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Ambient concentrations of polychlorinated biphenyls and organochlorine pesticides in selected Thai estuarine sediments and mussels

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Abstract—Over the past few decades, the occurrence of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in the environment is of great concern due to their persistent and long-range transportable nature as well as toxic biological effects. While most of developed countries have already banned or restricted the production and usage of these compounds, some developing countries still use OCPs for agricultural and the public health purposes. This paper presents data on the concentrations of PCBs and OCPs in selected Thai estuarine sediments and mussels. A total of 20 composite sediment samples and 10 composite mussel samples were collected from two estuaries draining to the inner Gulf of Thailand, namely the Thachin and Bangpakong estuary in 2004. Aldrin, dieldrin, endrin, and heptachlor were not detected in either the mussels or sediments from both study sites. The most frequently detected pesticides were DDTs and chlordanes (CHLs), with relatively low concentration of hexachlorocyclohexanes (HCHs). Low concentrations of PCBs were only detected in sediment and mussel samples from the Bangpakong estuary, with penta-, hexa- and hepta-chlorinated congeners are the dominant homologues. The results from this study demonstrate that ambient concentrations of PCBs and OCPs in Thai estuaries are low, and in most cases lower than concentrations reported for estuaries in many Asian countries.

Key words: polychlorinated biphenyls, PCBs, organochlorine pesticides, persistent organic pollutants, POPs, green mussels, Bangpakong, Thachin, Gulf of Thailand

Introduction

The contamination of persistent organic pollutants (POPs) in the environments has become a global concern due to their carcinogenic and mutagenic properties. POPs have been shown to cause serious immune and metabolic effects, neurological defects, reproductive anomalies and cancer in both humans and wildlife. In addition, they are highly toxic, remain in the environment for long periods, bioaccumulate, and can spread thousands of miles from the point of emission (Colborn, et al. 1993, Tanabe 2002, Helberg et al. 2005). Public concern about the adverse environmental and human health impacts of organochlorine contaminants led to strict regulations on their use in developed nations three decades ago. Nevertheless, DDT and several other organochlorine pesticides (OCPs) are still being used for agriculture and public health programs in developing countries in Asia. In Thailand, a broad spectrum of pesticides was used for agricultural activities as well as vector controls. Persistent OCPs, including aldrin/dieldrin, endrin, chlordane, heptachlor and DDTs, were widely used from the early 1960s until the official ban commenced in 1981. The main areas of use were agriculture, horticulture, timber treatment and public health. Polychlorinated biphenyls (PCBs) were used in a relatively large quantity as a dielectric fluid for electric capacitors and transformers by the electrical utility industry, with a small amount as industrial fluids for hydraulic systems, as lubricating oil, and as plasticizer until 1975. Although OCPs and PCBs have been officially banned for over 20 years, their residues can still be detected in foods, soils, sediments and biota (i.e. Watanabe et al. 1996, PCD 1997, Kanatireklap et al. 1997, Wilcke et al. 1999, Thapinta and Hudak 2000, Boonyatumanond et al. 2007).

In this study OCPs and PCBs in estuarine surface sediment and mussel samples from two selected estuaries in Thailand, namely the Thachin and Bangpakong, were investigated to evaluate the residue levels. Thachin River is located in central Thailand. It is actually an effluent tributary of the Chao Phraya River, which is the waterway draining the Central Plain of Thailand. The upstream provinces have some of the most fertile agricultural lands in the country while the

lower provinces have some highly industrialized zones. Bangpakong River is the most important catchments basin in the eastern part of Thailand. The river basin comprises of paddy fields, farmlands, pig farms, aquaculture ponds and some industrial areas. Hence, the land uses within the catchments of these two river basins are quite different, with the Thachin is more industrialized and the Bangpakong is relatively more agricultural influences.

Materials and Methods

All solvents used for extraction and clean-up procedures were nanograde or HPLC grade quality (Merck). Glass distillation was used when solvent quality did not meet the requirement of purity specified by standard operation procedures. All glassware, vials and extraction vessels were washed with detergent in an ultrasonic bath for 1hour, rinsed with acetone and dried at 100°C for 30 min followed by 2 h at 220°C in oven, and rinsed with hexane before use.

Sampling Sites and Sample Preparation

The locations of study areas and the sampling sites are shown in Fig. 1. Samples of surface sediment were collected at stations T1–T10 and stations B1–B10 along the Thachin and Bangpakong estuary respectively, using a grab sampler. The top 1 cm surface layer was carefully removed with a stainless steel spoon and stored in pre-cleaned glass bottles. The samples were stored at −20°C and freeze dried before analysis. Approximately 20 individual green mussels (*Perna viridis*), with a mean shell length of 7.9±0.8 cm, were collected from five different locations at the mouth of the Thachin and Bangpakong estuary. Mussel samples were kept in polyethylene bags, kept in ice box with ice, and kept in a deep freezer immediately after reaching the laboratory. Sediment samples were collected between January and February 2004 while mussel samples were collected in June 2004.

Chemical Analysis

OCPs and PCBs in sediment and mussel samples were analyzed following previously described methods by Sericano et al. (1990) and Wade et al. (1993) with some modifications. Briefly, sediment and mussel samples were extracted with methylene chloride in a soxhlet apparatus, cleaning up and fractionation by alumina:silica column chromatography. The identification and quantification of OCP and PCB compounds was made by an HP 5890 gas chromatograph equipped with a 30 m×0.32 mm×0.25 μm HP-5MS (5% Phenyl methyl siloxane) fused silica capillary column and a ^{63}Ni ECD as well as an HP7673 autoinjector (Hewlett-Packard, Palo Alto, CA, USA). The initial temperature of the oven was 100°C and the temperature programmed at 5°C/min until 140°C, 3°C/min until 250°C and 10°C/min to a final temperature of 300°C that was held during 5 min; using helium as the carrier gas and nitrogen as make-up gas. The detector temperature was 325°C and injector temperature was 250°C. A splitless technique was used to inject 1 μL of the purified extract.

Quantitative estimation of OCP residues was carried out by reference to the retention times obtained by chromato-

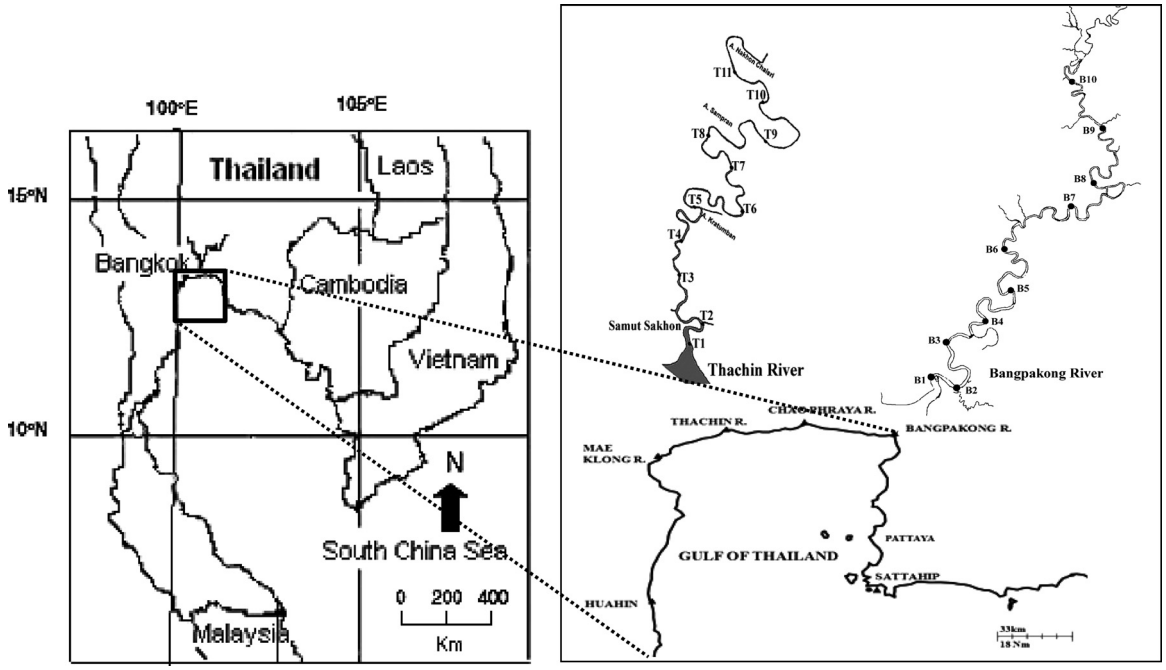

Fig. 1. Map of study areas showing Thachin and Bangpakong estuary with sediment sampling stations in the Thachin (T1–T10) and Bangpakong (B1–B10).

graphic separation of 18 standard solutions containing α-HCH, β-HCH, γ-HCH, δ-HCH, heptachlor, aldrin, heptachlor epoxide, trans-chlordane, cis-chlordane, o,p-DDE, p,p′-DDE, dieldrin, o,p-DDD, endrin, o,p-DDT, p,p′-DDD, p,p′-DDT and mirex (Supelco, U.S.A.). A PCB mixture consisting of Arochlor 1016, 1242, 1254, and 1260 (1 : 1 : 1 : 1) was used as the external standard to quantify the PCBs. Concentrations of individually resolved peaks were summed to obtain total PCB concentrations. Quality assurance of the analytical procedures included the addition of internal standards and the analysis of a procedural blank for each set of samples. Good recovery values were obtained for OCPs and PCBs in the range of 80–109%. All concentrations were corrected against blank levels and presented without recovery adjusted.

Results and Discussion

Polychlorinated Biphenyls (PCBs)

A summary of concentration data for PCBs determined in estuarine sediments and green mussels is provided in Table 1. PCBs were found below the limit of detection in surface sediment and mussel samples from Thachin estuary; however PCBs were detected in samples from Bangpakong estuary with total concentrations varied from 0.09 ng/g to 1.5 ng/g dry weight in surface sediments (average of 0.58 ng/g), and between 0.90 ng/g and 2.70 ng/g wet weight (average of 1.70 ng/g) in green mussels. PCB concentrations in green mussels were found to be comparable to the range of concentrations in green mussels along the coast of Thailand as reported by Kan-atireklap et al. (1997) and Cheevaporn et al. (2005), however these PCB levels were relatively low when compared to those reported in green mussels from coastal waters in more industrialized countries in Asia; such as Japan, South Korea, Hong Kong, and Taiwan (Tanabe et al. 2000).

Table 1. Mean and range (in parentheses) of PCB and OCP concentrations in surface sediment and mussel samples collecting from the respective estuaries.

PCB/OCP residues	Sediment (ng/g dw)		Mussel (ng/g ww)	
	Thachin	Bangpakong	Thachin	Bangpakong
PCBs	<0.01	0.58 (0.09–1.5)	<0.01	1.70 (0.9–2.70)
DDTs	6.33 (0.27–45.1)	2.27 (0.64–6.5)	1.65 (0.86–2.1)	2.20 (1.4–3.2)
CHLs	4.05 (0.65–11.6)	2.88 (0.75–5.5)	1.91 (0.47–2.0)	2.52 (1.4–2.8)
HCHs	0.68 (<0.01–2.0)	0.44 (<0.01–1.3)	0.07 (0.04–0.19)	0.04 (0.02–0.24)

DDTs: p,p′DDE+p,p′DDD+p,p′DDT
CHLs: trans-chlordane+cis-chlordane
HCHs: α-HCH+β-HCH+γ-HCH

For sediments, the highest PCB concentrations were found at stations B1–B3 with average PCBs concentrations of 1.44 ng/g dry weight. The lowest concentration (0.09 ng/g) was found at station B8, towards the upper reach of the estuary. The PCB homologues in both mussels and sediments were monitored from Arochlor-Mix standard peaks (not shown) indicating penta-, hexa- and hepta-chlorinated congeners as the predominant homologues. Highly chlorinated congeners are less volatile and could be resistant to biodegradation over a long period of time in comparison to lower chlorinated congeners (Iwata et al. 1993). The presence of high chlorine content PCBs can be attributed to local emissions along the Bangpakong, since they are less prone to travel long distances due to their high K_{ow}. In Thailand, the import of PCBs was banned in 1975. Capacitors and transformers containing PCBs and PCB wastes were normally exported for disposal overseas. However lack of awareness about handling PCBs in electrical equipment in the past had created some contaminated situations due to accidental leakage of PCBs from old transformers and condensers during awaiting disposal (Watanabe et al. 1996). Since then, it has been recognized that PCB-containing or contaminated electrical equipment in its electric utility is an important PCBs source of concern in Thailand (Boon-Long 1997). In our study site, the higher PCB concentrations in sediments at stations B1–B3 could have resulted from PCBs leaching from used capacitor storage at the site of the Bangpakong Power Plant located near the river mouth.

There is currently no regulatory limit for PCBs in sediments or shellfish in Thailand. However, the levels of PCBs observed in sediments from the Bangpakong estuary were much lower than the limit level (23.0 ng/g dry weight) for the Interim Sediment Quality Guidelines (ISQS) of Australian and New Zealand (ANZECC, 2000).

Organochlorine Pesticides (OCPs)

The concentrations of OCPs most frequently detected in green mussels and sediments from both study areas are also shown in Table 1. For both mussel and sediment samples, concentrations of DDTs (p,p′DDE+p,p′DDD+p,p′DDT) and chlordanes (CHLs: trans-chlordane + cis-chlordane) were the highest, followed by hexachlorocyclohexane (HCHs: α-HCH+β-HCH+γ-HCH). The o,p′-isomers of the DDT group were detected much less frequently, and concentrations of other OCPs such as aldrin, dieldrin, endrin and heptachlor were below the limits of detection in all samples analyzed. All of the organochlorine insecticides that were classified under the Stockholm Convention as POPs were prohibited or banned from use, import, export and production in the country on different occasions; aldrin (1988), chlordane (2000), DDT (1983), dieldrin (1988), endrin (1981), heptachlor

Table 2. Reported concentrations of organochlorine residues (ng/g ww) in green mussels (*Pema viridis*) from various locations.

Location	Year	PCBs	DDTs	HCHs	CHLs	References
Gulf of Thailand	1991	—	0.74–5.38	<0.02–0.09	—	Ruangwises et al. (1994)
Coastal waters,	1994	0.17–12	1.3–38	<0.01–0.09	—	Kan-atireklap et al. (1997)
Thailand	1995	<0.01–20	1.3–15.0	<0.01–0.43	—	Kan-atireklap et al. (1997)
Philippines	1994–97	0.69–36	0.19–4.20	<0.01–0.19	—	Prudente et al. (1999)
Viet Nam	1997	0.2–3.4	2.7–340	0.04–0.1	—	Monirith et al. (2000)
Cambodia	1998	<0.05–5.1	0.25–1.6	0.01–0.03	—	Monirith et al. (2000)
Malaysia	1998	0.1–5.1	0.2–5.7	0.01–0.15	—	Monirith et al. (2000)
Indonesia	1998	0.2–2.7	0.1–3.1	0.1–0.1	—	Monirith et al. (2000)
Philippines	1998	0.4–14.2	0.1–1.0	0.03–0.06	-	Monirith et al. (2000)
West coast, Malaysia	1998–99	—	0.00–7.8	0.32–11.28	—	Hossain (2001)
East coast, Thailand	2002–2003	0.2–3.7	1.2–3.9	<0.01–0.49	<0.01–1.4	Cheevaporn et al. (2005)
Thachin Estuary	2004	—	0.86–2.1	0.04–0.19	0.47–2.0	This study
Bangpakong Estuary	2004	0.9–2.7	1.4–3.2	0.02–0.24	1.4–2.8	This study

(1988), toxaphene (1983), and mirex (1995). As the ban on import and use of chlordane came into force only in recent years, there could still be continuing sources of chlordane releases from soil or sediments in the areas from recent and perhaps continuing applications of chlordane during the time of sampling. However, this pattern of contamination, in which DDTs are the predominant compounds indicating the extensive usage of DDTs in Thailand as compared to other pesticides.

In general, p,p′DDT and p,p′DDD were rarely found in most sediment and mussel samples, but p,p′DDE was more ubiquitous in their occurrence. The presence of significant concentrations of p,p′ DDE (average 90% and 78% of total DDTs in sediments from Thachin and Bangpakong, respectively; and >90% of total DDTs in mussels) suggesting that p,p′DDT had been converted under anaerobic and reducing conditions. This process is likely to have occurred in sediments prior to uptake by mussels. On the other hand, the presence of the elevated composition of p,p' DDT at stations T1 (54%), B4 (81%) and B8 (78%) indicates a more recent application of the chemical.

Of the three isomers of HCH, only γ-HCH was detected in green mussel samples from both study sites. This observation was also true for most sediment samples from both estuaries. However, α- and β-HCH isomers were found at rather high concentrations in sediments at stations T1, T4, T8 (Thachin) and B1, B2 (Bangpakong). On average α-HCH and β-HCH accounted for 34% and 42% of total HCHs concentration in these sediments. Since the α-isomer is the most volatile of the HCH isomers in this subtropical region (ATSDR 2005), the abundance of α-HCH suggests that technical HCH has been recently used in these areas. However, there is no available inventory on the import and use of technical HCH in Thailand, therefore contamination of HCHs in these sediments may be attributed to the long-range transport from other regions or illegal usage.

Concentration of all measurable OCPs residues in green mussels (Table 1) were found to be comparable to previously reported ranges of concentrations in green mussels along the coast of Thailand (i.e. Ruangwises et al. 1994, Kan-atireklap et al. 1997, Cheevaporn et al. 2005), which were lower than the Maximum Residue Limits (MRL) for aquatic animals recommended by the Ministry of Public Health of Thailand. In addition, the OCPs levels in both mussel (Table 2) and sediment samples from these two selected estuarine areas were relatively low when compared to those reported from many countries in Asia (Iwata et al. 1994, Tanabe et al. 2000, Hong et al. 2008).

Conclusions

Although OCPs and PCBs have been officially banned in Thailand for over 20 years, their residues can still be detected in sediments and mussel samples from estuarine environment such as the Thachin and Bangpakong. The major OCPs residues detected in sediment and mussel samples were DDTs, CHLs and HCHs. Concentrations of other OCPs such as aldrin, dieldrin, endrin and heptachlor were found to be below the limits of detection in all samples analyzed. Concentrations of DDTs and CHLs, although most frequently detected in the samples, were generally low suggesting that their levels were declining and that the Thachin and Bangpakong estuaries were only slightly contaminated with OCPs. Low concentrations of PCBs were only detected in sediment and mussel samples from the Bangpakong estuary, with penta-, hexa- and hepta-chlorinated congeners are the dominant homologues. The source of PCBs could have been from used capacitor storage at the site of the Bangpakong Power Plant located near the river mouth. However, further follow-up studies on POPs contamination in the areas are still needed in order to identify other possible sources of

PCBs and HCHs in Thailand.

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