	ND	ND	ND	ND	ND	ND	ND	ND	2.5	3.9	1.9	1.7	20	2
Br8	BDE-197	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20	2
	BDE-203	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	40	20
	BDE-196	57.2	34.3	43.7	ND	ND	ND	5.2	14.2	5.8	8.6	33.3	99.3	40	20
	BDE-208	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20	5
	BDE-207	0.57	ND	2.4	ND	ND	ND	3.6	6.65	7.50	8.40	17.3	23.5	20	20
	BDE-206	ND	0.45	5.56	0.45	ND	ND	15.7	16.3	0.75	0.64	3.1	23.5	30	4
	BDE-209	543	265	1990	428	136	4.09	ND	1.8	12	8.2	3.6	3.3	60	7
ΣPBDEs <sup>c</sup>		674	315	2070	457	149	30.4	66.6	91.1	35.1	31.5	65.8	160		
Batch number		4	4	4	4	4	4	4	4	3	3	3	3		
Sample dry wt. (g)		2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	3.00	3.00	3.00	3.00		

<sup>a</sup>Not Detected by the instrumental analysis. <sup>b</sup>Values in gray colors are below the Limit of Detection (LOD) of the corresponding BDE congeners, where LOD, pg = 3 x BDE congener concentration in the blank sample in pg. In units of pg/g dry wt.: LOD sample, pg/g dry wt. = LOD (pg) for corresponding batch / sample dry weight (g). To correlate individual samples to the corresponding LOD, the batch number for each sample is indicated in the row of "Batch number". A batch of analysis is composed of 8 samples with one blank sample; blank values varied among the batches. <sup>c</sup>ΣPBDEs includes concentrations below the LOD.

**4.2b. MB 18**

PBDEs		Concentration, pg/g dry wt.												LOD, pg	
Composite No.		1	2	3	4	5	6	7	8	9	10	11	12	Batch 2	Batch 3
Mean Depth, cm		3	9	16	22.5	27.5	32.5	37.5	42.5	47.5	55	65	73.5		
~ Year of sedimentation		~2008	~2003	~1997	~1992	~1987	~1982	~1977	~1972	~1967	~1959	~1950	~1942		
Br1	BDE-1	ND <sup>a</sup>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	200	70
	BDE-2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20	8
	BDE-3	7.3 <sup>b</sup>	ND	8.06	5.8	2.5	4.1	ND	ND	26.5	ND	ND	ND	20	6
Br2	BDE-10	ND	ND	ND	ND	2.7	ND	1.7	ND	0.68	4.8	ND	3.1	300	20
	BDE-7	ND	ND	ND	ND	1.8	ND	ND	ND	ND	ND	ND	ND	20	10
	BDE-11	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	30	10
	BDE-8	ND	ND	1.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	20	10
	BDE-12/13	3.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	30	20
	BDE-15	ND	ND	ND	2.4	ND	ND	ND	ND	ND	ND	ND	ND	20	20
	BDE-30	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	50	20
Br3	BDE-32	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	50	30
	BDE-17/25	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	60	30
	BDE-33/28	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	50	20
	BDE-35	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	200	40
	BDE-37	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	200	40
	BDE-75	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20	9
	BDE-49	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	40	20
Br4	BDE-71	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	30	20
	BDE-47	3.7	8.58	5.6	5.0	12.4	2.3	ND	2.3	ND	1.2	1.5	3.39	20	8
	BDE-66	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	40	20
	BDE-77	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	80	30
	BDE-100	ND	ND	ND	ND	1.5	ND	ND	ND	ND	ND	ND	ND	20	20
	BDE-119	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	30	20
	BDE-99	ND	2.7	ND	16.1	23.7	ND	ND	ND	5.2	ND	ND	ND	30	20
Br5	BDE-116	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	70	200
	BDE-118	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	40	40
	BDE-85	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	40	30
	BDE-126	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	60	20
	BDE-155	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20	7
	BDE-154	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.1	ND	ND	20	6
	BDE-153	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	30	10
Br6	BDE-138	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	30	20
	BDE-166	ND	ND	ND	3.7	ND	ND	ND	ND	ND	ND	ND	ND	30	8
	BDE-183	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	30	8
	BDE-181	ND	ND	ND	ND	ND	12.9	ND	ND	ND	ND	ND	ND	30	9
	BDE-190	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	40	9
	BDE-188	ND	1.9	6.52	ND	ND	ND	ND	ND	ND	ND	ND	ND	10	20
	BDE-202	268	190	299	189	179	166	131	130	ND	0.13	0.65	2.0	20	20
Br7	BDE-197	294	274	420	384	308	230	167	298	ND	ND	ND	ND	3	20
	BDE-203	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10	40
	BDE-196	194	199	365	292	233	312	75.9	219	ND	ND	12	33.9	40	40
	BDE-208	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	80	20
	BDE-207	104	71.7	69.6	92.6	69.3	83.2	87.6	90.4	0.95	4.7	9.08	21.0	50	20
	BDE-206	124	13	5.4	4.1	5.3	9.2	11	15	1.6	2.6	16.0	71.7	50	30
	BDE-209	4,160	2,580	2,740	2,040	818	133	80.5	274	6.4	21.8	33.4	10.3	200	60
ΣPBDEs <sup>c</sup>		5,160	3,340	3,920	3,030	1,660	952	555	1,030	41.4	36.4	72.6	146		
Batch number		2	2	2	2	2	2	2	2	3	3	3	3		
Sample dry wt. (g)		2.00	2.50	2.50	2.80	3.00	3.00	2.70	3.00	3.00	3.00	3.00	2.90		

<sup>a</sup>Not Detected by the instrumental analysis. <sup>b</sup>Values in gray colors are below the Limit of Detection (LOD) of the corresponding BDE congeners, where LOD, pg = 3 x BDE congener concentration in the blank sample in pg. In units of pg/g dry wt.: LOD sample, pg/g dry wt. = LOD (pg) for corresponding batch / sample dry weight (g). To correlate individual samples to the corresponding LOD, the batch number for each sample is indicated in the row of "Batch number". A batch of analysis is composed of 8 samples with one blank sample; blank values varied among the batches. <sup>c</sup>ΣPBDEs includes concentrations below the LOD.

Table 4.3 Concentrations of PBDEs in the sediment core sample from Thailand.

PBDEs		Concentration, pg/g dry wt. Composite No.								LOD Batch 1
Composite No.		1	2	3	4	5	6	7	8	pg
Mean Depth, cm		3	12	23	30.5	38	45.5	52	57.5	
~ Year of sedimentation		~2002	~1995	~1983	~1974	~1964	~1954	~1944	~1936	
Br1	BDE-1	ND <sup>a</sup>	ND	ND	ND	ND	ND	ND	ND	300
	BDE-2	ND	ND	ND	ND	ND	ND	ND	ND	30
	BDE-3	2.8 <sup>b</sup>	ND	ND	ND	ND	ND	ND	ND	20
Br2	BDE-10	19.7	29.5	ND	6.0	7.5	11	15.7	31.8	30
	BDE-7	ND	ND	ND	ND	3.9	ND	ND	ND	30
	BDE-11	ND	ND	ND	ND	ND	ND	ND	ND	40
	BDE-8	ND	ND	ND	ND	3.2	ND	6.5	ND	30
	BDE-12/13	ND	ND	ND	ND	ND	ND	ND	ND	30
	BDE-15	2.5	ND	ND	ND	3.7	ND	ND	ND	70
	BDE-30	ND	ND	ND	ND	ND	ND	ND	ND	70
Br3	BDE-32	ND	ND	ND	ND	ND	ND	ND	ND	70
	BDE-17/25	ND	ND	ND	ND	ND	ND	ND	ND	80
	BDE-33/28	ND	ND	ND	ND	ND	ND	ND	ND	70
	BDE-35	ND	ND	ND	ND	ND	ND	ND	ND	200
	BDE-37	ND	ND	ND	ND	ND	ND	ND	ND	200
	BDE-75	ND	ND	ND	ND	ND	ND	ND	ND	30
	BDE-49	ND	ND	ND	ND	ND	ND	ND	ND	50
Br4	BDE-71	ND	ND	ND	ND	ND	ND	ND	ND	30
	BDE-47	1.4	1.4	ND	ND	ND	ND	ND	ND	30
	BDE-66	ND	ND	ND	ND	ND	ND	ND	ND	60
	BDE-77	ND	ND	ND	ND	ND	ND	ND	ND	200
	BDE-100	1.5	ND	1.8	ND	ND	ND	ND	ND	30
	BDE-119	12	2.4	ND	ND	ND	ND	ND	ND	40
	BDE-99	2.3	ND	ND	ND	ND	2.2	2.4	ND	40
Br5	BDE-116	ND	ND	ND	ND	ND	ND	ND	ND	100
	BDE-118	ND	ND	ND	ND	ND	ND	ND	ND	50
	BDE-85	ND	ND	3.5	ND	ND	ND	ND	ND	50
	BDE-126	ND	ND	ND	ND	ND	ND	ND	ND	80
	BDE-155	ND	1.8	ND	ND	4.3	1.6	ND	ND	30
	BDE-154	3.3	1.5	ND	ND	ND	ND	ND	ND	20
	BDE-153	2.3	4.7	ND	ND	2.9	ND	ND	ND	40
Br6	BDE-138	2.3	6.6	4.0	5.9	ND	ND	ND	ND	40
	BDE-166	2.6	ND	ND	1.4	3.3	3.5	ND	ND	40
	BDE-183	ND	3.4	ND	46.3	ND	5.4	ND	ND	40
	BDE-181	10	3.4	8.2	3.3	ND	ND	ND	ND	40
	BDE-190	ND	ND	12	4.6	ND	ND	ND	ND	50
	BDE-188	ND	ND	ND	ND	ND	ND	ND	ND	7
	BDE-202	362	100	211	198	198	189	102	102	20
Br7	BDE-197	ND	ND	ND	ND	ND	ND	ND	ND	20
	BDE-203	ND	ND	ND	ND	ND	ND	ND	ND	60
	BDE-196	258	70.9	80.5	56.6	80.5	ND	ND	ND	20
	BDE-208	12.4	ND	ND	ND	ND	ND	ND	ND	5
Br8	BDE-207	8.16	28.0	54.6	39.7	32.9	54.2	29.6	32.7	5
	BDE-206	6.85	55.7	32.6	45.2	32.6	ND	ND	ND	7
	BDE-209	1,230	3,000	452	184	124	99.0	60.9	53.3	10
ΣPBDEs <sup>c</sup>		1,940	3,310	860	591	497	366	217	220	
Sample dry wt. (g)		2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	

<sup>a</sup>Not Detected by the instrumental analysis. <sup>b</sup>Values in gray colors are below the Limit of Detection (LOD) of the corresponding BDE congeners, where LOD, pg = 3 x BDE congener concentration in the blank sample in pg. In units of pg/g dry wt.: LOD sample, pg/g dry wt. = LOD (pg) / sample dry weight (g). <sup>c</sup>ΣPBDEs includes concentrations below the LOD.

Table 4.4 Concentrations of PCBs in the sediment core samples from the Philippines.

## 4.4a. MB 17

PCBs		Concentration, pg/g dry wt.												LOD, pg	
Composite No.		1	2	3	4	5	6	7	8	9	10	11	12	Batch 3	Batch 4
Mean Depth, cm		3	9	16	22.5	27.5	32.5	37.5	42.5	47.5	55	67.5	82.5		
CI2	CB-8	200	186	176	180	114	21.3	5.34	1.4 <sup>a</sup>	0.51	0.97	4.02	0.14	6	6
CI3	CB-18	207	161	84.1	118	112	34.5	32.9	18	8.0	ND <sup>b</sup>	11	3.7	40	40
	CB-28	270	242	323	274	140	26.2	17.6	12.2	5.3	8.4	6.9	4.2	30	7
CI4	CB-52	188	124	198	191	89.8	13.3	1.1	ND	1.7	ND	ND	ND	8	9
	CB-49	209	213	235	221	150	16.7	4.84	1.1	0.76	2.87	4.12	ND	7	8
	CB-44	77.2	63.7	85.4	71.9	30.2	0.82	ND	1.7	ND	ND	ND	ND	20	20
	CB-74	60.9	51.9	69.3	61.0	35.6	5.57	1.5	1.0	0.79	ND	2.13	ND	4	4
	CB-66	181	158	197	178	79.0	9.59	2.0	1.5	0.77	2.67	2.52	1.2	4	4
CI5	CB-101	115	103	150	79.3	46.0	10.8	2.0	ND	ND	2.28	2.39	0.32	5	5
	CB-99	195	145	185	130	85.2	15.6	3.56	0.81	0.32	ND	3.81	ND	5	4
	CB-87	43.9	47.0	63.3	22.3	16.8	1.1	ND	ND	ND	7.71	ND	0.60	10	9
	CB-110	49.6	41.1	53.0	34.4	23.8	2.69	3.13	1.3	0.21	ND	2.76	ND	3	3
	CB-118	96.6	132	105	68.6	61.2	1.8	2.73	1.6	2.47	11.1	ND	ND	6	5
	CB-105	56.4	46.5	65.2	26.5	18.6	3.22	0.60	ND	ND	ND	ND	ND	3	2
CI6	CB-151	102	44.5	100	73.4	27.0	ND	ND	ND	ND	ND	1.1	ND	10	9
	CB-149	253	114	302	188	127	11.4	6.55	2.4	ND	ND	5.45	ND	8	8
	CB-146	187	104	214	150	88.6	39.0	42.7	60.5	98.5	136	86.2	74.7	8	7
	CB-153	720	352	754	529	254	47.4	21.4	7.90	6.23	2.40	12.5	0.95	5	4
	CB-138	400	284	444	368	144	35.9	8.42	1.4	4.35	2.1	11.9	ND	8	7
	CB-158	21.9	17.9	20.5	17.1	7.57	0.69	0.42	ND	0.22	ND	ND	ND	4	4
	CB-128	84.4	71.8	54.9	76.9	29.2	1.4	ND	ND	ND	ND	ND	ND	20	20
	CB-167	15.1	12.8	9.07	9.77	4.04	0.40	0.44	ND	ND	0.14	0.89	ND	5	4
	CB-156	26.4	22.7	23.7	23.2	9.55	2.63	0.32	0.21	0.31	ND	0.58	ND	5	5
	CB-157	46.6	39.8	43.0	40.2	24.9	6.43	1.1	1.2	1.5	ND	2.11	ND	5	4
CI7	CB-178	49.4	37.6	69.4	44.0	18.1	ND	ND	ND	1.4	ND	ND	ND	20	20
	CB-187	316	261	372	286	142	40.7	12.9	2.6	2.1	ND	5.62	ND	8	10
	CB-183	86.2	54.0	118	70.7	25.9	5.43	1.4	ND	0.50	0.46	1.0	ND	6	6
	CB-177	101	66.3	115	69.2	9.3	11.3	2.3	ND	ND	ND	ND	ND	20	20
	CB-172	21.3	13.9	30.9	17.8	1.1	1.8	ND	ND	ND	ND	ND	ND	20	20
	CB-180	191	149	275	167	68.3	13.3	1.3	1.2	1.3	ND	3.18	ND	6	5
	CB-170	176	139	218	138	48.3	2.6	1.3	ND	ND	1.6	1.8	ND	20	10
	CB-189	3.55	0.93	5.45	4.28	10.9	2.50	1.2	0.19	0.57	ND	ND	0.29	4	4
CI8	CB-199	45.7	27.6	64.3	19.1	13.0	1.7	ND	ND	ND	ND	ND	ND	8	7
	CB-196/203	27.2	18.4	31.9	15.1	9.88	2.3	ND	ND	ND	ND	1.2	ND	5	5
	CB-195	19.0	6.6	14.3	8.4	4.7	ND	ND	0.79	1.4	0.10	ND	0.60	9	20
	CB-194	65.6	44.4	118	60.2	18.1	ND	1.3	ND	0.95	ND	ND	ND	20	20
CI9	CB-206	11.7	11.2	17.6	14.9	11.9	2.94	2.36	0.86	ND	0.063	ND	ND	6	3
CI10	CB-209	38.6	44.4	89.5	45.8	41.0	14.8	8.65	1.88	0.50	ND	ND	ND	3	3
$\Sigma$ PCBs <sup>c</sup>		4,960	3,650	5,490	4,090	2,140	408	191	122	141	179	173	86.6		
Batch number		4	4	4	4	4	4	4	4	3	3	3	3		
Sample, dry wt. (g)		2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	3.00	3.00	3.00	3.00		

<sup>a</sup>Values in gray colors are below the Limit of Detection (LOD) of the corresponding CB congeners, where LOD, pg = 3 x CB congener concentration in the blank sample in pg. In units of pg/g dry wt.: LOD sample, pg/g dry wt. = LOD (pg) for corresponding batch / sample dry weight (g). To correlate individual samples to the corresponding LOD, the batch number for each sample is indicated in the row of "Batch number". A batch of analysis is composed of 8 samples with one blank sample; blank values varied among the batches. <sup>b</sup>Not Detected by the instrumental analysis. <sup>c</sup> $\Sigma$ PCBs includes concentrations below the LOD.

#### 4.4b. MB 18

PCBs		Concentration, pg/g dry wt.											LOD, pg		
Composite No.		1	2	3	4	5	6	7	8	9	10	11	12	Batch 2	Batch 3
Mean Depth, cm		3	9	16	22.5	27.5	32.5	37.5	42.5	47.5	55	65	73.5		
Cl2	CB-8	151	115	145	121	118	129	90.6	51.6	114	12.5	0.39 <sup>a</sup>	0.82	7	6
Cl3	CB-18	144	97.8	68.9	188	97.2	67.2	64.6	52.0	179	49.6	ND <sup>b</sup>	ND	30	40
	CB-28	272	232	321	221	238	222	134	81.1	170	21.9	5.8	1.8	6	30
Cl4	CB-52	156	173	172	179	133	142	88.2	60.7	123	10.4	0.88	ND	20	8
	CB-49	213	197	223	231	174	136	160	79.5	164	11.2	1.54	ND	9	7
	CB-44	118	122	112	122	79.3	36.3	48.4	21.1	47.7	9.49	ND	1.5	20	20
	CB-74	58.4	49.3	65.2	57.7	50.5	48.6	30.7	21.4	57.4	1.44	1.60	ND	4	4
Cl5	CB-66	169	162	198	181	147	146	110	51.5	126	10.4	2.76	ND	5	4
	CB-101	236	188	171	161	143	ND	83.6	46.4	82.1	6.46	ND	0.38	7	5
	CB-99	300	209	197	157	159	145	140	65.8	101	7.44	0.31	1.0	6	5
	CB-87	115	17.7	25.6	39.6	21.3	ND	25.5	1.4	19.6	2.1	ND	ND	20	10
	CB-110	158	68.6	57.3	49.4	41.9	35.1	31.2	20.2	28.6	2.82	0.30	0.43	5	3
	CB-118	360	134	122	97.1	80.5	61.1	50.8	31.2	92.3	9.80	0.39	0.84	5	6
	CB-105	68.6	43.8	44.6	41.2	33.3	59.8	26	15	ND	ND	ND	ND	80	3
Cl6	CB-151	201	276	247	191	184	72.0	84.7	27.6	54.3	32.4	ND	ND	20	10
	CB-149	581	521	673	411	406	193	237	95.1	145	20.6	4.52	ND	9	8
	CB-146	413	347	526	335	333	142	213	88.7	162	142	68.4	90.0	20	8
	CB-153	1,180	1,060	1,280	941	907	650	532	301	451	39.4	ND	ND	6	5
	CB-138	1,010	953	1,010	809	725	351	492	286	259	26.9	0.52	ND	8	8
	CB-158	49.6	37.1	42.7	29.1	30.3	20.0	23.4	7.05	14.9	0.92	ND	ND	5	4
	CB-128	187	176	189	227	154	69.6	65.8	29.4	61.3	3.5	ND	ND	20	20
	CB-167	36.7	35.1	37.5	30.9	25.0	7.64	11.0	7.52	12.6	0.32	ND	ND	5	5
	CB-156	62.0	60.3	54.6	34.6	16.9	20.1	26.2	9.34	15.4	0.35	0.30	ND	6	5
	CB-157	80.1	95.3	76.7	63.6	70.3	34.0	60.9	25.6	31.6	1.3	0.28	ND	6	5
Cl7	CB-178	125	106	101	93.9	104	32.1	44.9	24.6	31.3	ND	ND	ND	30	20
	CB-187	547	505	604	431	455	275	326	198	223	22.1	ND	ND	9	8
	CB-183	177	145	165	124	125	69.7	67.9	33.1	50.7	2.00	ND	ND	8	6
	CB-177	414	336	287	241	243	88.1	33.2	7.9	31.3	ND	ND	ND	40	20
	CB-172	78.4	52.1	105	37.4	34.1	ND	3.3	4.6	6.84	ND	ND	ND	20	20
	CB-180	526	427	493	339	311	170	231	79.0	147	ND	ND	ND	7	6
	CB-170	508	385	301	274	293	148	137	45.1	110	1.8	ND	ND	20	20
	CB-189	64.2	20.5	52.4	60.8	56.7	13.6	11.9	21.8	20.3	11.0	ND	2.8	5	4
	CB-199	136	118	117	86.2	62.4	30.1	26.3	2.6	13.4	ND	0.57	ND	20	8
Cl8	CB-196/203	23.6	32.2	36.4	25.0	23.3	17.0	14.9	6.15	11.8	ND	0.38	ND	7	5
	CB-195	60.6	14.7	43.5	21.0	10.3	3.6	6.1	6.5	3.98	0.70	ND	ND	20	9
	CB-194	169	280	131	99.0	101	45.6	51.5	7.48	37.1	ND	ND	ND	20	20
	CB-206	28.7	19.4	8.97	8.92	9.20	2.3	4.64	5.07	1.2	ND	ND	ND	7	6
Cl9	CB-209	26.4	26.4	88.9	35.4	27.9	15.6	31.1	33.4	26.1	1.06	ND	ND	4	3
ΣPCBs <sup>c</sup>		9,200	7,840	8,590	6,800	6,220	3,700	3,820	1,950	3,230	462	89.0	99.4		
Batch number		2	2	2	2	2	2	2	2	3	3	3	3		
Sample, dry wt. (g)		2.00	2.50	2.50	2.80	3.00	3.00	2.70	3.00	3.00	3.00	3.00	2.90		

<sup>a</sup>Values in gray colors are below the Limit of Detection (LOD) of the corresponding CB congeners, where LOD, pg = 3 x CB congener concentration in the blank sample in pg. In units of pg/g dry wt.: LOD sample, pg/g dry wt. = LOD (pg) for corresponding batch / sample dry weight (g). To correlate individual samples to the corresponding LOD, the batch number for each sample is indicated in the row of "Batch number". A batch of analysis is composed of 8 samples with one blank sample; blank values varied among the batches. <sup>b</sup>Not Detected by the instrumental analysis. <sup>c</sup>ΣPCBs includes concentrations below the LOD.



Table 4.5 Concentrations of PCBs in the sediment core sample from Thailand.

PCBs		Concentration, pg/g dry wt. Composite No.								LOD Batch 1
Composite No.		1	2	3	4	5	6	7	8	pg
Mean Depth, cm		3	12	23	30.5	38	45.5	52	57.5	
CI2	CB-8	75.5	34.7	91.2	134	108	25.7	11.7	5.11	3
CI3	CB-18	50.8	25.8	113	69.6	111	48.8	38.6	28.5	40
	CB-28	109	65.3	125	123	96.5	57.8	19.9	8.09	6
CI4	CB-52	40.9	35.6	54.5	88.6	103	177	100	11.0	20
	CB-49	60.2	48.6	72.8	104	110	106	82.3	14.3	20
	CB-44	8.8 <sup>a</sup>	5.6	10	12.3	16.3	5.6	ND <sup>b</sup>	ND	20
	CB-74	17.0	11.1	23.4	32.5	17.2	2.2	1.3	ND	5
	CB-66	56.0	38.6	67.1	91.4	56.6	11.3	6.80	1.6	6
CI5	CB-101	43.6	26.0	44.5	45.0	53.0	21.6	10.3	3.4	8
	CB-99	56.9	42.0	65.7	81.6	74.7	24.4	9.18	1.5	7
	CB-87	15.9	14.0	22.8	18.5	8.2	ND	ND	1.2	20
	CB-110	30.1	31.4	37.9	37.1	25.1	15.3	3.80	2.0	5
	CB-118	42.3	35.2	56.7	52.0	32.7	8.64	4.27	1.0	5
	CB-105	28.0	25.5	30.9	24.0	20.6	11.6	8.96	3.66	5
CI6	CB-151	7.0	2.2	14.3	8.0	24.0	7.3	ND	ND	20
	CB-149	75.2	62.5	89.0	88.6	118	46.6	35.0	3.9	20
	CB-146	46.6	35.3	48.5	66.4	83.2	18.3	5.8	1.8	9
	CB-153	230	200	250	272	332	103	53.3	15.3	6
	CB-138	239	241	269	258	281	89.2	46.5	15.5	9
	CB-158	9.36	5.55	10.4	8.49	9.35	ND	ND	ND	5
	CB-128	36.8	17.6	39.1	42.6	6.4	8.2	ND	ND	20
	CB-167	14.5	4.33	6.84	5.03	3.53	0.87	ND	ND	5
	CB-156	29.6	11.8	23.9	13.4	9.19	3.22	1.0	ND	6
	CB-157	13.5	12.8	16.9	17.6	9.23	1.1	ND	ND	6
CI7	CB-178	3.4	7.7	8.1	7.5	ND	ND	ND	ND	20
	CB-187	66.1	58.7	60.6	103	130	31.7	18.8	4.4	20
	CB-183	17.6	18.0	20.8	16.1	37.9	4.4	2.0	ND	10
	CB-177	49.3	25.3	31.5	77.1	44.9	ND	ND	ND	30
	CB-172	14	6.3	3.3	ND	ND	ND	ND	ND	30
	CB-180	102	91.0	117	134	137	34.6	9.27	1.4	8
	CB-170	107	76.8	89.1	88.1	129	13.0	2.3	2.8	20
	CB-189	12.9	6.52	11.7	4.54	2.9	1.4	4.57	0.92	6
CI8	CB-199	24.6	21.5	23.4	36.4	19.4	ND	ND	ND	20
	CB-196/203	5.45	6.28	3.89	6.84	3.51	0.94	ND	ND	7
	CB-195	20.0	5.6	8.1	3.6	2.4	ND	ND	ND	20
	CB-194	26.6	20.3	28.9	26.6	16.6	ND	2.4	ND	20
CI9	CB-206	1.2	4.91	4.60	2.6	2.5	ND	1.1	ND	8
CI10	CB-209	3.98	2.29	3.21	2.42	0.79	ND	13.1	ND	4
	ΣPCBs <sup>c</sup>	1,790	1,380	2,000	2,200	2,240	879	493	127	
Sample, dry wt. (g)		2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	

<sup>a</sup>Values in gray colors are below the Limit of Detection (LOD) of the corresponding CB congeners, where LOD, pg = 3 x CB congener concentration in the blank sample in pg. In units of pg/g dry wt.: LOD sample, pg/g dry wt. = LOD (pg) for corresponding batch / sample dry weight (g). <sup>b</sup>Not Detected by the instrumental analysis. <sup>c</sup>ΣPCBs includes concentrations below the LOD.

Table 4.6 Comparison of the surface fluxes, inventories and doubling time of PBDEs and PCBs in Manila Bay, Philippines and in the upper Gulf of Thailand with those from other locations worldwide.

Sediment core/Location	Sampling Time Year	BDE-209			$\Sigma$ PBDEs <sup>a</sup>		$\Sigma$ PCBs <sup>b</sup>				Reference
		Surface flux ng/cm <sup>2</sup> -year	Inventory ng/cm <sup>2</sup>	Doubling time year	Inventory ng/cm <sup>2</sup>	Doubling time year	No. of PCB congeners analyzed	Surface flux ng/cm <sup>2</sup> -year	Inventory ng/cm <sup>2</sup>	Doubling time year	
Manila Bay, Philippines											
MB17	~2007	0.206	8.5	5.7	11	5.6	38	1.88	47	8.7	This study
MB18	~2008	1.46	22	7.5	34	7.3	38	3.22	92	8.1	This study
Upper Gulf of Thailand											
GT15	~2002	0.566	22	6	33	6	38	0.823	47	11	This study
References:											
Asia:											
Pearl River Estuary, China	2005	29.7	368	2.6-6.4							Chen et al., 2007
Tokyo Bay, Japan	1998-2000	17-58	590-1,700	NI <sup>c</sup>							Minh et al., 2007
Arctic:											
Canadian Arctic	1999	0.0028	0.11	NI			90	0.037	1.18	NI	Stern et al., 2005
Norwegian Arctic	~1994	NI	NI	15			18	NI	NI	NI	Evenset et al., 2007
Europe:											
Greifensee, Switzerland	2002	0.83	19	9							Kohler et al., 2008
Great Lakes, USA:											
Lake Erie	2002	3.71-8.93	68.0-76.2	NI			39	2.09-3.71	169-196	NI	Song et al., 2005b
Lake Erie	2003	3.6	40	5.3							Zhu and Hites, 2005
Lake Michigan	2004	0.98	38	7.5							Zhu and Hites, 2005
Lake Michigan	2002	0.64-2.04	48.6-82.0	10-13			39	0.26-1.14	27.3-48.1	NI	Song et al., 2005a
Lake Huron	2002	0.67-1.41	8.64-25.1	NI			39	0.23-0.73	6.21-56.3	NI	Song et al., 2005a
Lake Ontario	2002	6.50-7.33	86.7-141	NI			39	1.79-1.92	255-263	NI	Song et al., 2005b
Lake Superior	2001-2002	0.008-0.031	3.1-6.4	45			19	0.015-0.106	2.14-12.2	NI	Song et al., 2004

<sup>a</sup>  $\Sigma$ PBDEs is sum of 45 PBDEs: BDEs 1, 2, 3, 7, 8, 10, 11, 12/13, 15, 17/25, 30, 32, 33/28, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 116, 118, 119, 126, 138, 153, 154, 155, 166, 181, 183, 190, 188, 196, 197, 202, 203, 206, 207, 208, 209. <sup>b</sup>  $\Sigma$ PCB is sum of 38 PCBs: CBs 8, 18, 28, 44, 49, 52, 66, 74, 87, 99, 101, 105, 110, 118, 128, 138, 146, 149, 151, 153, 156, 157, 158, 167, 170, 172, 177, 178, 180, 183, 187, 189, 194, 195, 199, 196/203, 206, 209. <sup>c</sup> Not Indicated.

## **Chapter 5**

### **General Discussion and Conclusion**

## 5.1. General Discussion

This study investigated the distribution, debromination and transport processes of PBDEs in eight tropical Asian countries and their highly urbanized cities, such as Lao PDR (Vientiane), Cambodia (Phnom Penh), Vietnam (Can Tho and Hanoi), India (Kolkata, Chennai and Mumbai), Indonesia (Jakarta), Thailand (Bangkok), the Philippines (Metro Manila) and Malaysia (Kuala Lumpur). The study specifically covered three topics: the status and debromination of PBDEs in the leachates from MSWDS of highly urbanized cities; sedimentary PBDEs in the rivers and canals of urban areas; and the historical trends of PBDE deposition in typical tropical Asian environments, using radio-dated sediment cores from Manila Bay, Philippines and the upper Gulf of Thailand. The concentration levels of the PBDE congeners and their variability among countries, and with other countries worldwide were assessed. PBDE congener profiles were also examined to probe the occurrence of debromination in the MSWDS, in the rivers and canals, and in the sediment cores of tropical Asian countries because debrominated higher congeners can become the source of lower but more bioavailable and toxic congeners to the environment. Possible transport mechanisms of PBDEs to the environment were also investigated from the partitioning of the PBDEs in the dissolved and adsorbed phases of leachate samples, through the temporal trends of PBDEs in MSWDS, and from the spatial distribution of PBDEs in riverine and coastal sediments. The findings of the study are specifically described below.

**Chapter 2:** The results of this study showed the status of PBDEs in the MSWDS of tropical Asian countries. Higher PBDE concentrations were found in the more industrialized Asian countries, such as Thailand, India, the Philippines, Malaysia and Indonesia. In general, the concentrations of PBDEs in the leachates from the MSWDS of most of the tropical Asian countries studied were higher than those reported in northern Canada, the U.S., Sweden, Japan and South Africa. The PBDE congener profiles in the leachates reflected the composition of the technical PBDE products typically used in Asia (i.e., more of the technical deca-BDE than the penta- and octa-BDE products).

Further, the fate of PBDEs in MSWDS and possible transport mechanisms to the environment were revealed. Occurrence of debromination in the MSWDS was suggested by the

profiles of the PBDE congeners. Congeners which are not contained, or in trace concentrations in the technical PBDE products (e.g., BDEs 1, 8, 17/25, 49, 179, 188, 202, 206, 207, 208) were found at relatively higher concentrations in most of the leachate samples. The temporal trends also indicated the reduction of BDE-209 over time, with a corresponding increase in the concentrations, and/or emergence of lower brominated PBDE congeners. While it is possible that deca-BDE in consumer products may be debrominated before disposal in MSWDS, other indicators considered in this study (i.e., the methanogenic phase activity or the anaerobic conditions in the MSWDS, and the strong solar radiation in tropical Asian countries) indicated that debromination occurred in the MSWDS of tropical Asian countries.

PBDEs were found predominantly in the adsorbed phase of the leachates. However, the presence of PBDEs in the dissolved phase in some of the leachates samples may be associated with the presence of DOM such as humic matter, which was confirmed by the high concentrations of DOC than POC in those samples, and by the lower apparent organic carbon-normalized partition coefficients ( $K'_{oc}$ ) than the  $K_{oc}$  predicted from the octanol-water partition coefficients ( $K_{ow}$ ). Dissolution of PBDEs with DOM in the leachates may facilitate the transport of PBDEs from the dumping sites to the aquatic and terrestrial environments. Temporal trends showed lowest PBDE concentrations in a MSWDS (Smokey Mt. in the Philippines) which had been closed for ~16 years, possibly indicating the leaching out of PBDEs over the intervening time.

**Chapter 3:** Widespread occurrence of PBDEs in the surface sediments of rivers and canals in urban areas of the selected tropical Asian countries was verified in this study. BDE-209 was predominant in most of the sediment samples. A correlation was observed between the amount of PBDEs in the aquatic environment (i.e., in the sediments) and the GDP per capita of tropical Asian countries; and between the quantity of PBDEs found in the leachates from the MSWDS. Although higher GDP per capita may translate into high purchasing power for consumer goods laden with PBDEs, it may not always correspond to more PBDEs in the environment, as indicated by the relatively lower levels of PBDEs in the sediment samples from Japan, where waste management is very stringent. The concentrations of sedimentary BDE-209 in the selected tropical Asian countries (including countries with comparatively lower GDP per capita, such as Lao PDR and Cambodia)

were similar to or higher than those in highly urbanized and industrialized countries worldwide. Moreover, higher concentrations of PBDEs were observed in areas near to point sources. Spatial trends indicated that inland sources of PBDEs (i.e., rivers and canals) can impact coastal areas.

The congener profiles in the sediments were similar to those in the leachates from the MSWDS. Higher importation of technical deca-BDE than penta- and octa-BDE products into Asia was indicated by the congener profiles. The presence of PBDE congeners which are not contained in the technical PBDE mixtures (e.g., BDE 3, 7, 15 and 77) in the sediments; and the higher proportions of nona-BDEs relative to BDE-209, and of mono- to tri-BDEs in the sediments compared to their respective proportions in the technical deca-BDE mixture, and in the corresponding leachate samples in some countries, were identified as indicators of debromination in the riverine environments. BDE-209 was possibly debrominated in anaerobic sediment samples, although there was no occurrence of debromination in some anaerobic samples. Further studies are needed to verify the occurrence of debromination in aquatic environments, e.g., identifying specific microorganisms that will facilitate or suppress the occurrence of debromination in the aquatic environment.

**Chapter 4:** Vertical profiles of the cores indicated the high concentrations of BDE-209 and their increasing concentrations toward the surface; or correspondingly, the increasing consumption of technical deca-BDE products, presumably since it is the only technical product remaining in the market. The concentration profiles of total PBDEs in the cores also reflected the rapid economic growth in Asia until the mid-1990s, the Asian financial crisis in 1997 to 1999, and the economic recovery since the early 2000s.

Earlier occurrence of PCBs than of PBDEs was reflected in the cores from the Philippines and Thailand, and was consistent with the historical earlier usage of PCBs worldwide. Although the inventories of total PBDEs were lower than the total PCBs, the doubling times of PBDEs were faster than the PCBs, both in Manila Bay and in the upper Gulf of Thailand. With the current consumption pattern of PBDEs (i.e., with respect to a wider range of applications in consumer products, and with no existing regulations in the use of deca-BDE in most of these tropical Asian

countries), it can be deduced that accumulation of PBDEs in the aquatic environment will likely surpass those of the PCBs.

The congener profiles of the cores (i.e., the occurrence of BDEs 209, 207, 206, 197, 196, 99, and 47) also reflected the higher consumption of the technical deca- than the penta-BDE products in the Philippines and in Thailand, which would be consistent with the PBDE importation in Asia. BDEs 47 and 99 generally decreased toward the surface, which would reflect the phase-out of the technical penta-PBDE products and the regulation by the Stockholm Convention in recent years.

Occurrence of anaerobic debromination was also indicated in the sediment cores by the increasing ratios of the octa- and nona-BDEs to BDE-209 (BDE-196/209, 202/209, 206/209, 207/209), and the corresponding decreasing % BDE-209 down the core layer, at proportions that were higher and lower, respectively than their respective proportions in the technical deca-BDE mixture. The occurrence of BDE-202 which is not contained in the technical deca-BDE product in many layers of the sediment cores, and its increasing ratio relative to BDE-209 (BDE-202/209), particularly from the middle down to the bottom layers provided a strong evidence of the occurrence of anaerobic debromination in the sediment cores.

## **5.2. General Conclusion**

This study revealed the relatively high emissions of PBDEs in most of the selected tropical Asian countries included in this study. MSWDS are significant sources of PBDE emission to the aquatic environments of tropical Asian countries. PBDEs are also prevalent in the aquatic environments (i.e., in riverine sediments) of urban areas of the selected tropical Asian countries. Thailand, Cambodia, India, Philippines and Malaysia are possible hot spot areas of PBDE contamination. The high PBDE concentrations in Cambodia which has a lower GDP and population may be associated with the importation of e-waste.

Deca-BDE was debrominated in the MSWDS and in the urban riverine environments of tropical Asian countries, as well as in the sediment cores from two typical tropical Asian marine environments. Similar debromination profiles of BDE-209 (particularly the higher proportions of nona-BDEs relative to BDE-209 and to their proportions in the technical deca-BDE mixture, and

the occurrence of BDE-202) were consistently observed in the leachates, riverine sediments and in the sediment core samples. Anaerobic debromination likely occurred in the MSWDS, in the rivers and canals, and in the coastal areas where the sediment cores were obtained. Photolytic debromination, particularly in the MSWDS may have also occurred due to the long and intense solar radiation in these Asian countries. Although debromination in the MSWDS appeared to be significant, and possibly contributed to the load of lower brominated congeners in the rivers and canals, occurrence of debromination was indicated in some extremely anaerobic surface sediment samples, and in the more anaerobic middle to bottom layers of the sediment core samples. Thus, the results of the present study revealed the debromination of deca-BDE in the tropical Asian environment, and can be used as evidence toward the regulation of deca-BDE.

Trends on the historical accumulation and the increasing emission of deca-BDE were captured by the sediment cores from Manila Bay, Philippines and from the upper Gulf of Thailand, which are typical tropical Asian environments. Thus, sediment cores can be used to predict the increase of PBDE pollution in tropical Asian environments, and can provide the basis for the formulation of policies and strategies toward the appropriate management and containment of PBDEs in each country.

### **5.3. Recommendation**

Based on the findings of this study, action plans need to be focused on two interrelated areas, i.e., to reduce the emissions of PBDEs in tropical Asian countries, particularly the contribution from MSWDS, and to implement measures that will control or minimize the occurrence of debromination or the conversion of higher brominated congeners to lower brominated congeners. Three general approaches can be feasible, i.e., through research, regulations, and public awareness.

On the area of research, further laboratory studies on the occurrence of debromination are needed. The results of the present study indicated that debromination of BDE-209 did not occur even in some sediments that were extremely anaerobic. Microbial specificity has been hinted in some studies. There may be some indigenous microorganisms in the tropical Asian environments



that may suppress debromination, and may be utilized to control debromination in the dumping sites. Also, the association of PBDEs with DOM needs further studies as it can be a possible mechanism in the transport of PBDEs in leachates to the groundwater.

This study covered a limited number of samples and sampling locations (i.e., in most cases only one dumping site or urban city was examined, therefore they may not be considered as the true representative samples for each country). Thus, it will be necessary to examine more sampling locations or samples in order to verify the findings of this study, and to further examine the comparison of results among countries.

In addition, the contribution of photolysis from solar radiation in the debromination of deca-BDE in the tropical Asian environment needs further studies.. Another area of research is localized studies on the impact of PBDEs from MSWDS to specific environmental settings in each country, e.g., to a major water reservoir in Metropolitan Manila which is located adjacent to the dumpsite.

Regulations can be formulated both at the local and international levels. Local regulations on the segregation of waste, particularly PBDE-laden plastic waste including e-waste from biodegradable organic waste can effectively control the occurrence of anaerobic debromination in the MSWDS. This will also prevent facilitated transport of PBDEs by DOM to the environment. Similarly, indiscriminate disposal of raw waste and untreated waste water in rivers and coastal areas should be prevented in order to reduce the anaerobic conditions of riverine and coastal sediments. Also, local regulations on strict compliance to environmental standards for MSWDS leachates (e.g., requiring settling ponds with flocculating agents), prohibiting the entry of e-waste in each country and proper treatment of e-waste, particularly the small scale e-waste recycling operations in communities can reduce the emission of PBDEs in the environment.

At the international level, strengthening the initiatives of UNEP e.g., the Basel Convention for the trading of e-waste, and the on-going risk profile assessment for deca-BDE by the POP Review Committee of the Stockholm Convention can also reduce distribution of PBDEs in the tropical Asian region.

Another important component is the cooperation of the general public, particularly in the proper segregation and disposal of waste; thus, programs on public awareness through information campaigns should be put in place.

## REFERENCES

- Alaee, M., Arias, P., Sjödin, A., Bergman, Å., 2003. An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. *Environ. Int.* 29, 683-689.
- APIC (Asia Petrochemical Industry Conference). <http://www.apic-online.org>. Date accessed: 12 November 2012.
- Benninger, L.K., Aller, R.C., Cochran, J.K., Turekian, K.K., 1979. Effects of biological sediment mixing on the <sup>210</sup>Pb chronology and trace metal distribution in a Long Island Sound sediment core. *Earth Planet. Sc. Lett.* 43, 241-259.
- Binelli, A., Sarkar, S.K., Chatterjee, M., Riva, C., Parolini, M., deb Bhattacharya, B., Bhattacharya, A.K., Satpahty, K.K., 2007. Concentration of polybrominated diphenyl ethers (PBDEs) in sediment cores of Sundarban mangrove wetland, northeastern part of Bay of Bengal (India). *Mar. Pollut. Bull.* 54, 1220-1229.
- Boonyatumanond, R., Wattayakorn, G., Amano, A., Inouchi, Y., Takada, H., 2007. Reconstruction of pollution history of organic contaminants in the upper Gulf of Thailand by using sediment cores: First report from Tropical Asia Core (TACO) project. *Mar. Pollut. Bull.* 54, 554-565.
- Bożyk, P., 2006. Globalization and the Transformation of Foreign Economic Policy - (Transition and Development). Ashgate Publishing Ltd., Hampshire.
- Braekevelt, E., Tittlemier, S.A., Tomy, T.G., 2003. Direct measurement of octanol-water partition coefficients of some environmentally relevant brominated diphenyl ethers. *Chemosphere* 51, 563-567.
- BSEF (Bromine Science and Environmental Forum). <http://www.bsef.com>. Dates accessed: 18 October 2012; 26 October 2013.
- Burke, P.J., Ahmadi-Esfahani, F.Z., 2006. Aid and growth: A study of South East Asia. *J. Asian Econ.* 17, 350-362.
- Chen, J.W., Harner, T., Schramm, K.W., Quan, X., Xue, X.Y., Kettrup, A., 2003. Quantitative

- relationships between molecular structures, environmental temperatures and octanol-air partition coefficients of polychlorinated biphenyls. *Comput. Biol. Chem.* 27, 405-421.
- Chen, L., Huang, Y., Peng, X., Xu, Z., Zhang, S., Ren, M., Ye, Z., Wang, X., 2009. PBDEs in sediments of the Beijiang River, China: Levels, distribution, and influence of total organic carbon. *Chemosphere* 76, 226-231.
- Chen, S.-J., Luo, X.-J., Lin, Z., Luo, Y., Li, K.-C., Peng, X.-J., Mai, B.-X., Ran, Y., Zeng, E.Y., 2007. Time trends of polybrominated diphenyl ethers in sediment cores from the Pearl River Estuary, South China. *Environ. Sci. Technol.* 41, 5595–6000.
- Christiansson, A., Eriksson, J., Teclechiel, D., Bergman, Å., 2009. Identification and quantification of products formed via photolysis of decabromodiphenyl ether. *Environ. Sci. Pollut. Res.* 16, 312-321.
- Costa, L.G., Giordano, G., 2007. Developmental neurotoxicity of polybrominated diphenyl ether (PBDE) flame retardants. *NeuroToxicology* 28, 1047-1067.
- Covaci, A., Gheorghe, A., Voorspoels, S., Maervoet, J., Steen Redeker, E., Blust, R., Schepens, P., 2005. Polybrominated diphenyl ethers, polychlorinated biphenyls and organochlorine pesticides in sediment cores from the Western Scheldt river (Belgium): analytical aspects and depth profiles. *Environ. Int.* 31, 367–375.
- Danon-Schaffer, M., 2010. Polybrominated diphenyl ethers in landfills from electronic waste. Dissertation, University of British Columbia.
- Darnerud, P.O., 2003. Toxic effects of brominated flame retardants in man and in wildlife. *Environ. Int.* 29, 841-853.
- Daso, A.P., Fatoki, O.S., Odendaal, J.P., Olujimi, O.O., 2012. Polybrominated diphenyl ethers (PBDEs) and 2,2', 4,4', 5,5'-hexabromobiphenyl (BB-153) in landfill leachate in Cape Town, South Africa. *Environ. Monit. Assess.* doi: 10.1007/s10661-012-2565-5.
- de las Alas, J.G., Sodusta, J.A., 1985. A model for the wind driven circulation of Manila Bay. *Natur. Appl. Sci. Bull.* 37, 159-170.

- de Wit, C.A., 2002. An overview of brominated flame retardants in the environment. *Chemosphere* 46, 583-624.
- Ehrig, H.-J., 1989. Water and element balances of landfills. In: Baccini, P., (ed) *The landfill – lecture notes in earth sciences*. Springer-Verlag, Berlin, pp 83-115.
- Eljarrat, E., De La Cal, A., Larrazabal, D., Fernandez-Alba, A.R., Borrull, F., Marce, R.M., Barcelo, D., 2005. Occurrence of polybrominated diphenylethers, polychlorinated dibenzo-*p*-dioxins, dibenzofurans, biphenyls in coastal sediments from Spain. *Environ. Pollut.* 136, 493-501.
- EMB (Environmental Management Bureau). Proceedings: Seminar-workshop on river rehabilitation program for the Manila Bay Region. DENR-EMB, Quezon City, Philippines.
- Evenset, A., Christensen, G.N., Carroll, J., Zaborska A, Berger U, Herzke D, Gregor, D., 2007. Historical trends in persistent organic pollutants and metals recorded in sediment from Lake Ellasjøen, Bjørnøya, Norwegian Arctic. *Environ. Pollut.* 46, 196–205.
- Fang, L., Huang, J., Yu, G., Wang, L., 2008. Photochemical degradation of six polybrominated diphenyl ether congeners under ultraviolet irradiation in hexane. *Chemosphere* 71, 258-267.
- Gerecke, A.C., Hartmann, P.C., Heeb, N.V., Kohler, H.-P.E., Giger, W., Schmid, P., Zennegg, M., Kohler, M., 2005. Anaerobic degradation of decabromodiphenyl ether. *Environ. Sci. Technol.* 39, 1078-1083.
- Goldhaber, M.B., Aller, R.C., Cochran, J.K., Rosenfeld, J.K., Martens, C.S., Berner, R.A., 1977. Sulfate reduction, diffusion and bioturbation in Long Island Sound Sediments: Report of the FOAM group. *Am. J. Sci.* 277, 193-237.
- Guzzella, L., Roscioli, C., Binelli, A., 2008. Contamination by polybrominated diphenyl ethers of sediments from the Lake Maggiore basin (Italy and Switzerland). *Chemosphere* 73, 1684–1691.
- Hale, R.C., Alae, M., Manchester-Neesvig, J.B., Stapleton, H.M., Ikonomou, M.G., 2003. Polybrominated diphenyl ether flame retardants in the North American environment. *Environ. Int.* 29, 771-779.

- Hale, R.C., La Guardia, M.J., Harvey, E., Mainor, T.M., 2002. Potential role of fire retardant-treated polyurethane foam as a source of brominated diphenyl ethers to the US environment. *Chemosphere* 46, 729-735.
- Hardy, M.L., 2002. A comparison of the properties of the major commercial PBDPO/PBDE product to those of major PBB and PCB products. *Chemosphere* 46, 717–728.
- He, J., Robrock, K.R., Alvarez-Cohen, L., 2006. Microbial reductive debromination of polybrominated diphenyl ethers (PBDEs). *Environ. Sci. Technol.* 40, 4429-4434.
- Heskett, M., Takada, H., Yamashita, R., Yuyama, M., Ito, M., Geok, Y.B., Ogata, Y., Kwan, C., Heckhausen, A., Taylor, H., Powell, T., Morishige, C., Young, D., Patterson, H., Robertson, B., Bailey, E., Mermoz, J., 2012. Measurement of persistent organic pollutants (POPs) in plastic resin pellets from remote islands: Toward establishment of background concentrations for International Pellet Watch. *Mar. Pollut. Bull.* 64, 445-448.
- Hirai, H., Takada, H., Ogata, Y., Yamashita, R., Mizukawa, K., Saha, M., Kwan, C., Moore, C., Gray, H., Laursen, D., Zettler, E.R., Farrington, J.W., Reddy, C.M., Peacock, E.E., Ward, M.W., 2011. Organic micropollutants in marine plastics debris from the open ocean and remote and urban beaches. *Mar. Pollut. Bull.* 62, 1683–1692.
- Hites, R.A., Laflamme R.E., Farrington J.W., 1977. Sedimentary polycyclic aromatic hydrocarbons: the historical record. *Science* 198, 829–831.
- Hites, R.A., 2004. Polybrominated diphenyl ethers in the environment and in people: A meta-analysis of concentrations. *Environ. Sci. Technol.* 38, 945-956.
- Hong, S.H., Kannan, N., Jin, Y., Won, J.H., Han, G.M., Shim, W.J., 2010. Temporal trend, spatial distribution, and terrestrial sources of PBDEs and PCBs in Masan Bay, Korea. *Mar. Pollut. Bull.* 60, 1836-1841.
- Horowitz, A.J., Lum, K.R., Garbarino, J.R., Hall, G.E.M., Lemieux, C., Demas, C.R., 1996. Response to comments on “Problems associated with using filtration to define dissolved trace element concentrations in natural water samples”. *Environ. Sci. Technol.* 30, 3398-3400.

- <http://www.plasticsindustry.org/AboutPlastics/content.cfm?ItemNumber=670>. Date accessed: 21 July 2013.
- <http://www.solarischemtech.com>. Decabromodiphenyl oxide product sheet. Date accessed: 12 November 2012.
- <http://www.unep.org/roap/Activities/HarmfulSubstances/BaselandRotterdamConventions/tabid/6821/Default.aspx>. Date accessed: 30 October 2013.
- <http://www.unstats.un.org/unsd/demographic/products/dyb/dyb2001/Table08.pdf>. Date accessed: 27 January 2014.
- Hung, C.-C., Gong, G.-C., Jiann, K.-T., Yeager, K.M., Santschi, P.H., Wade, T.L., Serricano, J.L., Hsieh, H.-L., 2006. Relationship between carbonaceous materials and polychlorinated biphenyls (PCBs) in the sediments of the Danshui River and adjacent coastal areas, Taiwan. *Chemosphere* 6, 1452-1461.
- Ilyas, M., Sudaryanto, A., Setiawan, I.T., Isobe, T., Takahashi, S., Tanabe, S., 2010. Characterization of polychlorinated biphenyls and polybrominated diphenyl ethers in sediments from leachates and control wells of Benowo dumping site, Surabaya, Indonesia: A preliminary report. In: Isobe, T., Nomiya, K., Subramanian, A., Tanabe, S. (eds) *Interdisciplinary studies on environmental chemistry, Volume 4 TERRAPUB*, Tokyo, pp 161-166.
- Ilyas, M., Sudaryanto, A., Setiawan, I.E., Riyadi, A.S., Isobe, T., Takahashi, S., Tanabe, S., 2011. Characterization of polychlorinated biphenyls and brominated flame retardants in sediments from riverine and coastal waters of Surabaya, Indonesia. *Mar. Pollut. Bull.* 62, 89-98.
- Isobe, K.O., Zakaria, M.P., Chiem, N.H., Minh, L.Y., Prudente, M., Boonyatumanond, R. Saha, M., Sarkar, S., Takada, H., 2004. Distribution of linear alkyl benzenes (LABs) in riverine and coastal environments in South and Southeast Asia. *Water Res.* 38, 2449-2459.
- Jiang, J.-J., Lee C.-L., Fang, M.-D., Ko, F.-C., Baker, J.E., 2011. Polybrominated diphenyl ethers and polychlorinated biphenyls in sediments of southwest Taiwan: Regional characteristics and potential sources. *Mar. Pollut. Bull.* 62, 815-823.

- Johannessen, S.C., Macdonald, R.W., Wright, C.A., Burd, B., Shaw, D.P., van Rodselaar, A., 2008. Joined by geochemistry, divided by history: PCBs and PBDEs in Strait of Georgia sediments. *Mar. Environ. Res.* 66, S112-S120.
- Kajiwara, N., Noma, Y., Takigami, H., 2008. Photolysis studies of technical decabromodiphenyl ether (DecaBDE) and ethane (DeBDethane in plastics under natural sunlight. *Environ. Sci. Technol.* 42, 4404-4409.
- Kim, Y.-J., Osako, M., Sakai, S., 2006. Leaching characteristics of polybrominated diphenyl ethers (PBDEs) from flame-retardant plastics. *Chemosphere* 65, 506-513.
- Klosterhaus, S.L., Stapleton, H.M., La Guardia, M.L., Greig, D.J., 2012. Brominated and chlorinated flame retardants in San Francisco Bay sediments and wildlife. *Environ Int.* 47, 56-65.
- Knoth, W., Mann, W., Meyer, R., Nebhuth, J., 2007. Polybrominated diphenyl ether in sewage sludge in Germany. *Chemosphere* 67, 1831-1837.
- Koh, A., 2007. Green productivity approaches to SWM. Turning waste into profit. In: *Solid waste management: issues and challenges in Asia*. Asian productivity organization, Tokyo, pp 11-12.
- Kohler, M., Zennegg, M., Bogdal, C., Gerecke, A., Schmid, P., Heeb, N.V., Sturm, M., Vonmont, H., Kohler, H.-P.E., Giger, W., 2008. Temporal trends, congener patterns, and sources of octa-, nona-, and decabromodiphenyl ethers (PBDE) and hexabromocyclododecanes (HBCD) in Swiss Lake sediments. *Environ. Sci. Technol.* 42, 6378-6384.
- La Guardia, M.J., Hale, R.C., Harvey, E., 2006. Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. *Environ. Sci. Technol.* 40, 6247-6254.
- La Guardia, M.J., Hale, R.C., Harvey, E., 2007. Evidence of debromination of decabromodiphenyl ether (BDE-209) in biota from a wastewater receiving stream. *Environ. Sci. Technol.* 41, 6663-6670.



- Li, B., Danon-Schafer, M.N., Li, L.Y., Ikonomou, M.G, Grace, J.R., 2012. Occurrence of PFCs and PBDEs in landfill leachates from across Canada. *Water Air Soil Poll.* 223, 3365-3372.
- Liu, Y., Zheng, G.J., Yu, H., Martin, M., Richardson, B.J., Lam, M.H.W., Lam, P.K.S., 2005. Polybrominated diphenyl ethers (PBDEs) in sediments and mussel tissues from Hong Kong marine waters. *Mar. Pollut. Bull.* 50, 1173-1184.
- Lloyd, P.J., MacLaren, D., 2000. Openness and growth in East Asia after the Asian crisis. *J. Asian Econ.* 11, 89–105.
- Martin, M., Lam, P.K.S., Richardson, B.J., 2004. An Asian quandary: where have all of the PBDEs gone? *Mar. Pollut. Bull.* 49, 375-382.
- Mato, Y., Isobe, T., Takada, H., Kanehiro, H., Ohtake, C., Kaminuma, T., 2001. Plastic resin pellets as a transport medium for toxic chemicals in the marine environment. *Environ. Sci. Technol.* 35, 318-324.
- McDonald, T.A., 2002. A perspective on the potential health risks of PBDEs. *Chemosphere* 46, 745-755.
- Minh, N.H., Isobe, T., Ueno, D., Matsumoto, K., Mine, M., Kajiwara, N., Takahashi, Tanabe, S., 2007. Spatial distribution and vertical profile of polybrominated diphenyl ethers and hexabromocyclododecanes in sediment core from Tokyo Bay, Japan. *Environ. Pollut.* 148, 409–417.
- Ministry of Interior. Population in Bangkok metropolis, vicinity area and whole kingdom during 2000–2011 and forecast of 2012 and 2013. [http://www.office.bangkok.go.th/pipd/05-Stat/08Stat\(En\)/Stat\(En\)54/pdf%20\(not%20edit\)/stat-eng2011%20\(not%20edit\).pdf](http://www.office.bangkok.go.th/pipd/05-Stat/08Stat(En)/Stat(En)54/pdf%20(not%20edit)/stat-eng2011%20(not%20edit).pdf). Date accessed: 27 May 2013.
- Mizukawa, K., Takada, H., Takeuchi, I., Ikemoto, T., Omori, K., Tsuchiya, K., 2009. Bioconcentration and biomagnification of polybrominated diphenyl ethers (PBDEs) through lower-trophic-level coastal marine food web. *Mar. Pollut. Bull.* 58, 1217-1224.
- Mizukawa, K., Takada, H., Ito, M., Geok, Y.B., Hosoda, J., Yamashita, R., Saha, M., Suzuki, S., Miguez, C., Frias, J., Antunes, J.C., Sobral, P., Santos, I., Micaelo, C., Ferreira, M., 2013.

- Monitoring of a wide range of organic micropollutants on the Portuguese coast using plastic resin pellets. *Mar. Pollut. Bull.* 70, 296-302.
- Moon, H.-B., Kannan, K., Choi, M., Choi, H.-G., 2007. Polybrominated diphenyl ethers (PBDEs) in marine sediments from industrialized bays of Korea. *Mar. Pollut. Bull.* 54, 1402-1412.
- Nickell, L.A., Black, K.D., Hughes, D.J., Overnell, J., Brand T., Nickell, T.D., Breuer, E., Harvey, S.M., 2003. Bioturbation, sediment fluxes and benthic community structure around a salmon cage farm in Loch Creran, Scotland. *J. Exp. Mar. Biol. Ecol.* 285-286, 221-233.
- Ngoc, U.N., Schnitzer, H., 2009. Sustainable solutions for solid waste management in Southeast Asian countries. *Waste Manage.* 29, 1992-1995.
- Noël, M., Dangerfield, N., Hourston, R.A.S., Belzer, W., Shaw, P., Yunker, M., Ross, P., 2009. Do trans-Pacific air masses deliver PBDEs to coastal British Columbia, Canada? *Environ. Pollut.* 157, 3404-3412.
- NSO (National Statistics Office), 2010. 2010 Census of population and housing. <http://www.census.gov.ph/statistics/census/population-and-housing>. Date accessed: 27 May 2012.
- Nylund, K., Asplund, L., Jansson, B., Jonsson, P., Litzén, K., Sellström, U., 1992. Analysis of some polyhalogenated organic pollutants in sediment and sewage sludge. *Chemosphere* 24, 1721–1730.
- Odusanya, D.O., Okonkwo, J.O., Botha, B., 2009. Polybrominated diphenyl ethers (PBDEs) in leachates from selected landfill sites in South Africa. *Waste Manage.* 29, 96-102.
- OECD (Organisation for Economic Co-operation and Development) Environment Directorate, 1994. Risk Reduction Monograph No. 3: Selected brominated flame retardants—background and national experience with reducing risk. <http://www.oecd.org>. Date accessed: 12 November 2012.
- Ogata, Y., Takada, H., Mizukawa, K., Hirai, H., Iwasa, S., Endo, S., Mato, Y., Saha, M., Okuda, K., Nakashima, A., Murakami, M., Zurcher, N., Boonyatumanond, R., Zakaria, M.P., Dung, L.Q., Gordon, M., Miguez, C., Suzuki, S., Moore, C., Karapanagioti, H., Weerts, S.,

- McClurg, T., Burres, E., Smith, W., Velkenburg, M.V., Lang, J.S., Lang, R.C., Laursen, D., Danner, B., Stewardson, N., Thompson, R.C., 2009. International pellet watch: Global monitoring of persistent organic pollutants (POPs) in coastal waters. 1. Initial phase data on PCBs, DDTs, and HCHs. *Mar. Pollut. Bull.* 58, 1437-1446.
- Oliaei, F., King, P., Phillips, L., 2002. Polybrominated flame retardants: Occurrence and concentrations of polybrominated diphenyl ethers (PBDEs) in Minnesota environment. *Organohalogen Compd.* 58, 185-188.
- Öman, C.B., Junestedt, C., 2008. Chemical characterization of landfill leachates - 400 parameters and compounds. *Waste Manage.* 28, 1876-1891.
- Oros, D.R., Hoover, D., Rodigari, F., Crane, D., Sericano, J., 2005. Levels and distribution of polybrominated diphenyl ethers in water, surface sediments, and bivalves from the San Francisco Estuary. *Environ. Sci. Technol.* 39, 33-41.
- Osako, M., Kim, Y.-J., Sakai, S., 2004. Leaching of brominated flame retardants in leachate from landfills in Japan. *Chemosphere* 57, 1571-1579.
- Peralta, G.L., Fontanos, P.N., 2006. E-waste issues and measures in the Philippines. *J. Mater. Cycles Waste Manag.* 8, 34-39.
- Philippine Information Agency (<http://www.pia.gov.ph>) and the Mines and Geosciences Bureau (<http://www.mgb.gov.ph>). Geohazard maps. Accessed 5 March 2013.
- Philippine Institute of Volcanology and Seismology. Liquefaction hazard map of Metro Manila. <http://www.phivolcs.dost.gov.ph>. Date accessed: 5 March 2013.
- Pozo, K., Harner, T., Shoeib, M., Urrutia, R., Barra, R., Parra, O., Focardi, S., 2004. Passive-sampler derived concentrations of persistent organic pollutants on a north-south transect in Chile. *Environ. Sci. Technol.* 38, 6529-6537.
- Pozo, K., Harner, T., Wania, F., Muir, D.C.G., Jones, K.C., Barrie, L.A., 2006. Toward a global network for persistent organic pollutants in air. Results from the GAPS study. *Environ. Sci. Technol.* 40, 4867-4873.

- Rahman, F., Langford, K.H., Scrimshaw, M.D., Lester, J.N., 2001. Polybrominated diphenyl ether (PBDE) flame retardants. *Sci. Total Environ.* 275, 1-17.
- Rinawati, Koike, T., Koike, H., Kurumizawa, R., Ito, M., Shigeaki, S., Togo, A., Saha, M., Arifin, Z., Takada, H., 2012. Distribution, source identification, and historical trends of organic micropollutants in coastal sediment in Jakarta Bay, Indonesia. *J. Hazard. Mater.* 217-218, 208-216.
- Roberts, S.C., Noyes, P.D., Gallagher, E.P., Stapleton, H.M., 2011. Species-specific differences and structure-activity relationships in the debromination of PBDE congeners in three fish species. *Environ. Sci. Technol.* 45, 1999-2005.
- Robinson, B.H., 2009. E-waste: An assessment of global production and environmental impacts. *Sci. Total Environ.* 408, 183-191.
- Robrock, K.R., Korytár, P., Alvarez-Cohen, L., 2008. Pathways for the anaerobic microbial debromination of polybrominated diphenyl ethers. *Environ. Sci. Technol.* 42, 2845-2852.
- Ross, P.S., Couillard, C.M., Ikonou, M.G., Johannessen, S.C., Lebeuf, M., Macdonald, R.W., Tomy, G.T., 2009. Large and growing environmental reservoirs of Deca-BDE present an emerging health risk for fish and marine mammals. *Mar. Pollut. Bull.* 58, 7-10.
- Sakai, S., 1996. Municipal solid waste management in Japan. *Waste Manage.* 16, 395-405.
- Samara, F., Tsai, C.W., Aga, D.S., 2006. Determination of potential sources of PCBs and PBDEs in sediments of the Niagara River. *Environ. Pollut.* 139, 489-497.
- Santiago, E.C., Cayetano, M., 2011. Organochlorine pesticides in ambient air in selected urban and rural residential areas in the Philippines derived from passive samplers with polyurethane disks. *Bull. Environ. Contam. Toxicol.* 86, 50-55.
- Santiago, E.C., Rivas, F., 2012. Polychlorinated biphenyls in selected sites in Pasig River and Laguna Lake in the Philippines before and after a big flood event investigated under the UNU East Asia regional POPs monitoring project. *Bull. Environ. Contam. Toxicol.* 89, 407-411.
- Schumacher, B.A., 2002. Methods for the determination of total organic carbon (TOC) in soils and

sediments. U.S. Environmental Protection Agency, Office of Research and Development, Ecological Risk Assessment Support Center, Las Vegas.

Stockholm Convention (Secretariat of the Stockholm Convention), 2009. The New POPs. <http://chm.pops.int/Convention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx>. Date accessed: 23 January 2012.

Seth, R., Mackay, D., Muncke, J., 1999. Estimating the organic carbon partition coefficient and its variability for hydrophobic chemicals. *Environ. Sci. Technol.* 33, 2390-2394.

Sims, J.L., Suflita, J.M., Russell, H.H., 1991. Reductive dehalogenation of organic contaminants in soils and ground water. <http://www.epa.gov/superfund/remedytech/tsp/download/reddehal.pdf>. Date accessed: 31 January 2014.

Söderström, G., Sellström, U., de Wit, C.A., Tysklind, M., 2004. Photolytic debromination of decabromodiphenyl ether (BDE-209). *Environ. Sci. Technol.* 38, 127-132.

Song, W., Ford, J.C., Li, A., Mills, W.J., Buckley, D.R., Rockne, K.J., 2004. Polybrominated diphenyl ethers in the sediments of the Great Lakes. 1. Lake Superior. *Environ. Sci. Technol.* 38, 3286–3293.

Song, W., Li, A., Ford, J.C., Sturchio, N.C., Rockne, K.J., Buckley, D.R., Mills, W.J., 2005a. Polybrominated diphenyl ethers in the sediments of the Great Lakes. 2. Lakes Michigan and Huron. *Environ. Sci. Technol.* 39, 3474–3479.

Song, W., Ford, J.C., Li, A., Sturchio, N.C., Rockne, K.J., Buckley, D.R., Mills, W.J., 2005b. Polybrominated diphenyl ethers in the sediments of the Great Lakes. 3. Lakes Ontario and Erie. *Environ. Sci. Technol.* 39, 5600–5605.

Sta. Maria, E.J., Siringan, F.P., Bulos, A.d.M., Sombrito, E.Z., 2009. Estimating sediment accumulation rates in Manila Bay, a marine pollution hot spot in the Seas of East Asia. *Mar. Pollut. Bull.* 59, 164–174.

- Stapleton, H.M., Brazil, B., Holbrook, R.D., Mitchelmore, C.L., Benedict, R., Konstantinov, A., Potter, D., 2006. In vivo and in vitro debromination of decabromodiphenyl ether (BDE 209) by juvenile rainbow trout and common carp. *Environ. Sci. Technol.* 40, 4653-4658.
- Stapleton, H.M., Keller, J.M., Schantz, M.M., Kucklick, J.R., Leigh, S.D., Wise, S.A., 2007. Determination of polybrominated diphenyl ethers in environmental standard reference materials. *Anal. Bioanal. Chem.* 387, 2365-2379.
- Stapleton, H.M., Dodder, N.G., 2008. Photodegradation of decabromodiphenyl ether in house dust by natural sunlight. *Environ. Toxicol. Chem.* 27, 306-312.
- Stern, G.A., Braekevelt, E., Helm, P.A., Bidleman, T.F., Outridge, P.M., Lockhart, W.L., McNeeley, R., Rosenberg, B., Ikononou, M.G., Hamilton, P., Tomy, G.T., Wilkinson, P., 2005. Modern and historical fluxes of halogenated organic contaminants to a lake in the Canadian arctic, as determined from annually laminated sediment cores. *Sci. Total Environ.* 342, 223-243.
- Takada, H., Eganhouse, R., 1998. Molecular markers of anthropogenic waste: Their use in determining sources, transport pathways and fate of wastes in the environment. In: Meyers, R. (Ed.), *The Encyclopedia of Environmental Analysis and Remediation*. Wiley and Sons, New York, pp. 2883-2940.
- Takada, H., Ishiwatari, R., 1990. Biodegradation experiments of linear alkylbenzenes (LABs): isomeric composition of C<sub>12</sub> LABs as an indicator for the degree of LAB degradation in the aquatic environment. *Environ. Sci. Technol.* 24, 86-91.
- Tokarz, J.A., Ahn, M.-Y., Leng, J., Filey, T.R., Nies, L., 2008. Reductive debromination of polybrominated diphenyl ethers in anaerobic sediment and a biomimetic system. *Environ. Sci. Technol.* 42, 1157-1164.
- Toms, L.-M.L., Mortimer, M., Symons, R.K., Paepke, O., Mueller, J.F., 2008. Polybrominated diphenyl ethers (PBDEs) in sediment by salinity and land-use type from Australia. *Environ. Int.* 34, 58-66.

- UNEP (United Nations Environmental Program), Division of Technology, Industry and Economics, International Environmental Technology Centre, 2007. E-waste Volume 1: Inventory Assessment Manual.  
[http://www.unep.or.jp/ietc/Publications/spc/EWasteManual\\_Vol1.pdf](http://www.unep.or.jp/ietc/Publications/spc/EWasteManual_Vol1.pdf). Date accessed: 25 October 2013
- UNDESA (United Nations Department of Economic and Social Affairs), Population Division, 2010. World Population Prospects: The 2010 Revision. CD-ROM ed.  
<http://esa.un.org/wpp/Excel-Data/population.htm>. Date accessed: 24 April 2012.
- Verslycke, T.A., Vethaak, A.D., Arijs, K., Janssen, C.R., 2005. Flame retardants, surfactants, organotins in sediment and mysid shrimp of the Scheldt estuary (The Netherlands). *Environ. Pollut.* 136, 19-31.
- Wang, Y, Jiang, G., Lam, P.K.S., Li, A., 2007. Polybrominated diphenyl ether in the East Asian environment: A critical review. *Environ. Int.* 33, 963-973.
- Watanabe, I., Tatsukawa R., 1990. Anthropogenic brominated aromatics in the Japanese environment. In: Freiji L (ed). *Proceedings of workshop on brominated aromatic flame retardants*. Swedish National Chemicals Inspectorate (KemI), Sweden, pp. 63-71.
- Wong, M.H., Wu, S.C., Deng, W.J., Yu, X.Z., Luo, Q., Leung, A.O.W., Wong, C.S.C., Wong, A.S., 2007. Export of toxic chemicals - a review of the case of uncontrolled electronic-waste recycling. *Environ. Pollut.* 149, 131-140.
- World Bank. 2010 GDP per capita. <http://data.worldbank.org/indicator/NY.GDP.PCAP.CD>. Date accessed: 24 April 2012.
- World Bank Urban Development Division, 1999. What a waste: solid waste management in Asia.  
[http://www.worldbank.org/urban/solid\\_wm/erm/CWG%20folder/uwp1.pdf](http://www.worldbank.org/urban/solid_wm/erm/CWG%20folder/uwp1.pdf). Date accessed: 24 April 2012.
- Wurl, O., Obbard, J.P., 2005. Organochlorine pesticides, polychlorinated biphenyls and polybrominated diphenyl ethers in Singapore's coastal marine sediments. *Chemosphere* 58, 925-933.

- Zegers, B.N., Lewis, W.E., Booij, K., Smittenberg, R.H., Boer, W., de Boer, J., Boon, J.P., 2003. Levels of polybrominated diphenyl ether flame retardants in sediment cores from Western Europe. *Environ. Sci. Technol.* 37, 3803–3807.
- Zennegg, M., Kohler, M., Hartmann, P.C., Sturm, M., Gujer, E., Schmid, P., Gerecke, A.C., Heeb, N.V., Kohler, H.-P.E., Giger, W., 2007. The historical record of PCB and PCDD/F deposition at Greifensee, a lake of the Swiss plateau, between 1848 and 1999. *Chemosphere* 67, 1754–1761.
- Zheng, G.J., Martin, M., Richardson, B.J., Yu, H., Liu, Y., Zhou, C., Li, J., Hu, G., Lam, M.H.W., Lam, P.K.S., 2004. Concentrations of polybrominated diphenyl ethers in Pearl River Delta sediments. *Mar. Pollut. Bull.* 49, 514-524.
- Zhu, L.Y., Hites, R.A., 2005. Brominated flame retardants in sediment cores from Lakes Michigan and Erie. *Environ Sci Technol* 39, 3488-3494, 5904.



## **ANNEX**



Lao PDR: Km. 18 Xaythang District



Cambodia: Stung Mean Chey



Vietnam: Dong Thanh



India: Dhapa



Indonesia: Bantar Gebang



Malaysia: Tamang Beringin



Philippines: Payatas in 2002



Payatas in 2011

Fig. 2.1a. MSWDS in Lao PDR, Cambodia, India, Indonesia, the Philippines and Malaysia that were operational at the time of sampling (2002-2011).





Vietnam: Tay Mo



Grab sampling of leachate from a tank



Collected leachate sample



Thailand: Kukot



Philippines: Smokey Mt.



Leachate samples from drippings

Fig. 2.1b. MSWDS in Vietnam, Thailand and the Philippines that were no longer operational at the time of sampling (2002-2003), and sampling of leachate samples.

## Lao PDR

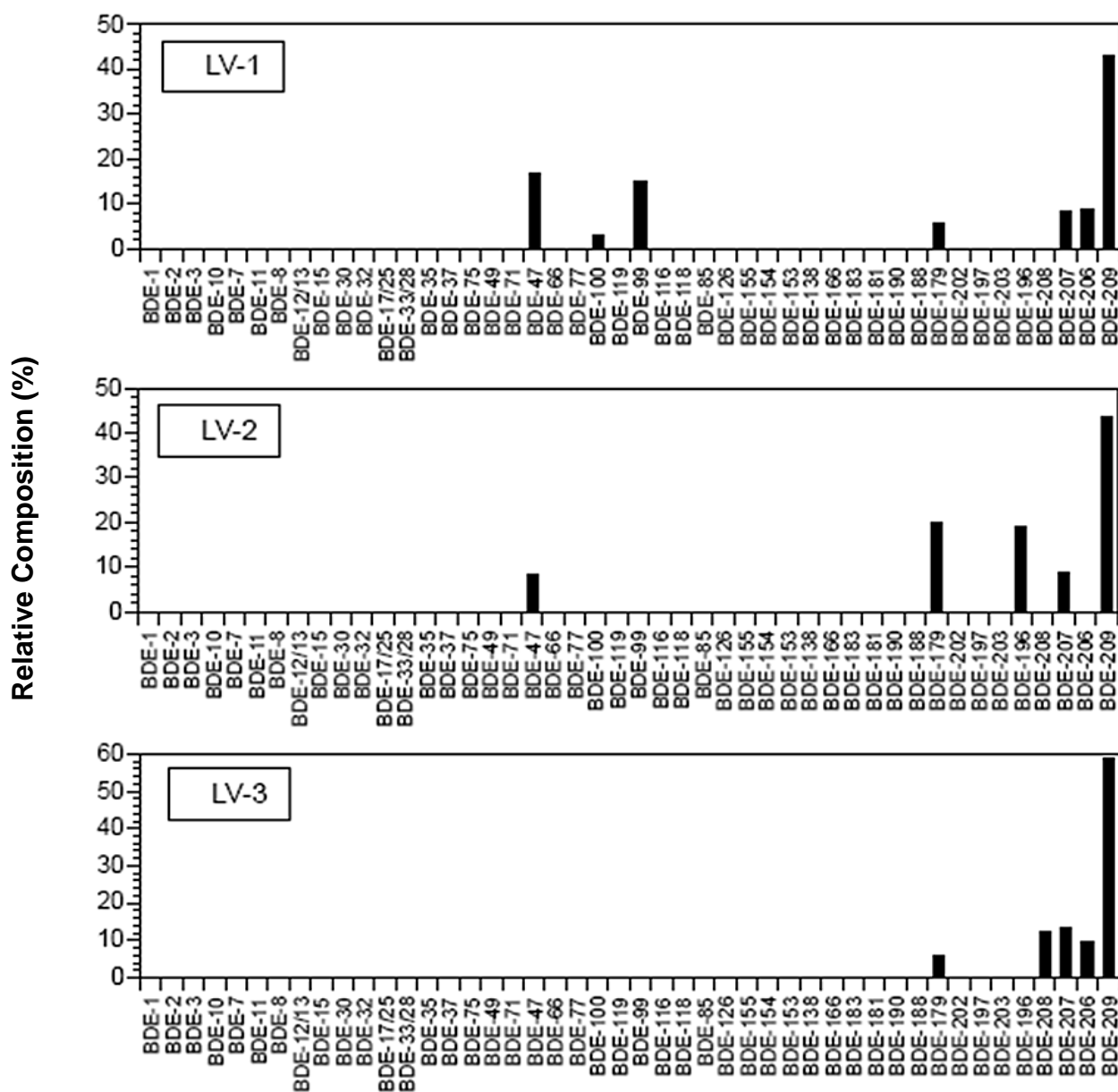
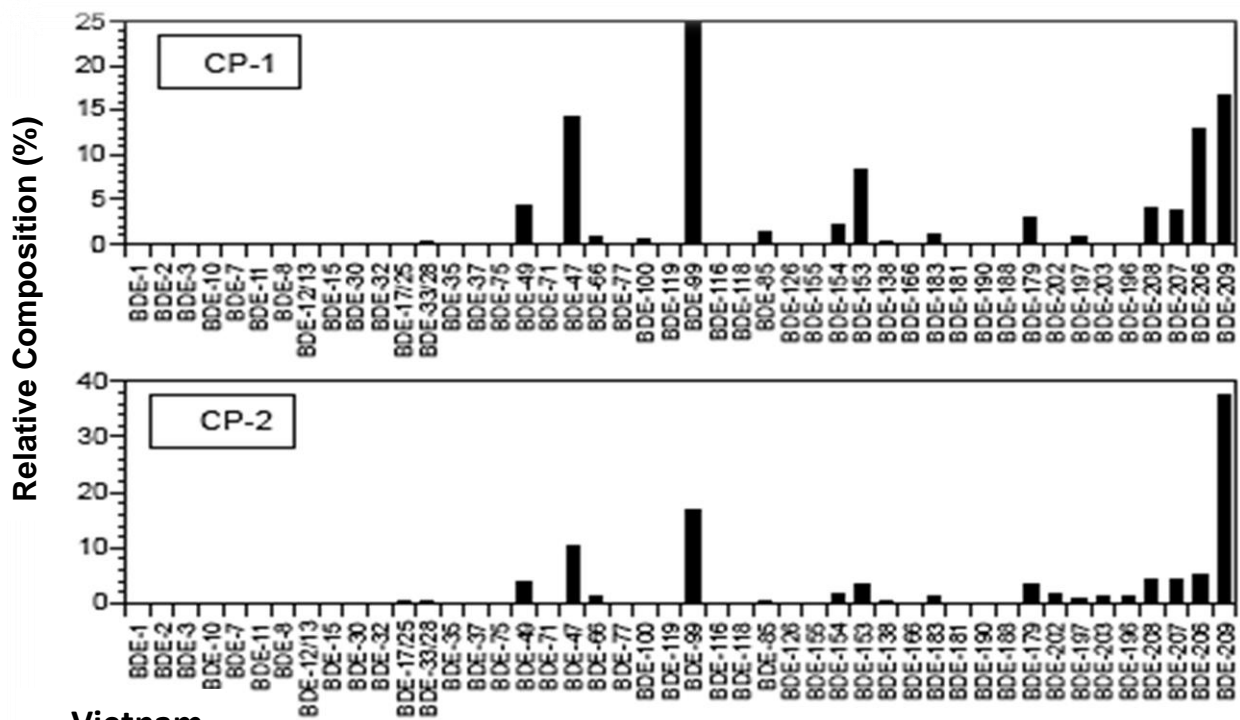


Fig. 2.2a. Congener profiles of PBDEs in the landfill leachates from Lao PDR.

## Cambodia



## Vietnam

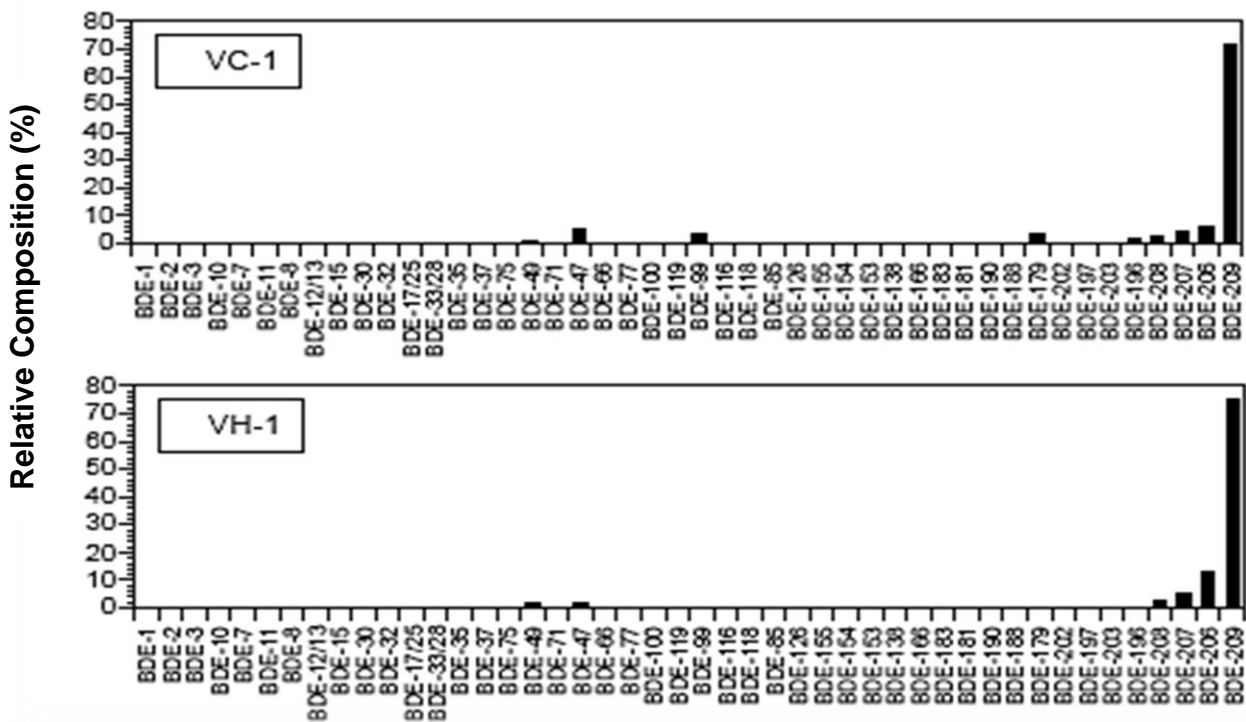


Fig. 2.2b. Congener profiles of PBDEs in the landfill leachates from Cambodia and Vietnam.

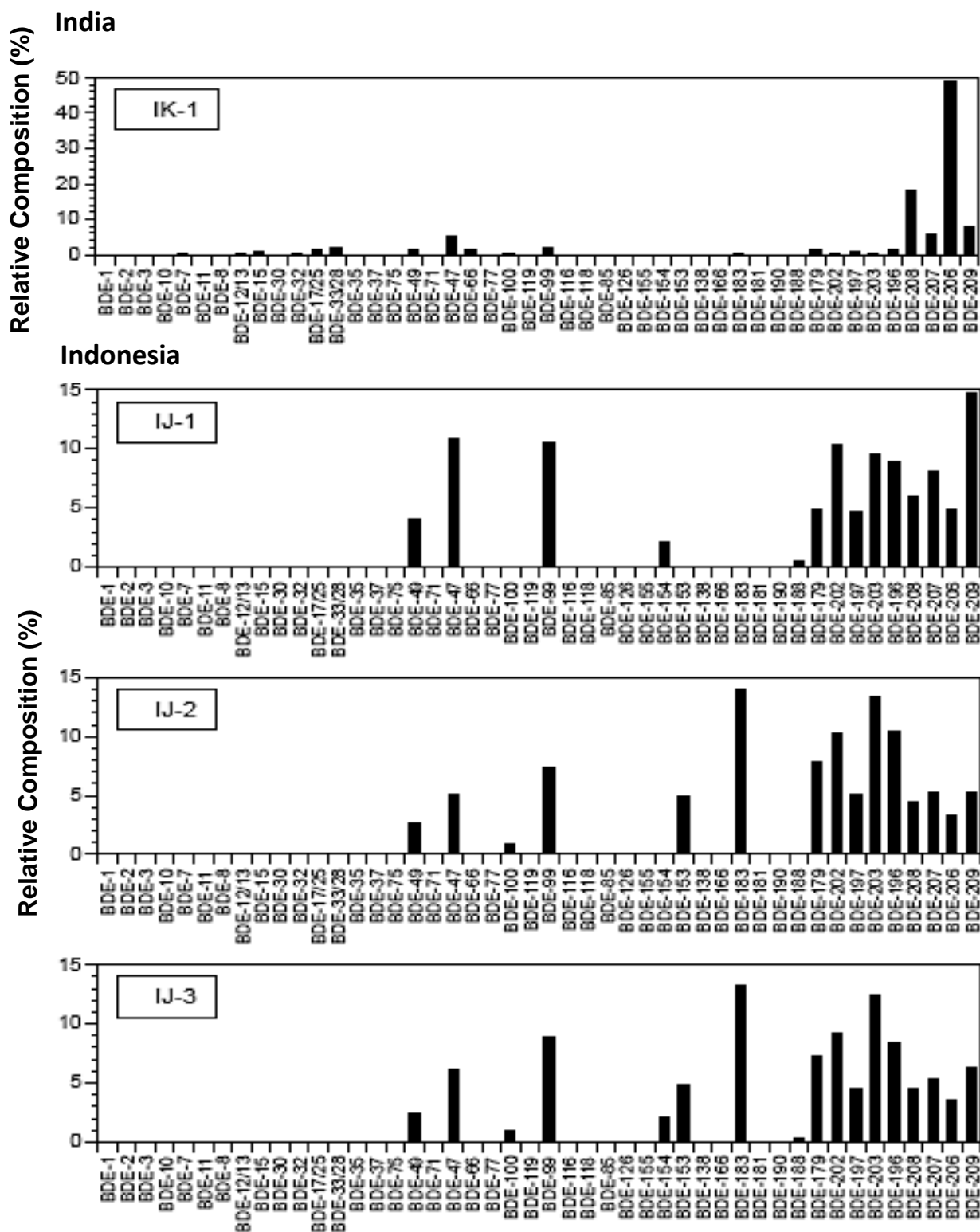


Fig. 2.2c. Congener profiles of PBDEs in the landfill leachates from India and Indonesia.

## Thailand

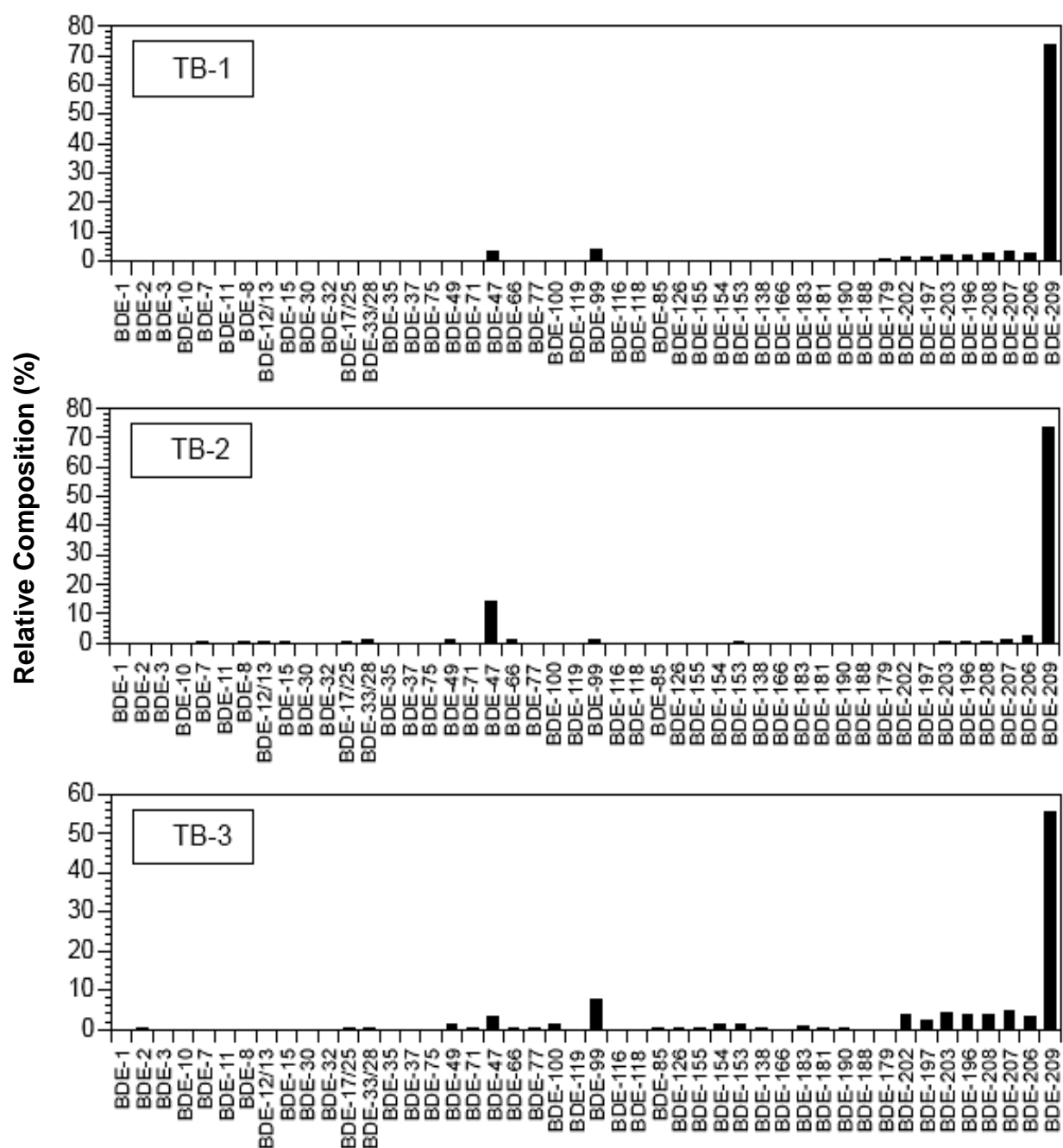


Fig. 2.2d. Congener profiles of PBDEs in the landfill leachates from Thailand.

## Philippines (Payatas)

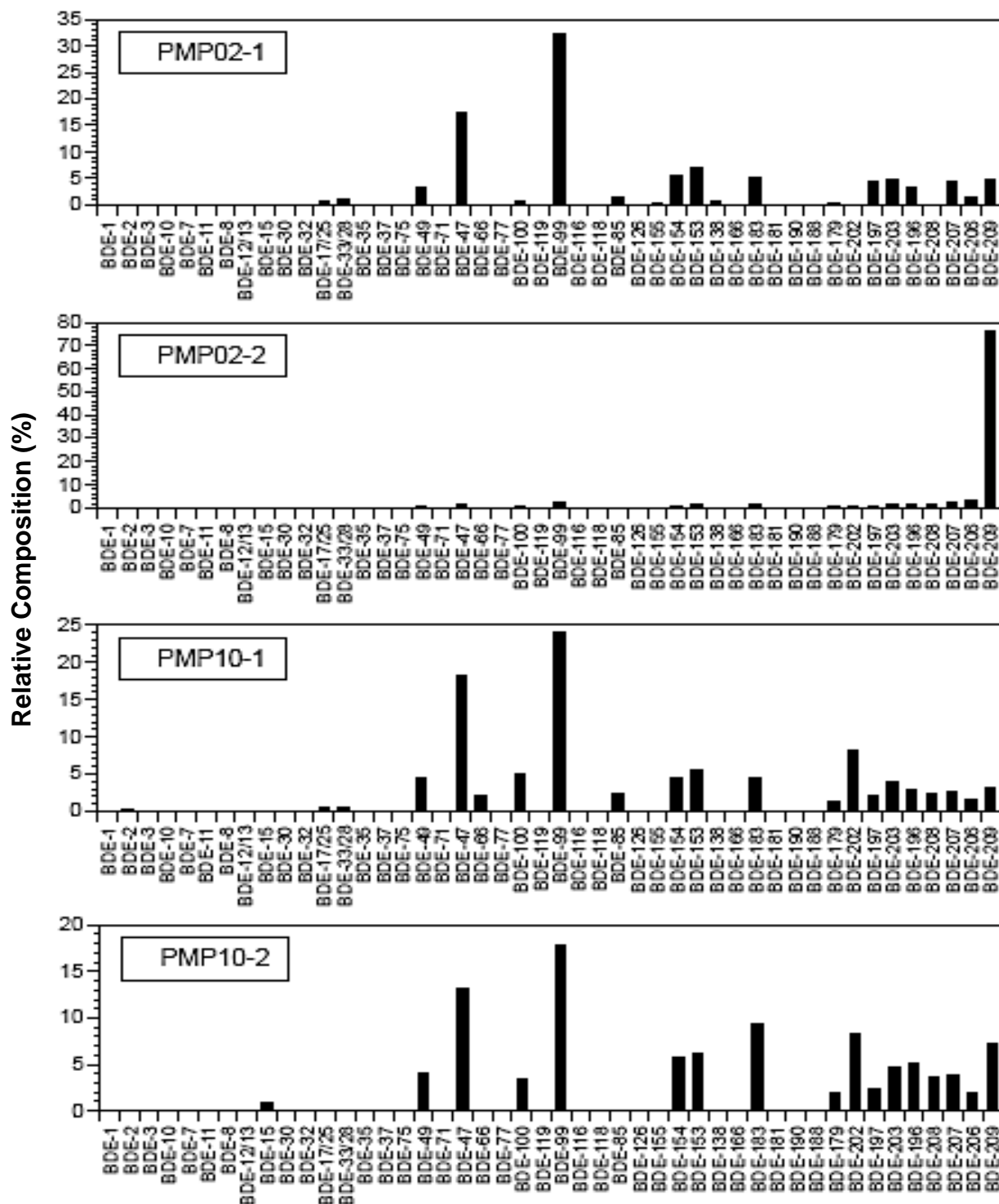


Fig. 2.2e. Congener profiles of PBDEs in the landfill leachates from the Philippines (Payatas).



### Philippines (Smokey Mountain)

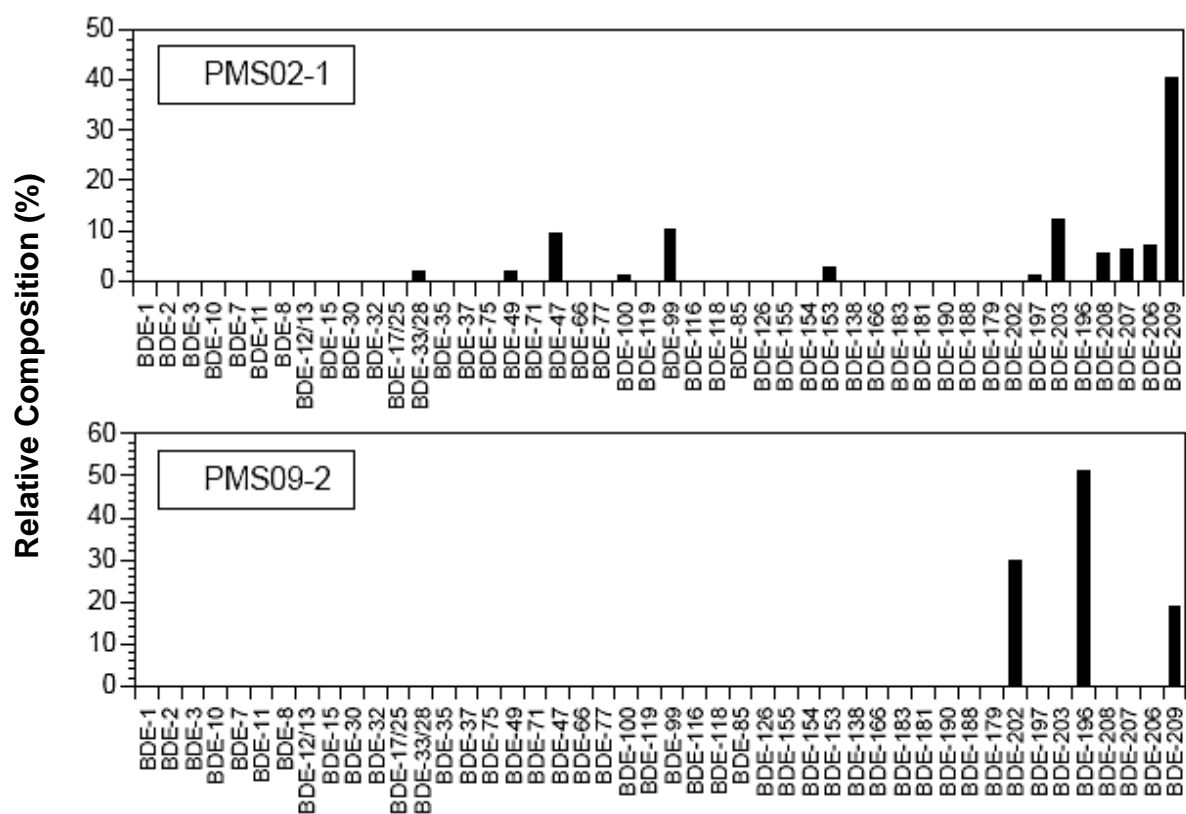


Fig. 2.2f. Congener profiles of PBDEs in the landfill leachates from the Philippines (Smokey Mountain).

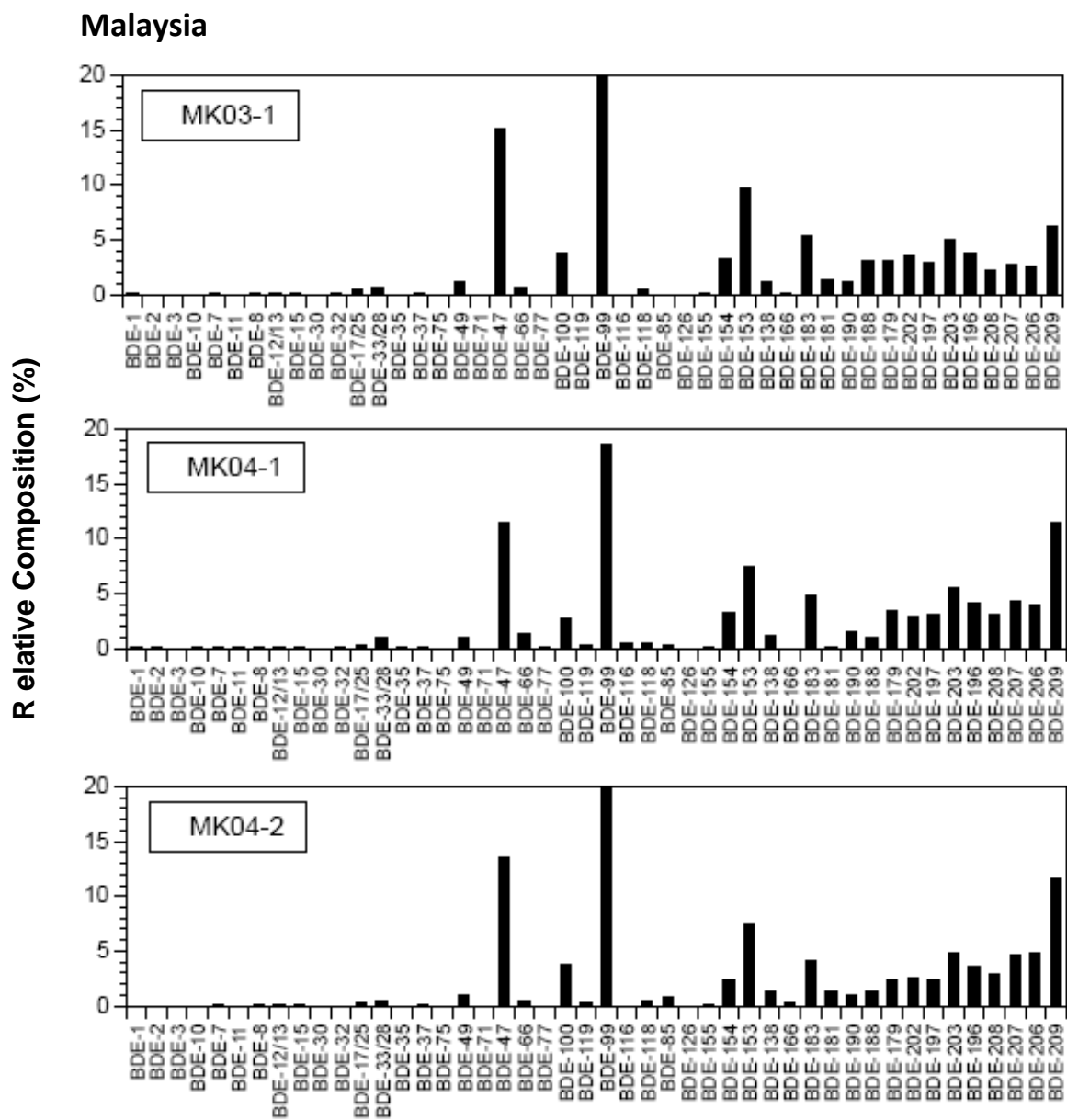


Fig. 2.2g. Congener profiles of PBDEs in the landfill leachates from Malaysia.

Table 2.1 Sample information for the sediment samples from the Pasig River, Manila, Philippines.

Sample code	Location	Coordinates (deg. min. sec., deg. min. sec.)	Date of sampling	Depth (m)
PR2	Roxas Bridge / Del Pan St.	N 14 36 45, E 120 58 59	2002 September 11	10
PR3	Jones Bridge / Q. Paredes St.	N 14 35 45, E 120 58 38	2002 September 12	10
PR7	Nagtahan Bridge / Pres. Quirino Ave.	N 14 36 46, E 121 0 8	2002 September 12	5
PR8	Pandacan Bridge / Paco-Sta. Mesa Railway	N 14 36 31, E 121 1 58	2002 September 12	5
PR12	Junction of Marikina River and Pasig River	N 14 33 30, E 121 4 2	2002 September 12	2

Table 2.2 Instrumental conditions for the analysis of PBDEs in the leachate samples.

2a GC/MS conditions

GC-MS system	: Thermo Scientific Trace GC Ultra : ITQ 1100 Ion Trap Quadrupole MS : AS Triplus Autoinjector		
Column	: Agilent Technologies HP-5MS narrow bore capillary column 30 m x 0.25 mm i.d. x 0.25 µm film thickness		
Carrier gas	: Helium at 100 kPa		
Injector temperature	: 285 °C		
Ion source temperature	: 250 °C		
Injection mode	: Splitless and purged 2 min after injection		
Column temperature	: 90 °C for 1 min Ramp 1 at 20°C/min to 180°C Ramp 2 at 3°C/min to 290°C Ramp 3 at 30°C/min to 320°C, hold 10 min (sample), or 5 min (standards)		
MS conditions			
	Parent Ion (m/z)	Product Ion (m/z)	
Br1	BDE-1, 2, 3	250.0	141.0
	BDE-3' ( <sup>13</sup> C <sub>12</sub> )	260.0	152.0
Br2	BDE-10, 7, 11, 8, 12/13, 15	328.0	168.0, 221.0
	BDE-15' ( <sup>13</sup> C <sub>12</sub> )	340.0	180.0, 230.0
Br3	BDE-30, 32, 17/25, 33/28, 35, 37	405.7	246.0
	BDE-28' ( <sup>13</sup> C <sub>12</sub> )	417.9	258.0
Br4	BDE-75, 49, 71, 47, 66, 77	486.0	326.0
	BDE-47' ( <sup>13</sup> C <sub>12</sub> )	496.0	338.0
Br5	BDE-100, 119, 99, 116, 118, 85, 126	564.0	404.0
	BDE-99' ( <sup>13</sup> C <sub>12</sub> )	575.9	416.0
Br6	BDE-155, 154, 153, 138, 166	484.0	377.0
	BDE-154', 153', 139' ( <sup>13</sup> C <sub>12</sub> )	496.0	386.0
Br7	BDE-183, 181, 190	562.0	455.0
	BDE-183' ( <sup>13</sup> C <sub>12</sub> )	574.0	466.0

2b GC-ECD conditions

GC System	: Agilent Technologies 7890A GC and 7683 Series Injector
Detector	: Electron Capture Detector
Column	: J&W Scientific DB-5 fused silica capillary column 15 m x 0.25 mm i.d. x 0.25 µm film thickness
Carrier Gas	: Helium at 100 kPa
Injector Temp.	: 250 °C
Detector Temp.	: 300 °C
Injection Mode	: Splitless and purged 2 min after injection
Column Temp.	: 80 °C for 2 min Ramp at 15°C/min to 290 °C, hold at 2 min

Table 2.3 Verification of the analytical method for dissolved PBDEs in leachate samples<sup>a</sup>: comparison of methanol and dichloromethane as extraction solvents, and recovery and reproducibility.

Native PBDEs	Extraction Solvents				Recovery and Reproducibility of the	
	Methanol		Dichloromethane		Analytical Method <sup>b</sup> (n=2)	
	Mean Conc., pg/L	% Extraction	Mean Conc., pg/L	% Extraction	Mean % Recovery	% RSD
BDE-1	ND <sup>c</sup>		ND			
BDE-2	ND		ND			
BDE-3	ND		ND			
BDE-10	ND		ND			
BDE-7	ND		ND			
BDE-11	ND		ND			
BDE-8	ND		ND			
BDE-12/13	ND		ND			
BDE-15	ND		ND			
BDE-30	ND		ND			
BDE-32	ND		ND			
BDE-17/25	4,850	100	ND			
BDE-33/28	ND		ND		112 (BDE-28)	6
BDE-35	ND		ND			
BDE-37	ND		ND			
BDE-75	ND		ND			
BDE-49	23,500	100	ND			
BDE-71	ND		ND			
BDE-47	69,700	85	12,200	15	69	9
BDE-66	17,000	100	ND			
BDE-77	ND		ND			
BDE-100	5,070	100	ND			
BDE-119	ND		ND			
BDE-99	39,200	100	ND		102	12
BDE-116	ND		ND			
BDE-118	ND		ND			
BDE-85	14,600	100	ND			
BDE-126	ND		ND			
BDE-155	ND		ND			
BDE-154	ND		ND		90	5
BDE-153	ND		ND		99	8
BDE-138	ND		ND			
BDE-166	ND		ND			
BDE-183	ND		ND		88	3
BDE-181	ND		ND			
BDE-190	ND		ND			
BDE-188	ND		ND		114	5
BDE-179	ND		ND		115	3
BDE-202	3,220	100	ND		109	12
BDE-197	829	100	ND		110	3
BDE-203	2,910	66	1,520	34	117	1
BDE-196	1,440	75	470	25	114	1
BDE-208	ND		ND		120	1
BDE-207	1,360	89	171	11	123	2
BDE-206	679	84	130	16	116	0
BDE-209	1,310	83	275	17	77	3

<sup>a</sup>Test sample was 20 mL of leachate filtrate, Philippines PMP10-1 (n=2)

<sup>b</sup>As described in Section 2.2 of the paper using another 20 mL aliquot of PMP10-1 (n=2) spiked with 6,250 pg of mono- to hepta- native PBDE congeners and 5000 pg of octa- to deca- native PBDE congeners using methanol as extraction solvent

<sup>c</sup>Not Detected by the instrumental analysis

Table 2.4 Partition coefficients of the PBDE congeners in the leachate samples from tropical Asian countries.

PBDEs		Partition coefficients			
		log K' <sub>oc</sub> <sup>a</sup> apparent		log K <sub>oc</sub> <sup>b</sup> predicted	log K <sub>ow</sub> <sup>c</sup>
		Mean	s (n)		
Br3	BDE-17/25	4.02	0.64 (3)	5.30	5.74 (BDE-17)
	BDE-33/28	3.56	0 (1)	5.51	5.94 (BDE-28)
Br4	BDE-47	4.14	0.49 (8)	6.40	6.81
Br5	BDE-100	4.07	0.70 (6)	6.85	7.24
	BDE-99	4.22	0.59 (8)	6.93	7.32
	BDE-85	4.39	0.25 (2)	6.98	7.37
Br6	BDE-154	3.91	0.23 (6)	7.44	7.82
	BDE-153	3.99	0.17 (6)	7.53	7.90
Br7	BDE-183	3.96	0.20 (5)	7.91	8.27
Br10	BDE-209	4.14	0.73 (8)	9.66	9.97

<sup>a</sup>log K'<sub>oc</sub> apparent = C<sub>adsorbed</sub>/C<sub>dissolved</sub>/f<sub>oc</sub>

<sup>b</sup>log K<sub>oc</sub> predicted = 1.03 x logK<sub>ow</sub> - 0.61

<sup>c</sup>Reference: K<sub>ow</sub> for all the congeners are cited from Braekvelt et al. (2003) except for BDE-209 which is cited from Watanabe and Tatsukawa (1990).

Table 2.5 Comparison of the PBDE concentrations in the adsorbed phase of the leachates with samples from other countries.

Location	Sample	Concentration, ng/g dry wt.						Reference
		BDE-15	BDE-33/28	BDE-47	BDE-99	BDE-100	BDE-153	
Lao PDR	solid phase, leachate	ND	ND	<LOD-2.0	<LOD-1.8	ND-0.38	ND	This study
Cambodia	solid phase, leachate	ND	0.43-0.72	15-17	24-30	ND-0.71	5.0-9.9	This study
Vietnam	solid phase, leachate	ND	ND	0.41-3.2	<LOD-2.1	<LOD	ND	This study
India	solid phase, leachate	0.71	1.7	4.0	1.4	0.08	<LOD	This study
Indonesia	solid phase, leachate	ND-<LOD	ND-<LOD	3.5-7.3	4.6-11	<LOD-1.1	ND-5.9	This study
Thailand (TB-1,-3)	solid phase, leachate	ND-<LOD	ND-0.40	1.6-4.0	2.0-8.9	0.19-1.3	0.18-1.7	This study
Thailand (TB-2)	solid phase, leachate	9.9	26	396	33	1.6	8.8	This study
Philippines (PMP)	solid phase, leachate	ND-3.6	ND-3.7	16-100	20-131	3.4-27	11-30	This study
Malaysia	solid phase, leachate	0.21-0.31	1.2-3.4	41-56	61-72	10-14	23-36	This study
Reference values <sup>a</sup> :								
Sweden	sediments, raw leachate			0.21-12 (Tetra)	0.05-69 (Penta)		<LOD-0.70 (Hexa)	Öman and Junestedt, 2008
Canada, North	soils, landfills			0.055-35.4	0.022-56.7	0.008-11.0	0.002-47.4	Danon-Schaffer (2010)
Location	Sample	Concentration, ng/g dry wt.						
		BDE-154	BDE-183	BDE-206	BDE-207	BDE-209		
Lao PDR	solid phase, leachate	ND	ND-<LOD	<LOD-1.1	0.83-1.5	4.1-6.7		This study
Cambodia	solid phase, leachate	2.5-2.6	1.4-1.9	7.4-15	4.6-6.3	20-56		This study
Vietnam	solid phase, leachate	ND	ND-<LOD	2.4-3.8	0.98-2.6	14-44		This study
India	solid phase, leachate	<LOD	<LOD	38	4.5	6.1		This study
Indonesia	solid phase, leachate	<LOD-2.4	<LOD-16	2.1-4.2	3.6-6.5	3.6-7.6		This study
Thailand (TB-1,-3)	solid phase, leachate	0.21-1.3	ND-1.2	1.2-3.9	1.6-5.5	33-66		This study
Thailand (TB-2)	solid phase, leachate	1.6	3.8	64	36	2,072		This study
Philippines (PMP)	solid phase, leachate	5.3-24	18-36	6.1-34	14-24	18-698		This study
Malaysia	solid phase, leachate	7.2-12	13-20	9.2-15	10-16	22-44		This study
Reference values <sup>a</sup> :								
Sweden	sediments, raw leachate							Öman and Junestedt, 2008
Canada, North	soils, landfills	0.001-12.0	0.002-199.3	ND-19.8	ND-32.4	0.449-597.3		Danon-Schaffer (2010)

<sup>a</sup>Reference values converted to units ng/g.

## LAO PDR

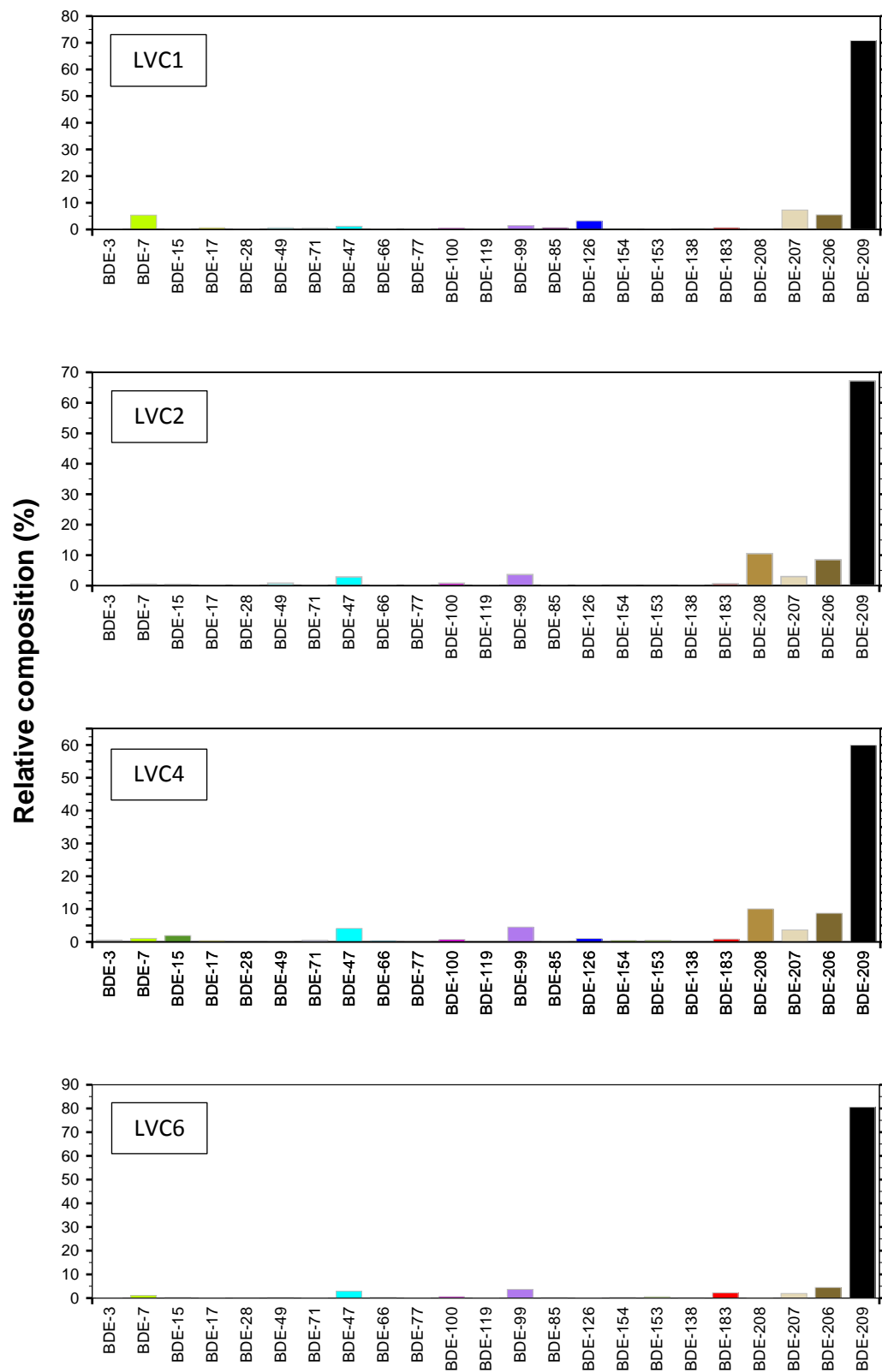


Fig. 3.1a. Congener profiles of sedimentary PBDEs in Lao PDR.



## CAMBODIA

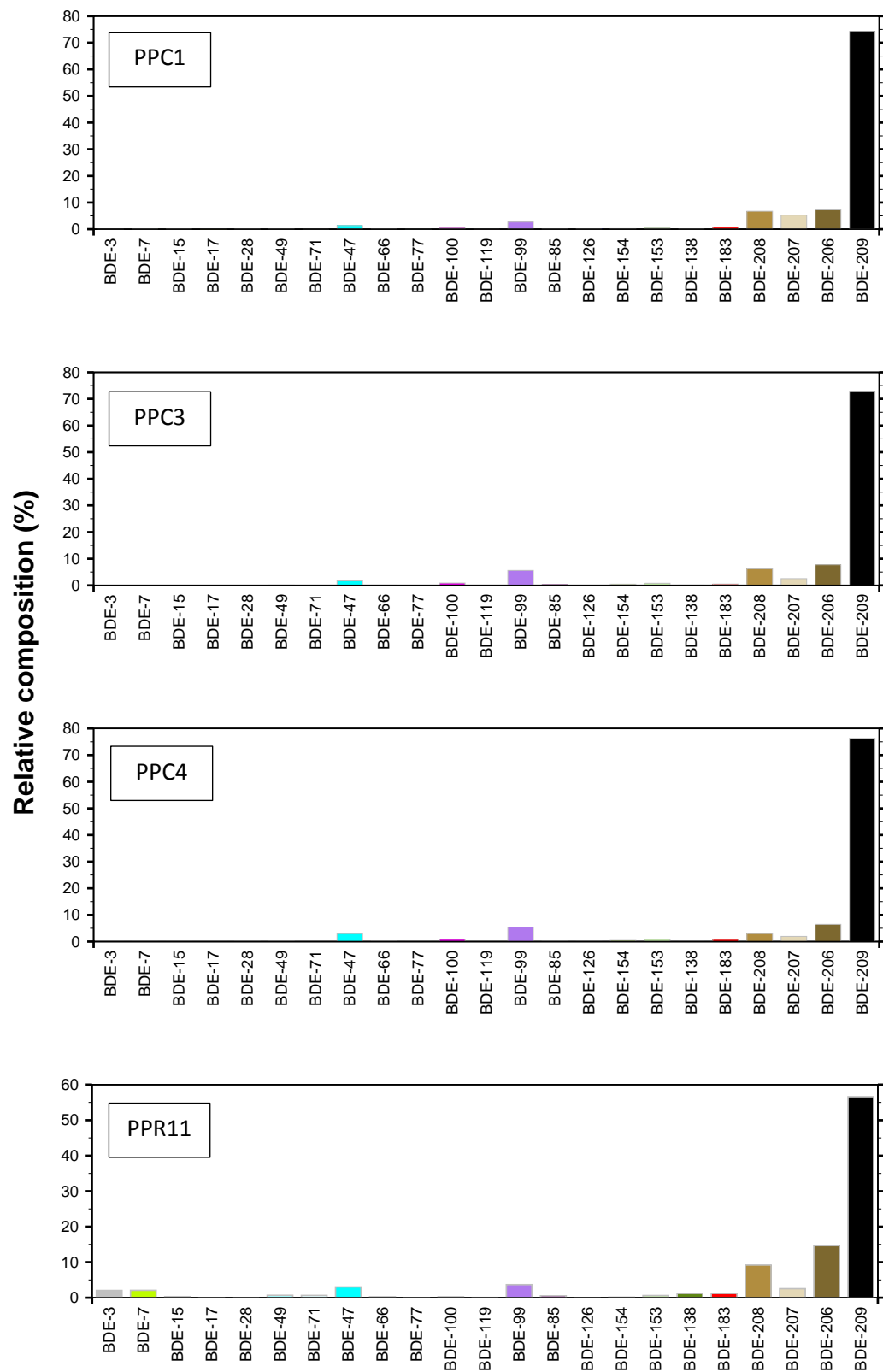


Fig. 3.1b. Congener profiles of sedimentary PBDEs in Cambodia.

## VIETNAM

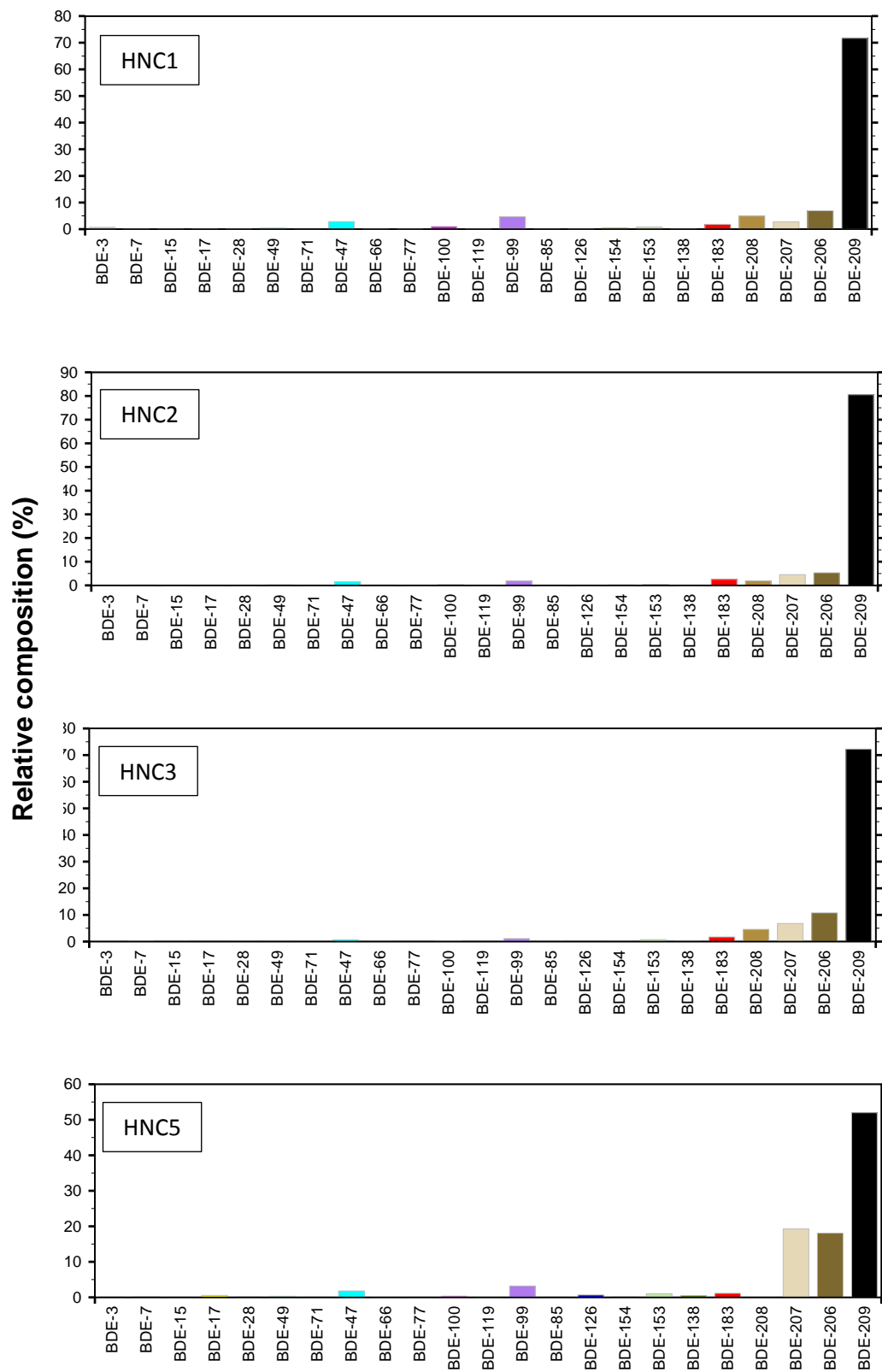


Fig. 3.1c. Congener profiles of sedimentary PBDEs in Vietnam.

# INDIA (Kolkata)

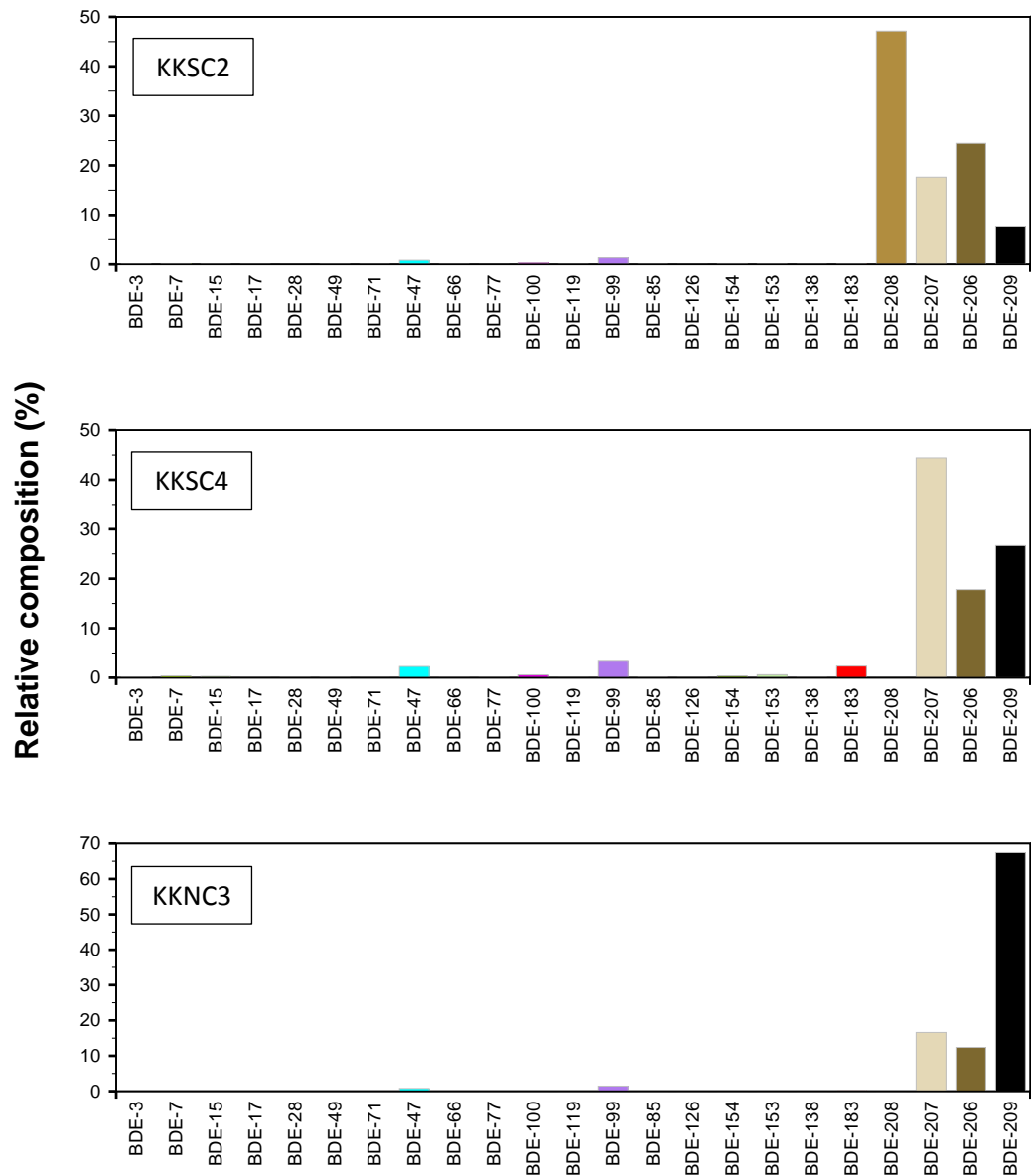


Fig. 3.1d. Congener profiles of sedimentary PBDEs in India (Kolkata).

# INDIA (Chennai)

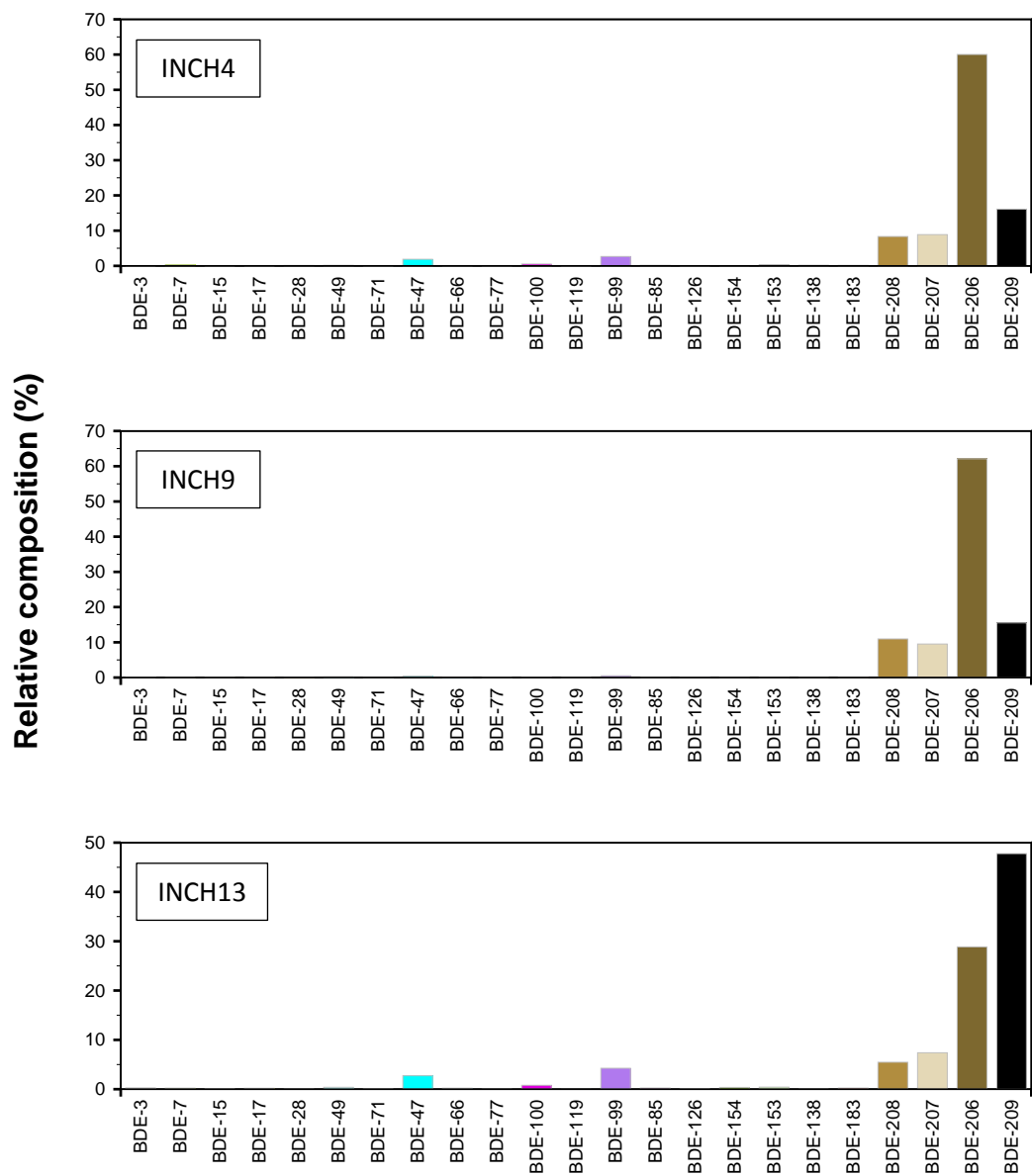


Fig. 3.1e. Congener profiles of sedimentary PBDEs in India (Chennai).

## INDIA (Mumbai)

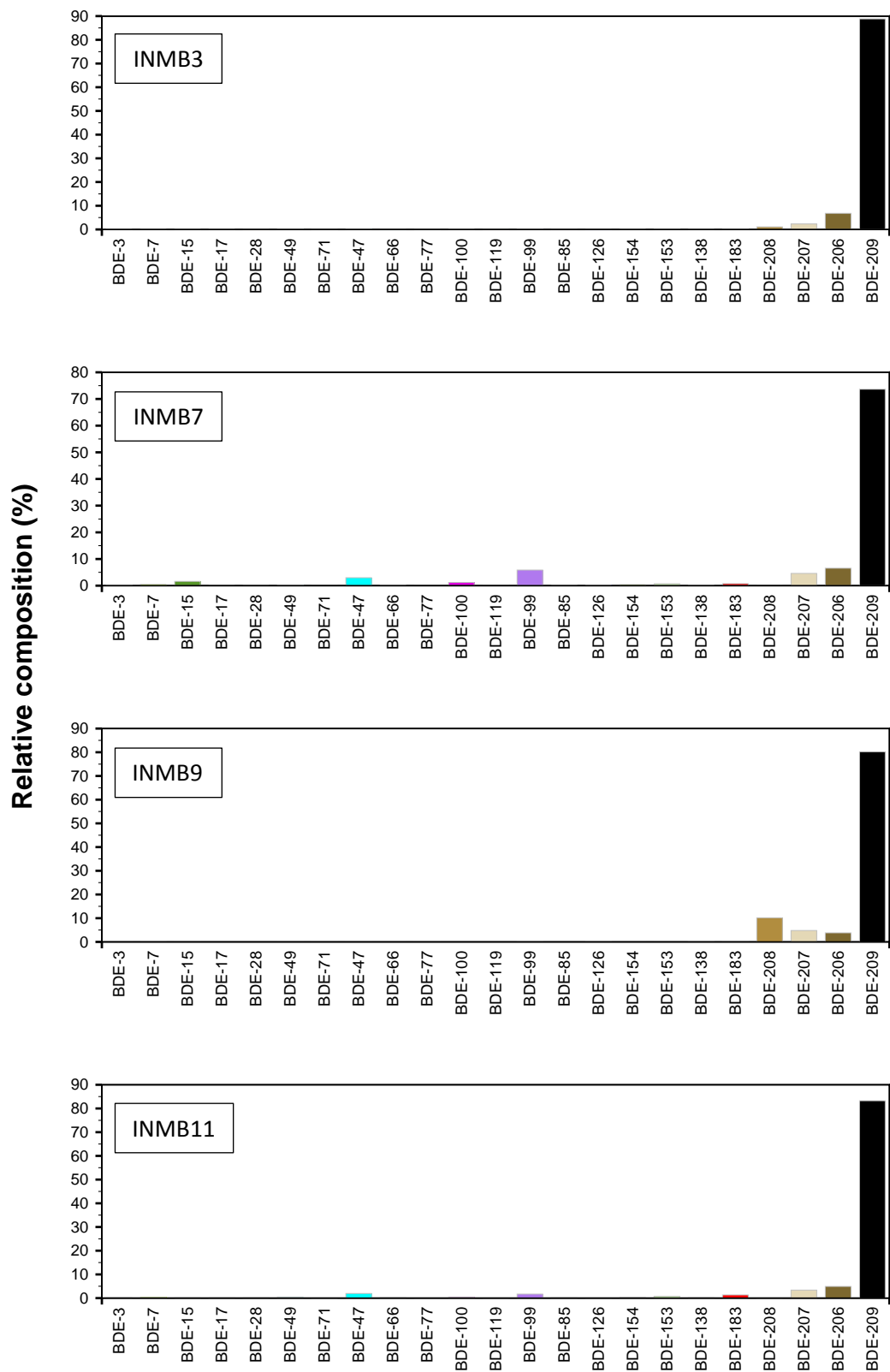


Fig. 3.1f. Congener profiles of sedimentary PBDEs in India (Mumbai).

## INDONESIA

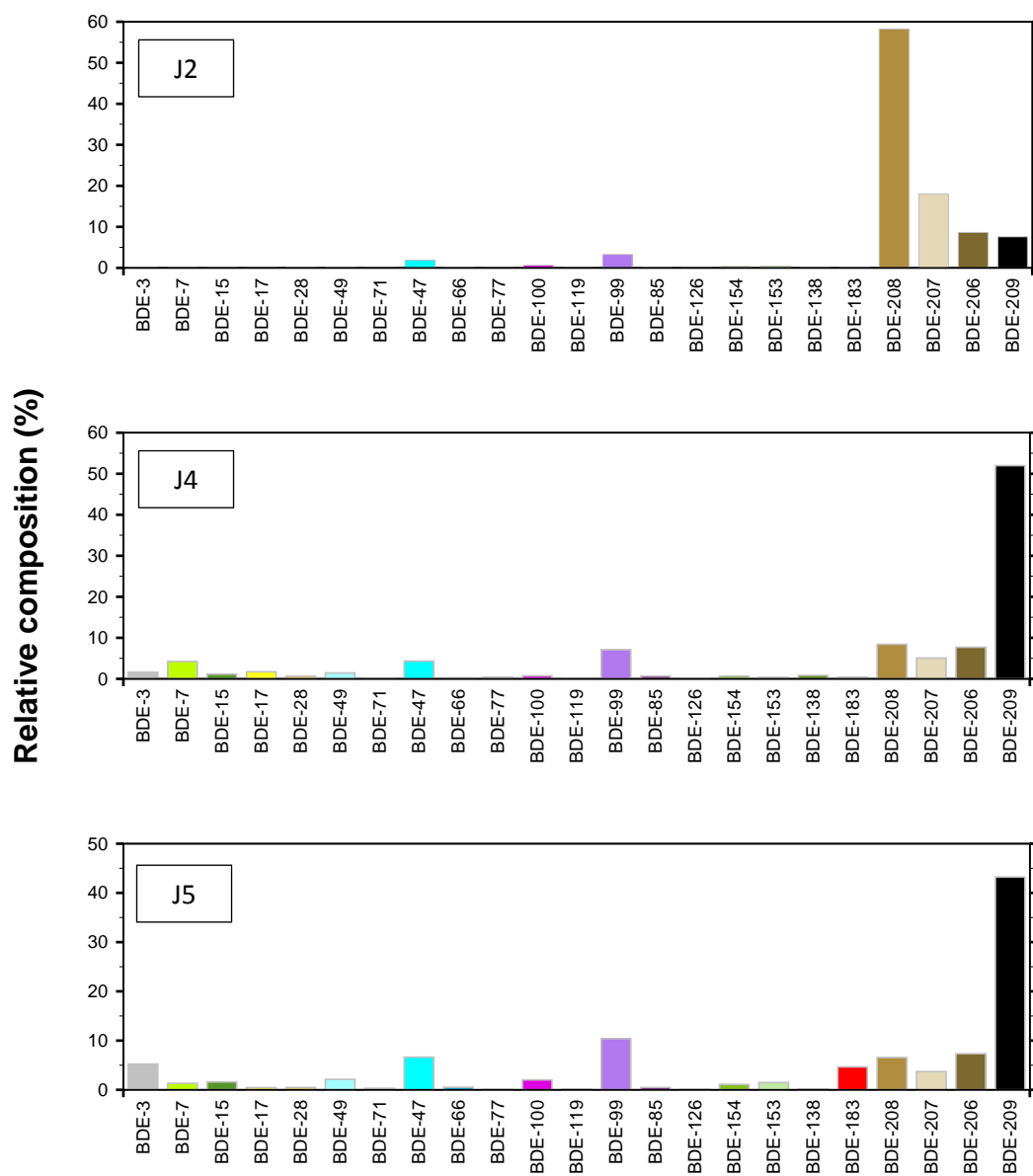


Fig. 3.1g. Congener profiles of sedimentary PBDEs in Indonesia.

## THAILAND

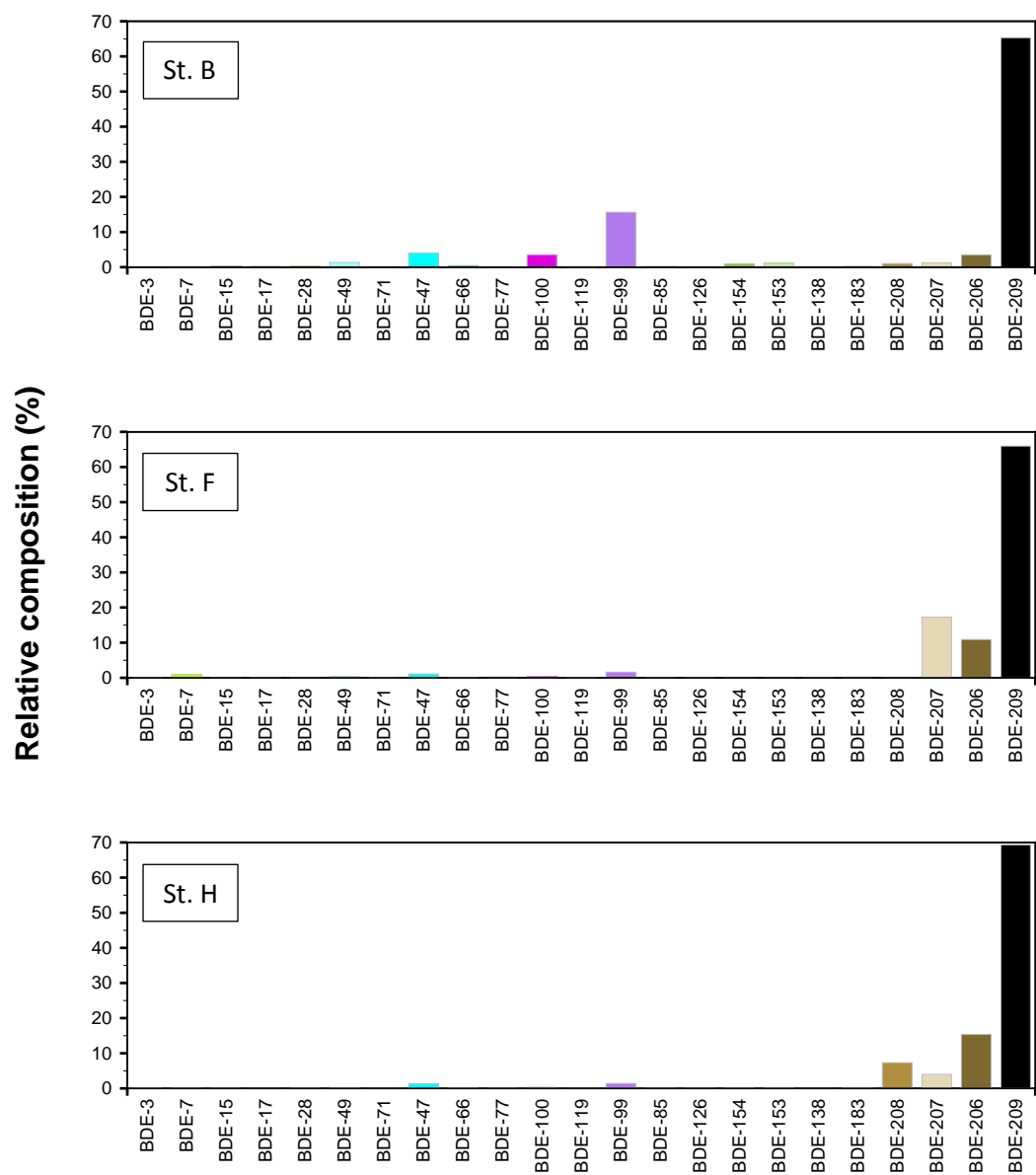


Fig. 3.1h. Congener profiles of sedimentary PBDEs in Thailand.

# **PHILIPPINES (Pasig River 1, 2, 3)**

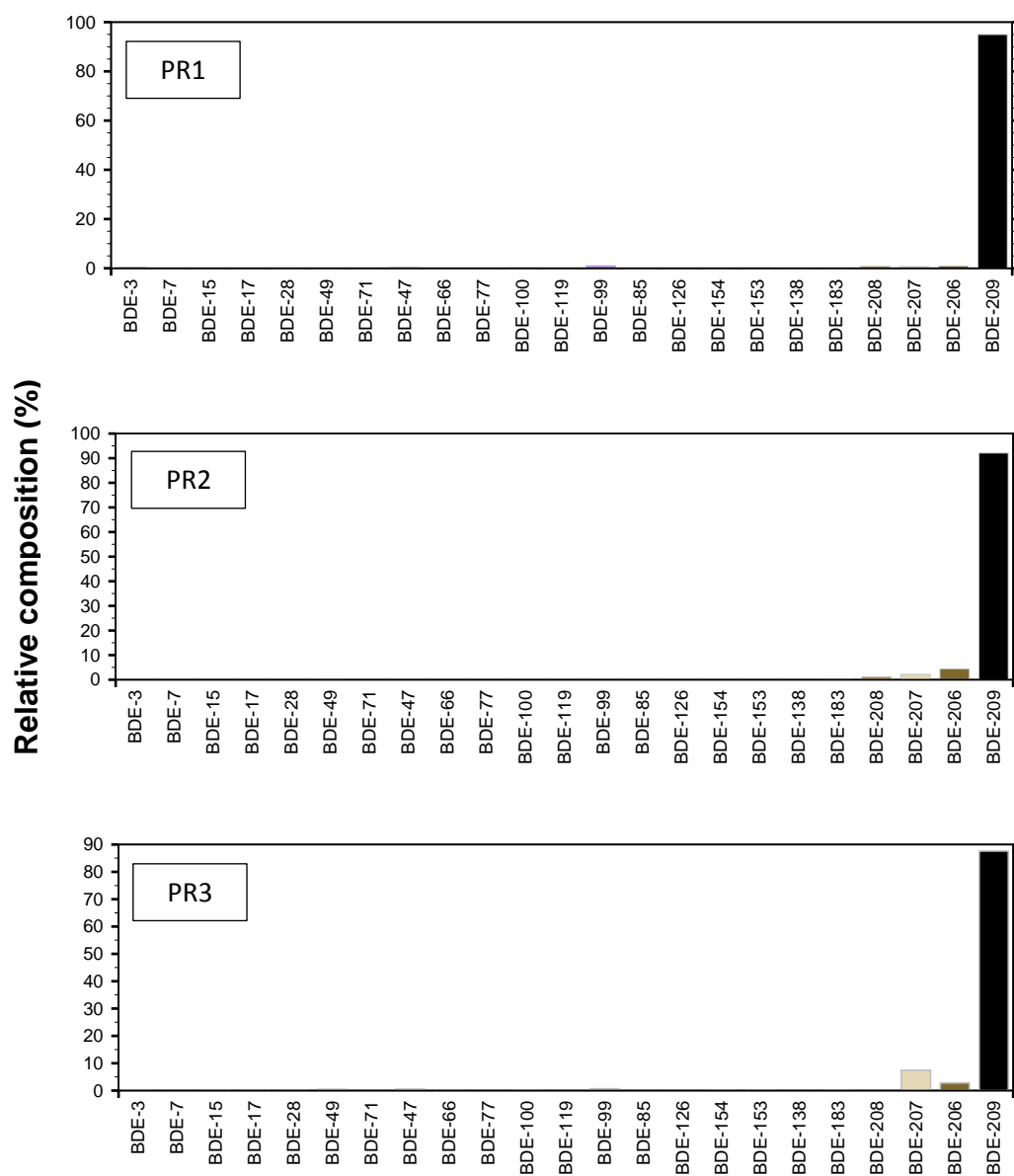


Fig. 3.1ia. Congener profiles of sedimentary PBDEs in the Philippines (Pasig River: PR1, PR2, PR3).



# PHILIPPINES (Pasig River 7, 8, 12)

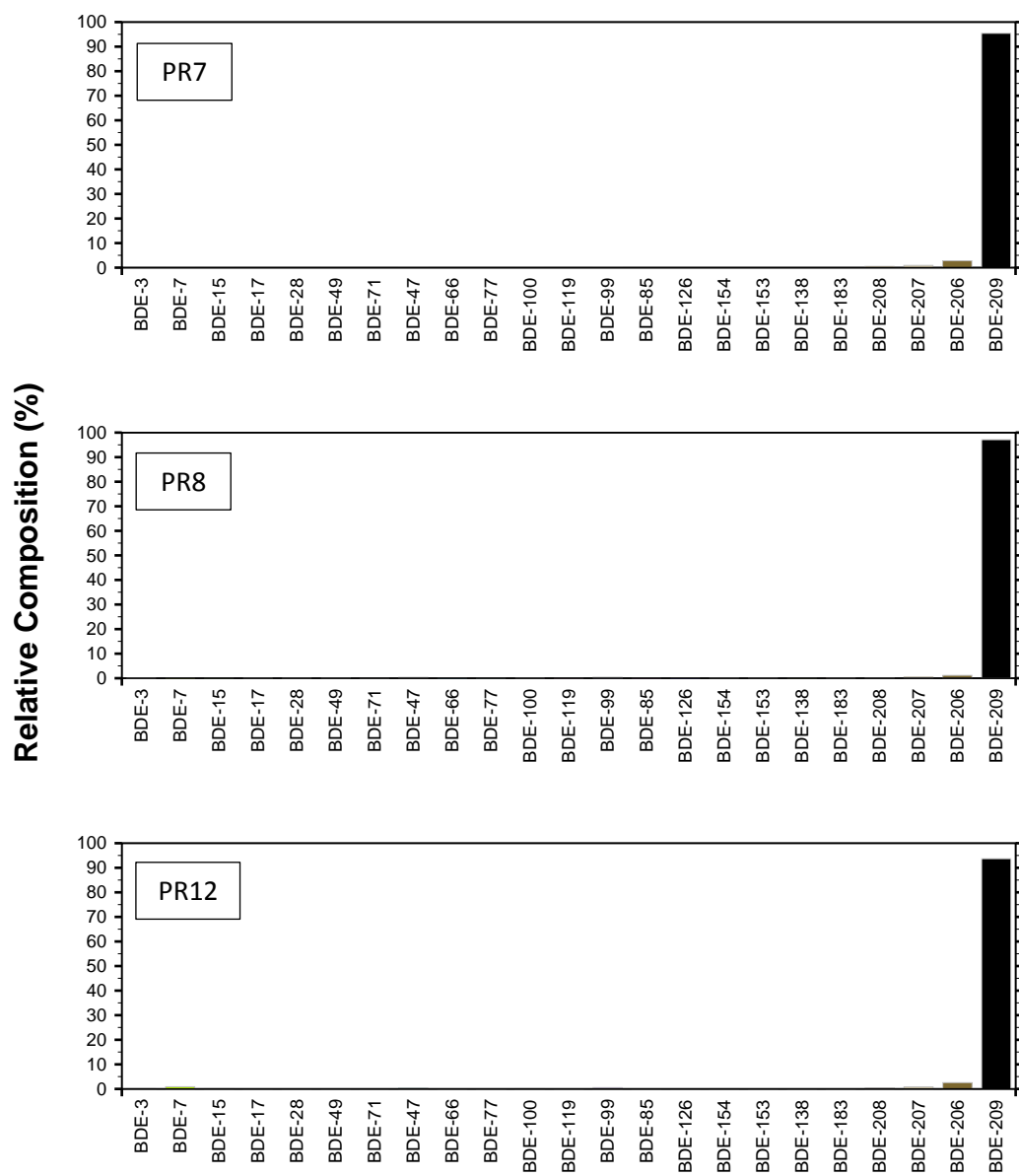


Fig. 3.1ib. Congener profiles of sedimentary PBDEs in the Philippines (Pasig River: PR7, PR8, PR12).

# PHILIPPINES (Manila Bay)

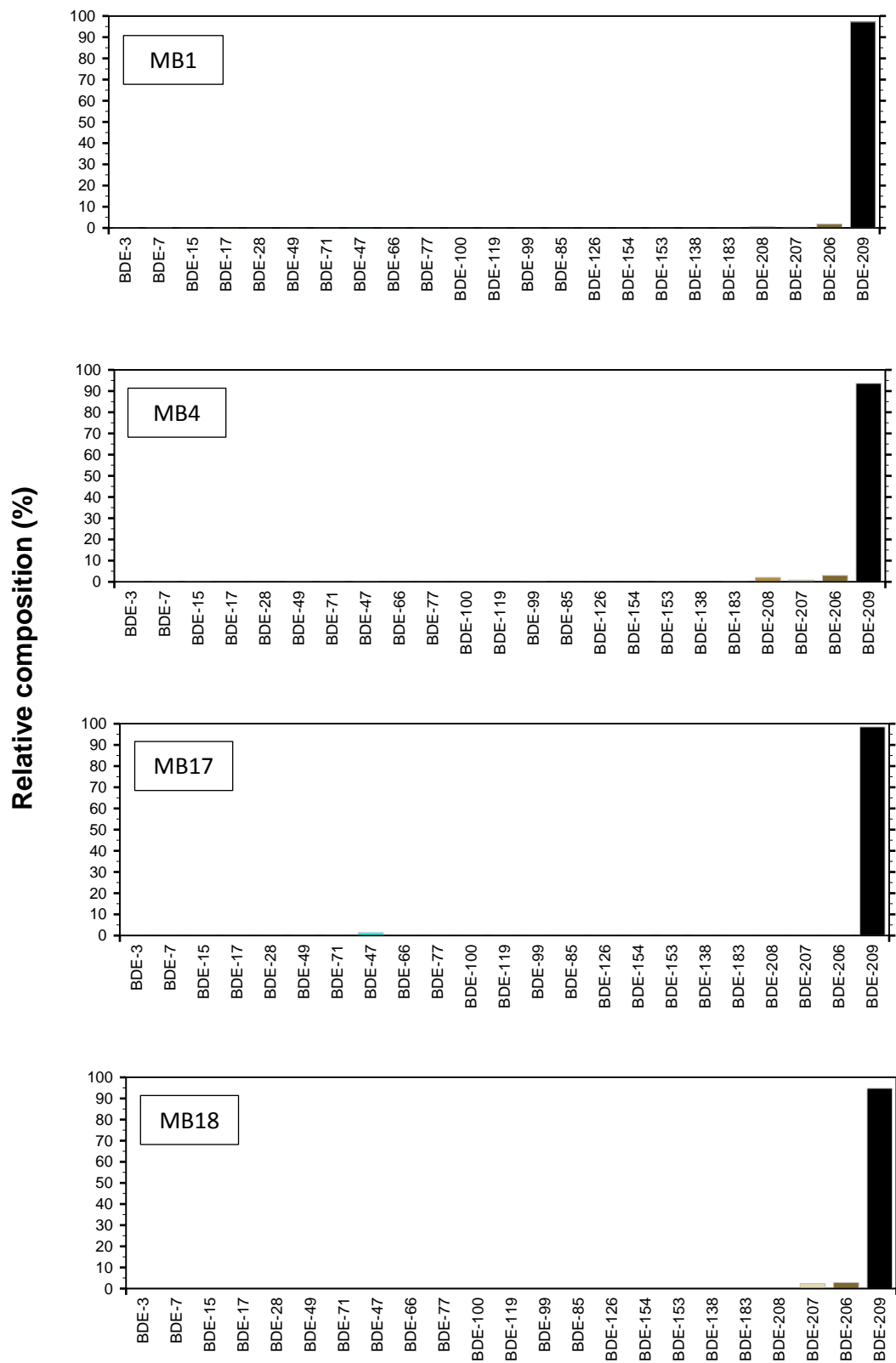


Fig. 3.1j. Congener profiles of sedimentary PBDEs in the Philippines (Manila Bay).

### PHILIPPINES (Pasig River tributaries: Manila Canals)

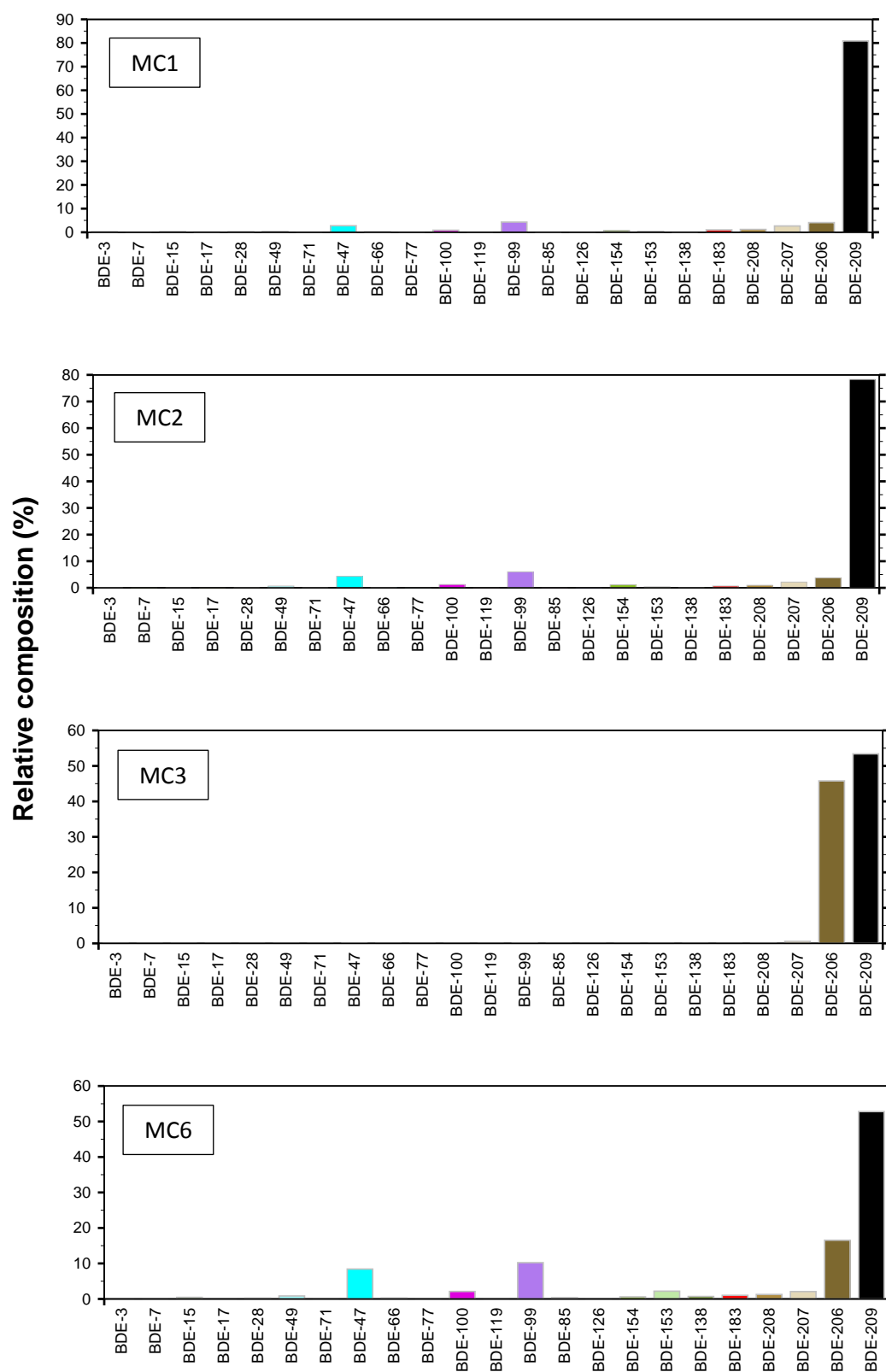


Fig. 3.1k. Congener profiles of sedimentary PBDEs in the Philippines (Pasig River tributaries: Manila Canals).

## MALAYSIA

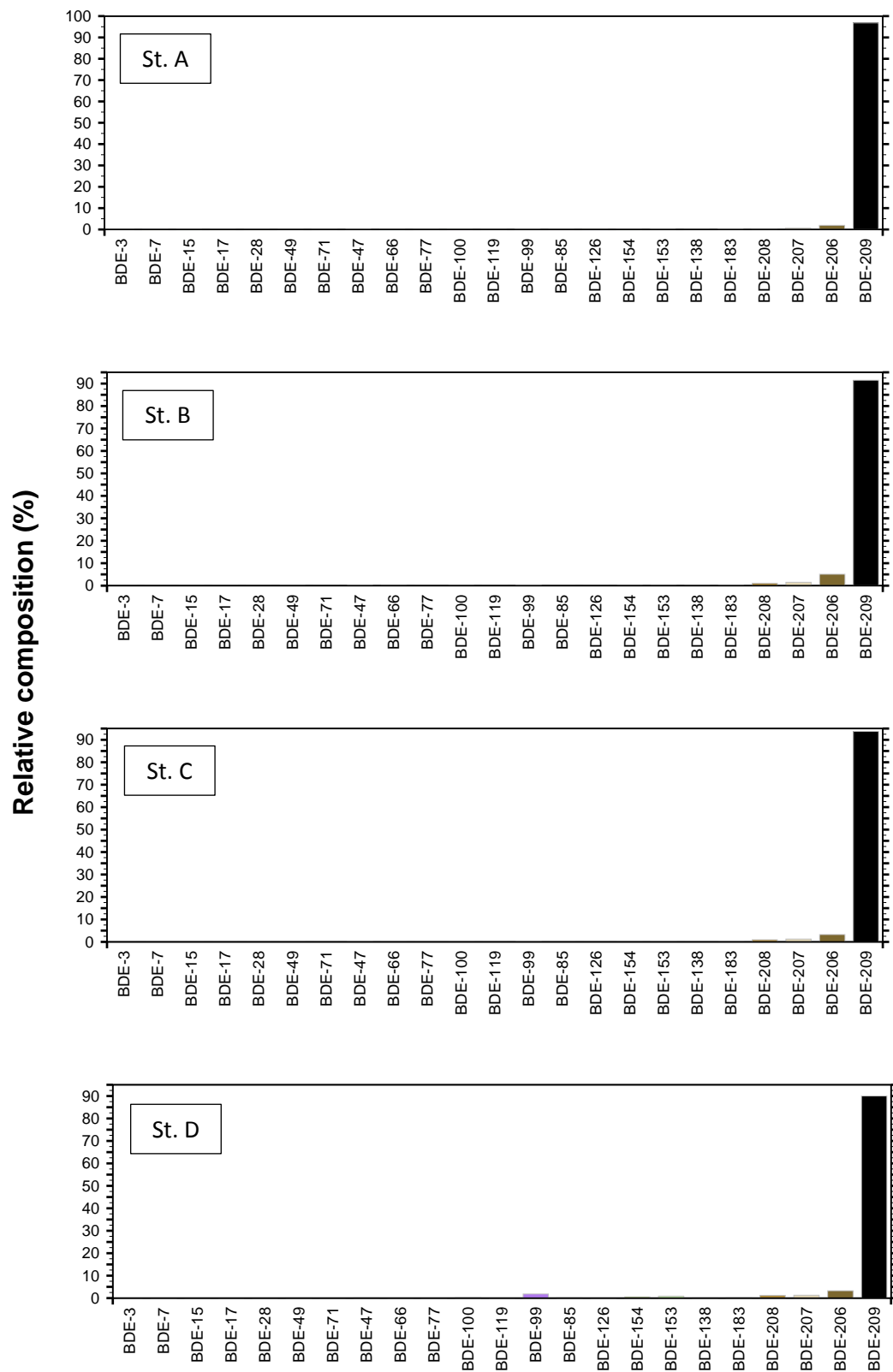


Fig. 3.11. Congener profiles of sedimentary PBDEs in Malaysia.

## JAPAN

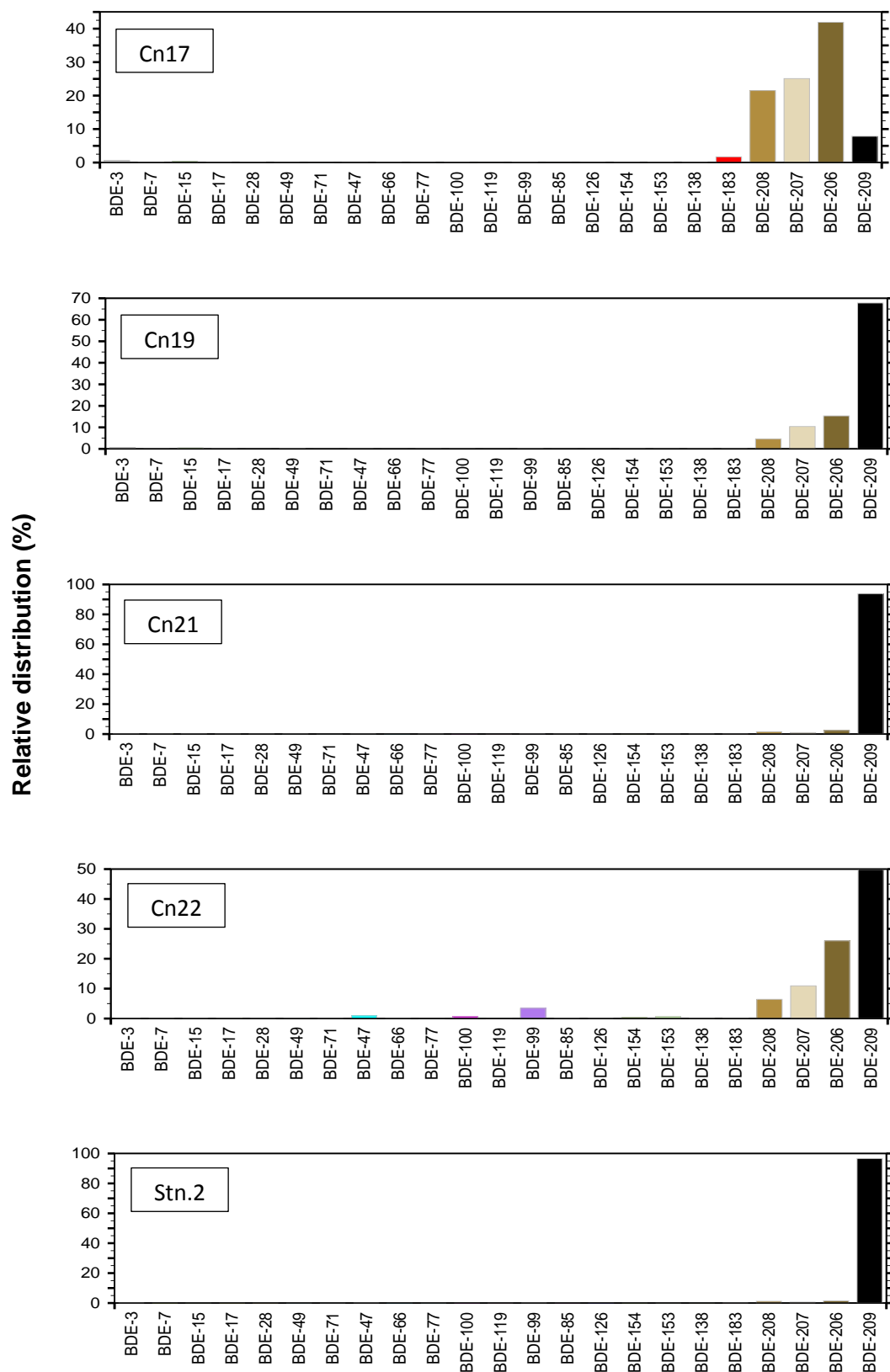
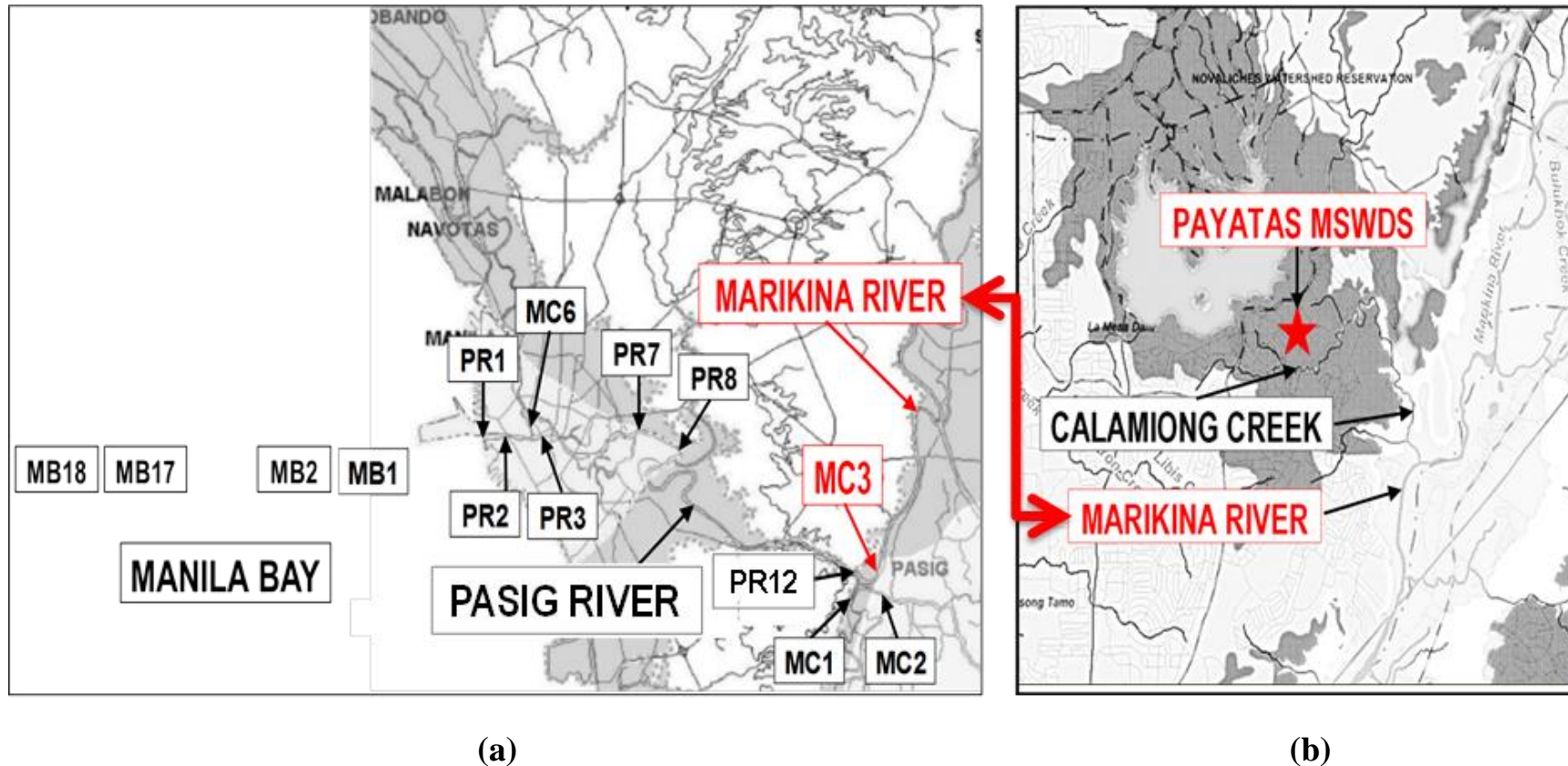


Fig. 3.1m. Congener profiles of sedimentary PBDEs in Japan.



Figs. 3.2a. Sampling locations in the Philippines: the Pasig River (PR 12, 8, 7, 3, 2, 1) flowing into Manila Bay (MB1, 2, 17, 18) and its river tributaries or canals (MC1, MC2, MC3, MC6). The coordinates of the sampling locations are tabulated in Table 3.1.

Fig. 3.2b. Location of the Payatas Municipal Solid Waste Dumping Site and the confluence of the Calamiong Creek to the upper portion of the Marikina River (MC3).

Map sources: (a) Liquefaction Hazard Map of Metro Manila. Philippine Institute of Volcanology and Seismology (<http://www.phivolcs.dost.gov.ph>). (b) Geohazard Maps. Philippine Information Agency (<http://www.pia.gov.ph>) and the Mines and Geosciences Bureau (<http://www.mgb.gov.ph>).

Table 3.1 Instrumental conditions for the analysis of PBDEs in sediments.

### 3.1a. GC/MS conditions

GC/MS system	: Thermo Electron Corporation Trace GC Ultra : Thermo Electron Corporation Polaris Q MS : Thermo Electron Corporation AS3000 Autosampler		
Column	: J&W Scientific DB-5 fused silica capillary column 30 m x 0.25 mm i.d. x 0.25 µm film thickness		
Carrier gas	: Helium at 100 kPa		
Injector temperature	: 285 °C		
Ion source temperature	: 250 °C		
Injection mode	: Splitless and purged 2 min after injection		
Column temperature	: 90 °C for 1 min Ramp 1 at 20°C/min to 180°C Ramp 2 at 3°C/min to 290°C Ramp 3 at 30°C/min to 320°C, hold 10 min (sample), or 5 min (standards)		
MS conditions		Parent Ion (m/z)	Product Ion (m/z)
Br1	BDE-3	250.0	141.0
	BDE-3' ( <sup>13</sup> C <sub>12</sub> )	260.0	152.0
Br2	BDE-7, 15	328.0	168.0, 221.0
	BDE-15' ( <sup>13</sup> C <sub>12</sub> )	340.0	180.0, 230.0
Br3	BDE-17, 28	405.7	246.0
	BDE-28' ( <sup>13</sup> C <sub>12</sub> )	417.9	258.0
Br4	BDE- 49, 71, 47, 66, 77	486.0	326.0
	BDE-47' ( <sup>13</sup> C <sub>12</sub> )	496.0	338.0
Br5	BDE-100, 119, 99, 85, 126	564.0	404.0
	BDE-99' ( <sup>13</sup> C <sub>12</sub> )	575.9	416.0
Br6	BDE-154, 153, 138	484.0	377.0
	BDE-154', 153', 139' ( <sup>13</sup> C <sub>12</sub> )	496.0	386.0
Br7	BDE-183	562.0	455.0
	BDE-183' ( <sup>13</sup> C <sub>12</sub> )	574.0	466.0

### 3.1b. GC-ECD conditions

GC System	: Agilent Technologies 7890A GC
Detector	: Electron Capture Detector
Column	: J&W Scientific DB-5 fused silica capillary column 15 m x 0.25 mm i.d. x 0.25 µm film thickness
Carrier Gas	: Helium at 100 kPa
Injector Temp.	: 250 °C
Detector Temp.	: 300 °C
Injection Mode	: Splitless and purged 2 min after injection
Column Temp.	: 80 °C for 2 min Ramp at 15°C/min to 290 °C, hold at 2 min

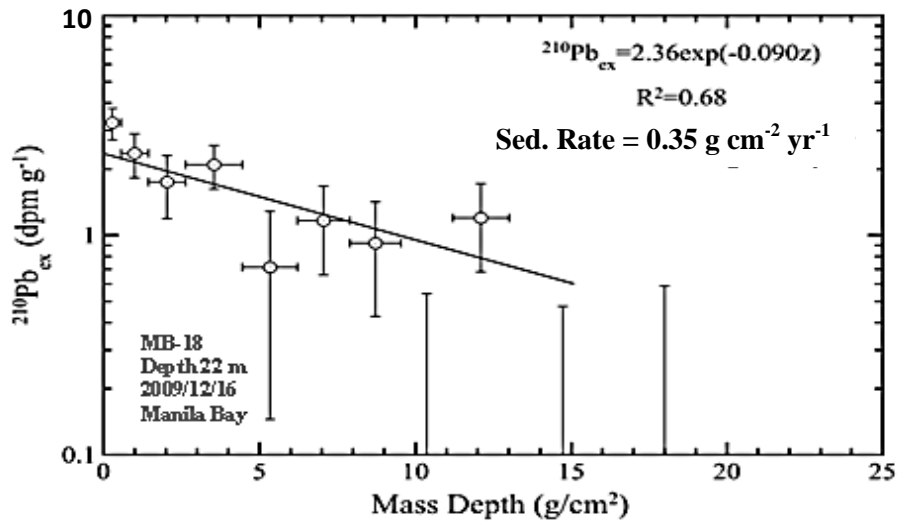
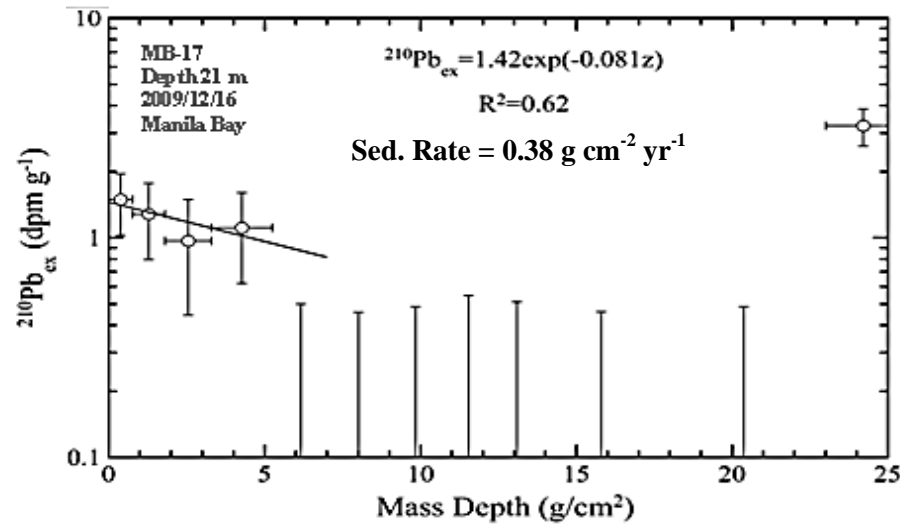
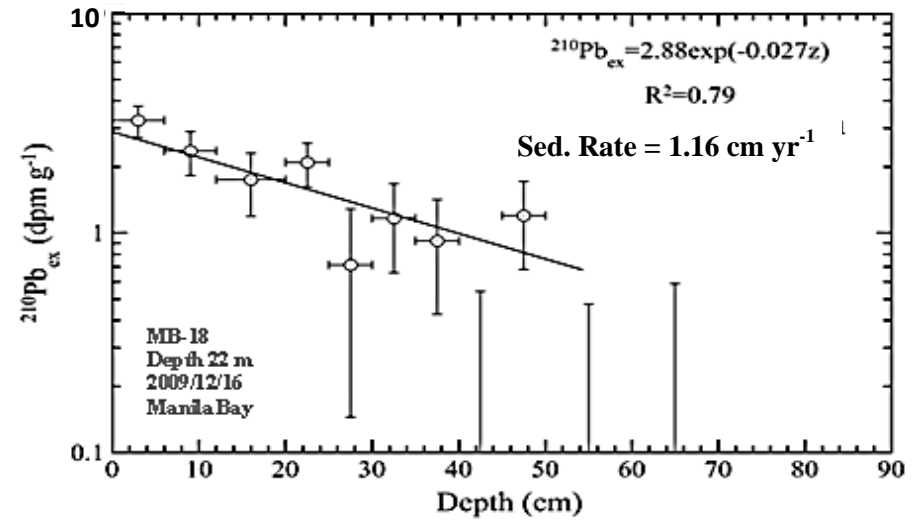
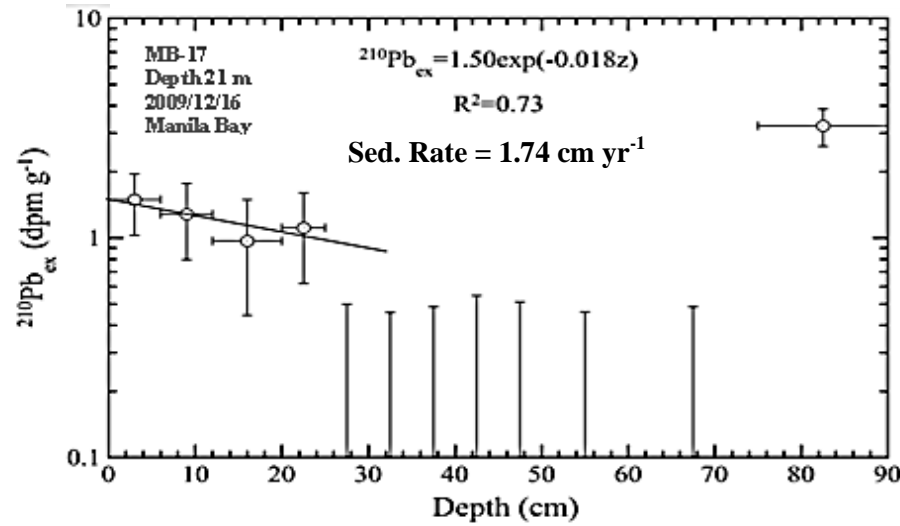


Fig. 4.1 Sedimentation accumulation rates in the sediment core samples from the Philippines.



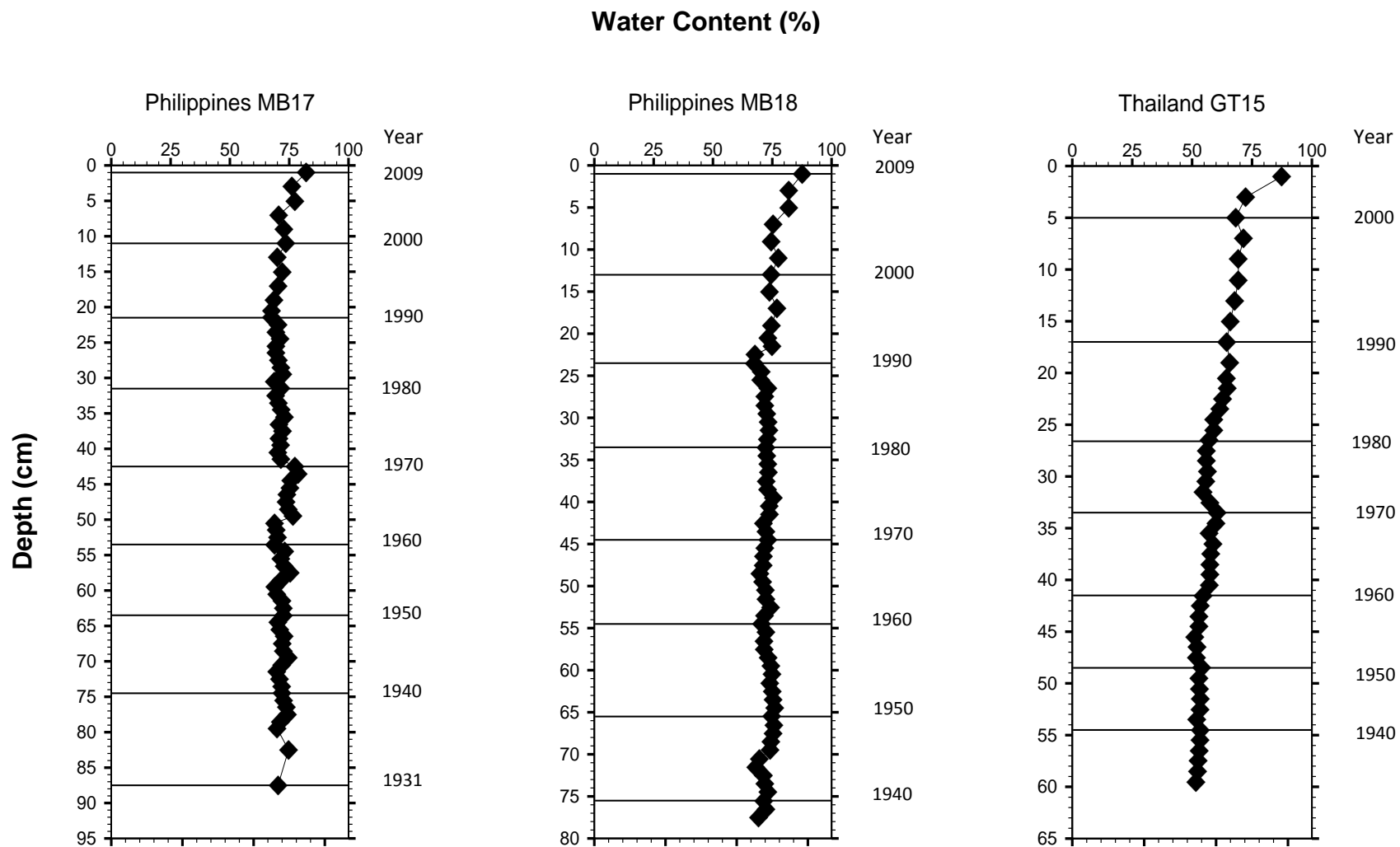


Fig. 4.2. Vertical profiles of the water content in the sediment core samples from the Philippines and Thailand.

Data for the water content in GT15 was taken from Boonyatumanond et al. (2007).

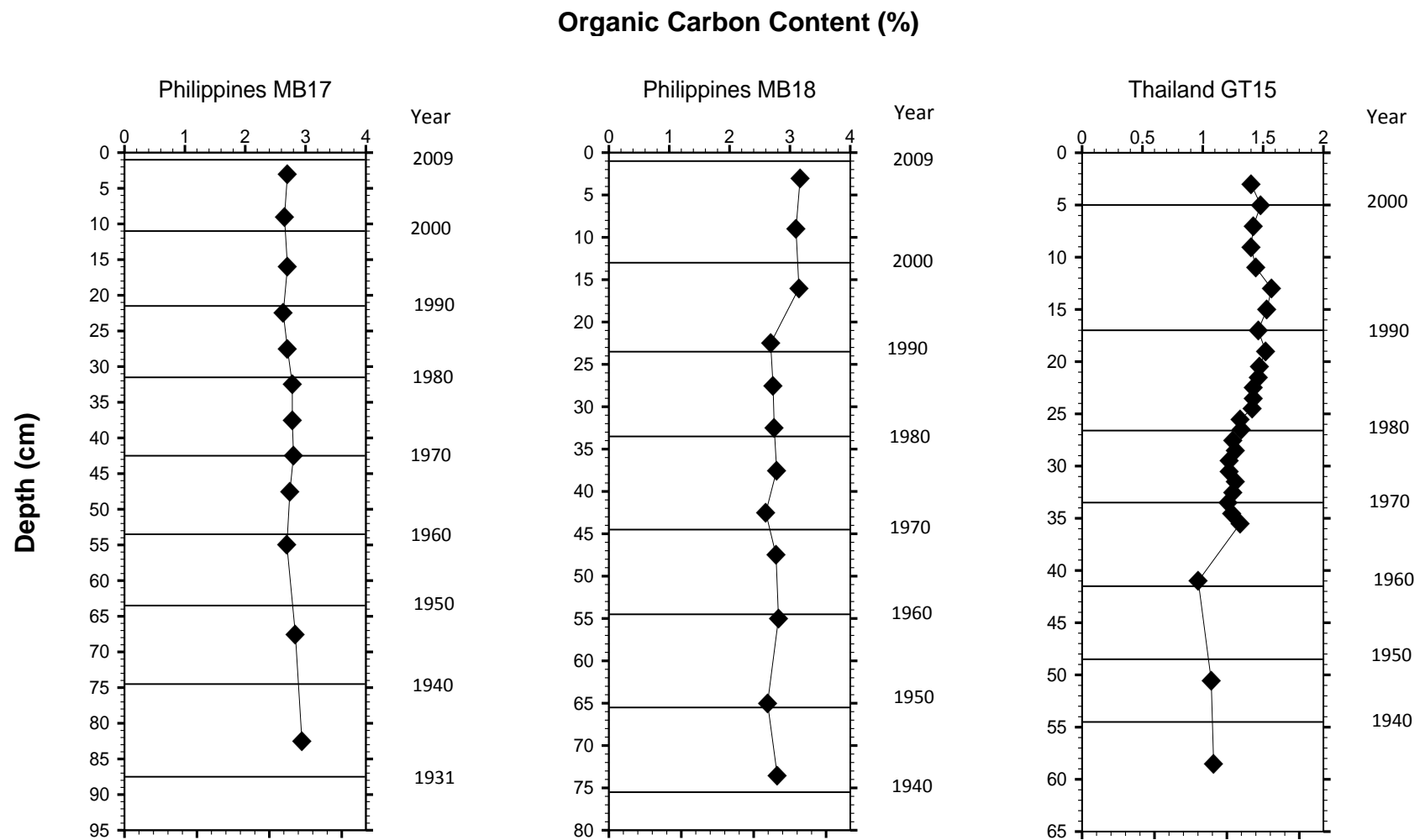


Fig. 4.3. Vertical profiles of the organic carbon content in the sediment core samples from the Philippines and Thailand. Data for the organic carbon content in GT15 was taken from Boonyatumanond et al. (2007).

Table 4.1 Sampling information for the beached plastic resin pellets from Asian countries.

Country	Beach location	Code	Date of Sampling	Coordinates	
				(deg. min. sec)	(deg. min. sec)
Philippines	Cavite City	09122000	2009 December	N 14 27 53.6	E 120 52 57.9
Vietnam	Minh Chau Island	07100600	2007 October	N 20 56 13.5	E 107 33 24
	Balat Estuary	08100700	2008 October	N 20 1 21.1	E 106 13 3.5
Malaysia	Langkawi	05081500	2008 August	N 6 27, 21.7	E 99 49 22.1
	Penang	05092700	2009 September	N 5 22 20	E 100 18 55
	Borneo	06082000	2006 August	N 6 7 3	E 116 6 39
	Port Dickson	11120400	2011 November	N 2 24 53.3	E 101 51 32.7
Japan	Tokyo (Winter)	11122300	2011 December	N 35 37 53	E 139 46 30
	Tokyo (Summer)	12082801	2012 August	N 35 37 53	E 139 46 30

Table 4.2 Sample information for the passive air samples using PUF disk from Asian countries

Country	Location	Code	Date of sampling		Exposure time (d)	Coordinates		% Recovery of DC <sup>a</sup>	Sampling rate (m <sup>3</sup> ·d <sup>-1</sup> )	Mean Temp <sup>b</sup> (°C)	Air volume (m <sup>3</sup> )
			Start	End		(deg min sec)	(deg min sec)				
Philippine	Cavite City	F11112800	9/19/2011	11/21/2011	63	N 14 29 06	E 120 54 46	5	8.0	27	504
	Cavite City	F12080600	6/6/2012	8/1/2012	56	N 14 29 06	E 120 54 46	7	7.19	28	403
Vietnam	Ninh Hai, Haiphong	F11121400	9/16/2011	11/16/2011	61	N 20 45 38.4	E 106 40 31	7	7.8	27	478
	Ninh Hai, Haiphong	F12072300	4/18/2012	7/9/2012	82	N 20 45 38.4	E 106 40 31	2	7.56	28	620
	Ninh Hai, Haiphong	F12111501	7/10/2012	10/16/2012	98	N 20 45 38.4	E 106 40 31	2	6.33	28	621
	Ngu Phuc, Haiphong	F11121401	9/14/2011	11/28/2011	75	N 20 46 13.5	E 106 42 6.6	10	5.9	26	442
	Ngu Phuc, Haiphong	F12072301	4/16/2012	7/10/2012	85	N 20 46 13.5	E 106 42 6.6	2	6.84	28	582
	Ngu Phuc, Haiphong	F12111500	7/10/2012	10/16/2012	98	N 20 46 13.5	E 106 42 6.6	3	5.72	28	561
Malaysia	Port Dicskon (Penang)	F11120201	9/2011	11/24/2011	60 <sup>c</sup>	N 2 24 53.3	E 101 51 32.7	13	5.3	28	321
	Port Dicskon (Penang)	F12100400	6/23/2012	9/20/2012	89	N 2 24 53.3	E 101 51 32.7	2	7.37	27	656
Japan	Tokyo	F11081400	6/15/2011	8/14/2011	60	N 35 41 6.0	E 139 39 2.1	19	4.1	29	245
	Tokyo	F12112500	10/10/2012	11/25/2012	46	N 35 41 6.0	E 139 39 2.1	64	5.09	15	234

<sup>a</sup>Depuration compound, PCB-30. <sup>b</sup>Mean temperature during the deployment period. <sup>c</sup>Estimated exposure time

Table 4.3 Mass depth,  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  activities of the sediment core samples from the Philippines

Sample / Composite No.	Ave. Depth (cm)	Mass Depth (g/cm <sup>2</sup> )	$^{210}\text{Pb}_{\text{ex}}$ (dpm/g)	Error (dpm/g)	$^{137}\text{Cs}$ (dpm/g)	Error (dpm/g)
<b>1a. MB17</b>						
1	3.0	0.383	1.49	0.47	0.03	0.40
2	9.0	1.283	1.28	0.49	0.07	0.04
3	16.0	2.546	0.97	0.53	0.05	0.04
4	22.5	4.269	1.11	0.49	0.13	0.04
5	27.5	6.160	ND	0.50	0.06	0.04
6	32.5	8.006	ND	0.46	ND	0.04
7	37.5	9.840	ND	0.49	0.04	0.04
8	42.5	11.535	ND	0.55	ND	0.05
9	47.5	13.091	ND	0.51	ND	0.05
10	55.0	15.793	ND	0.46	ND	0.43
11	67.5	20.371	ND	0.49	ND	0.05
12	82.5	24.214	3.24	0.63	0.02	0.05
<b>1b. MB18</b>						
1	3.0	0.282	3.25	0.54	0.02	0.05
2	9.0	1.001	2.36	0.54	ND	0.05
3	16.0	2.035	1.75	0.56	0.11	0.05
4	22.5	3.543	2.09	0.47	0.07	0.04
5	27.5	5.334	0.72	0.57	0.06	0.04
6	32.5	7.055	1.17	0.51	0.01	0.05
7	37.5	8.717	0.92	0.50	0.08	0.04
8	42.5	10.365	ND	0.54	0.05	0.04
9	47.5	12.100	1.20	0.52	0.04	0.04
10	55.0	14.729	ND	0.47	0.00	0.04
11	65.0	17.994	ND	0.59	ND	0.05
12	74.0	20.790	ND	0.00	ND	0.05