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Contamination of Organochlorine Pesticides and PCBs in Sediments Collected from the East Coast of Thailand

Jakkapan Potipat and Voravit Cheevaporn

Department of Environmental Science, Faculty of Science and Technology, Rambhai Barni Rajabhat University, Chantaburi, 22000 Thailand

Abstract

Organochlorine pesticides (OCs) and PCBs concentration were analyzed in sediments from east coast of Thailand. The samples were collected in April 2013 and were analyzed by GC/ECD. Organochlorine pesticide concentrations were detected in sediments in the range of 1.06–3.71 ng/g calculated on dry weight basis. T-DDTs concentrations were the highest in OCs group compared to other groups in most of the samples. PCBs concentrations were detected in sediments in the range of 0.04–3.03 ng/g calculated on dry weight basis. This study suggests that there is no correlation between the results of different stations but proximity to the sources of contamination may be the most important determining factor for the dominance of these contaminants. Probably this contamination seems to be localized due to the presence of urban runoff, municipal sewage, industrial waste, outflow from agricultural area and chemical spill.

Keywords: organochlorine pesticides; PCBs; sediment

1. Introduction

Organochlorines such as PCBs (Polychorinated biphenyls), DDTs (Dichloro Diphenyl Trichloroethanes), HCHs (Hexachlorocyclohexane), CHLs (Chlodane related compounds), and HCB (Hexachlorobenzene) etc. were widespread organic compounds which is ubiquitous in the environment. Owing to their stable physiochemical properties, once they come in to the environment they remain for a long time. Actually these compounds were restricted at many of countries in 1970s, but they have been detected almost of compartments including air, water, biota and sediment until now (Hong *et al*., 2001). In the aquatic environment, organochlorine compounds are removed from the water column and adsorbed on the particulate matters due to their high affinity for organic matter, and finally accumulated in sediments, which may play a role as secondary contamination source. These contaminants also accumulate in the sediment-dwelling organisms which maybe transferred to higher tropic levels through the food chain (Lee *et at*., 2001). Sediment is a useful tool to monitor the surroundings, through which we can identify pollution status for recent several years. (Hong *et al*., 2001).

2. Materials and Methods

2.1. Sample collection

Sediments were collected in summer season (April 2013) from east coast of Thailand from 8 sampling sites (Fig. 1). Samples were collected from the field. Sediment samples stored in pre-combusted and hexane-rinsed amber glass jar. In most of the sampling sites, several samples were collected and pooled in order to obtain a more representative sample of the area. All the samples were kept in a cooler box with ice and transported to the laboratory where they were stored deep frozen. Frozen sediments were thawed and scraped clean and re-frozen at -20ºC before analysis.

2.2. Samples analysis

Frozen samples were allowed to thaw at room temperature. About 15 g of homogenized sediment sample was dehydrated with activated sodium sulfate. About 20 µl of surrogate standard (Dibromooctafluorobiphenyl, PCB 103 and PCB 198) was added. The samples were placed in thimble and were soxhlet extracted with 200 ml of dichloromethane as solvent for

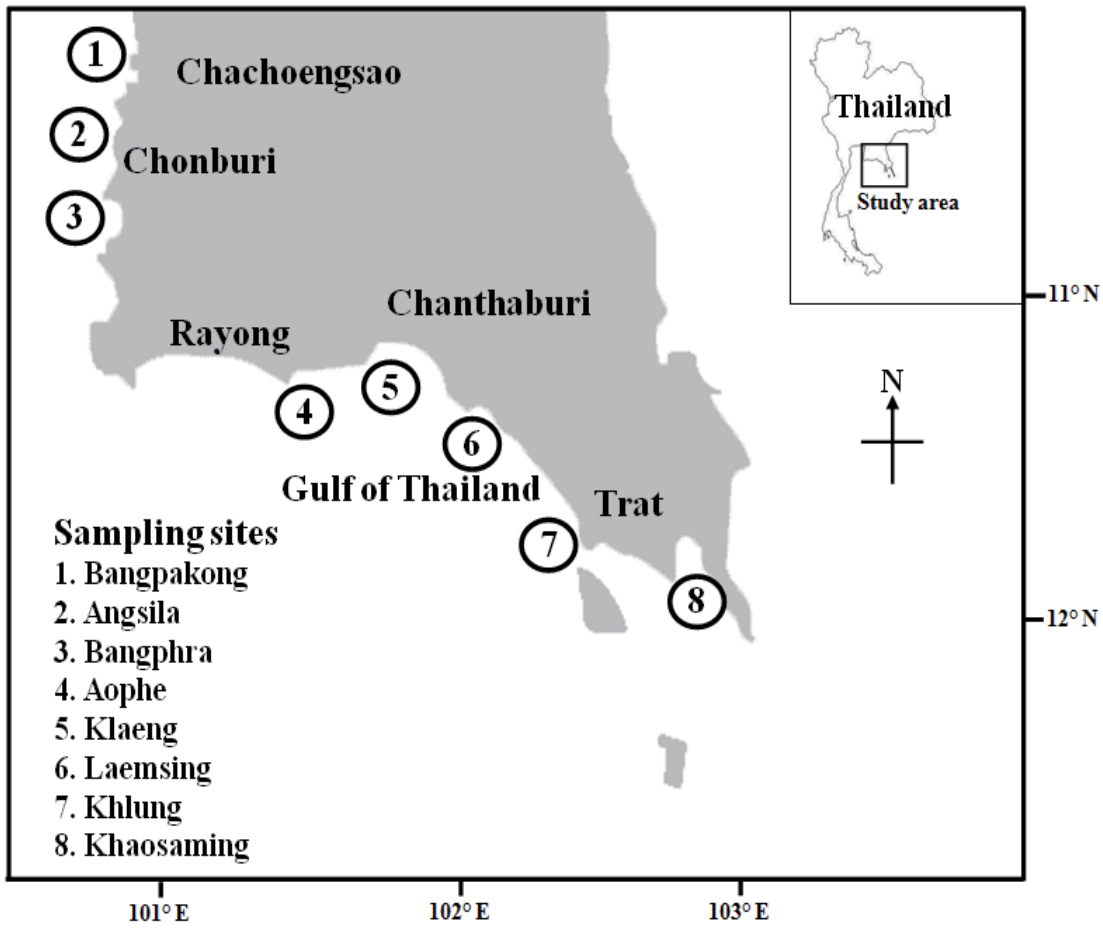

Figure 1. The sampling sites along the east coast of Thailand

16 hr. Sulfur was removed by activated Cu. Dry weight was determined 2 g of an each sample. The solvent was evaporated to about 2-3 ml on a water bath. The extract was cleaned up by liquid chromatography using silica gel/alumina column. The column was filled with 10 g of alumina and 20 g of silica gel (deactivated with about 1% and 5% water, respectively), and eluted with 200 ml of dichloromethane. The extract was separated with a high performance liquid chromatography (HPLC; 250 x 22.5 mm I.D. of size-exclusion column) using dichloromethane for further clean-up and fractionation. Collection time of OCs fraction was determined based on retention times of dibromooctafluorobihenyl and perlyene in HPLC calibration solution using an UV detector. When the retention time of both compounds stabilized, the sample was loaded into a HPLC, and OCs fraction was collected. The fraction was concentrated and re-constituted with hexane. The sample was concentrated with a gentle stream of N_2 to 0.5 ml, and 10 ng of internal standard (tetrachloro-*m*-xylene) was added.

A Hewlett-Packard 5890 gas chromatograph (GC) with an electron capture detector was used for identification and quantification of OCs in samples. The column used for analyses was fused silica capillary DB-5 (30 m x 0.25mm i.d. x 0.25 μm thickness). Helium gas was used as the carrier gas and argon: methane (95:5) used as the make-up gas. The GC temperature was programmed as follows; 100C (1 min holding time), heated to 140ºC at a rate of 5ºC/min (1 min holding time) and heated to 300ºC at a rate of 10ºC/min (5 min holding time). The extracts were concentrated in a steam bath with a three-ball Snyder column. The extracts then were cleaned up by: (1) silica gel and alumina column chromatograpy, and (2) High-Performance Liquid Chromatography (HPLC). The final extracts were

analyzed by Hewlett-Packard 5890 series II Gas Chromatograph with a ^{63}Ni Electron Capture Detector (ECD).

2.3. Quality control and quality assurance

Spike sample recoveries of PCB 103, DBOFB and PCB 198 in sediments were 83.28±10.86%, 87.34± 8.16% and 102.82±12.67%, respectively. Blanks were carried out with all sediment samples. The whole analytical procedure was validated by analyzing sediment reference materials, EC-4 from Environment Canada and 1941a from NIST (Fig. 2). The results of analyzing the reference materials fell within the range of the certified value for almost of the target OCs (Table 1).

3. Results and Discussion

3.1. Organochloride residues concentration

The concentrations of organochorine residues (OCs) detected in sediment is given in Fig. 3. Higher values of OCs concentration are observed at sampling site 1 where the sampling site 1 is located near the developing industrial facilities. The city also has co-developed with the industrial complex and is urbanized. So this high amount can be attributed to the industrial and sewage disposal in the coastal waters. In this study, the grain size were correlated with TOC content $r^2 = .79$, $p < 0.05$, while no correlation was found with T-OCs and TOC or grain size.

DDT is the most prominent type of organochlorine pesticides and PCBs are the major organochlorines in the study area. Concentrations of T-DDTs is in the range of 0.11-2.60 ng/g dry wt. A decreasing trend of DDT is noticed from sampling site 1 to 4, where it shows the least value. Other types of organochlorine pesticides are <1 ng/g in the sediment samples (Fig. 3). Concentration of T-DDTs correlate with T-OCs ($r^2 = .86$, $p < 0.01$), indication that T-DDTs in the sediments is one of major factor for influencing distribution of the concentration of organochlorine pesticides. The usage of DDT for agricultural purposes has been banned in Thailand since 1983, but still being used for malaria vector control (Ruangwises *et al*., 1994).

Although monitoring data on CHL residues in sediments are scarce even on an international basis, comparable levels were found in Thailand with Asian countries such as Sri Lanka, Japan and Korea. Total CHLs-concentrations (Sum of α-Chlordane, γ-Chlordane, cis-nonachlor and trans-nonachlor) were

Table 1. The results of certified reference material (EC-4 and SRM 1941a) analysis (*n=10*) in comparison with the certified values (ng/g dry wt.)

	This study (mean±SD)	Certified values (mean±SD)
PCB18 [a]	3.4±0.2	3.7±1.6
PCB28 [a]	7.2±0.5	6.8±1.8
PCB44 [a]	8.9±0.9	7.5±2.9
PCB52 [a]	13.3±1.5	12.5±5.7
PCB87 [a]	8.4±0.8	8.3±1.5
PCB101 [a]	20.5±3.5	22.4±9.5
PCB105 [a]	7.0±1.4	8.1±3.2
PCB110 [a]	26.3±2.7	29.1±11.5
PCB118 [a]	18.3±0.7	17.8±7.7
PCB128 [a]	5.9±0.5	4.6±2.2
PCB138 [a]	31.0±5.6	28.7±9.7
PCB153 [a]	27.0±6.9	27.3±7.5
PCB170 [a]	13.3±0.8	11.8±2.5
PCB180 [a]	24.5±4.2	26.1±11
PCB206 [a]	3.7±0.3	3.2±1.6
PCB209 [a]	1.9±0.5	1.6±0.2
Hexachlorobenzene [b]	48.5±0.03	70±25
cis-Chlordane [b]	2.30±0.07	2.33±0.56
trans-Nonachlor [b]	1.10±0.03	1.26±0.13
p,p′-DDE [b]	6.09±0.03	6.59±0.56
p,p′-DDD [b]	5.27±0.03	5.06±058

[a] EC-4; A Toronto harbor sediment for toxic organics produced by National Water Research Institute, Environment Canada.
[b] SRM 1941a; marine sediment for organics produced by National Institute of Standards & Technology (NIST).

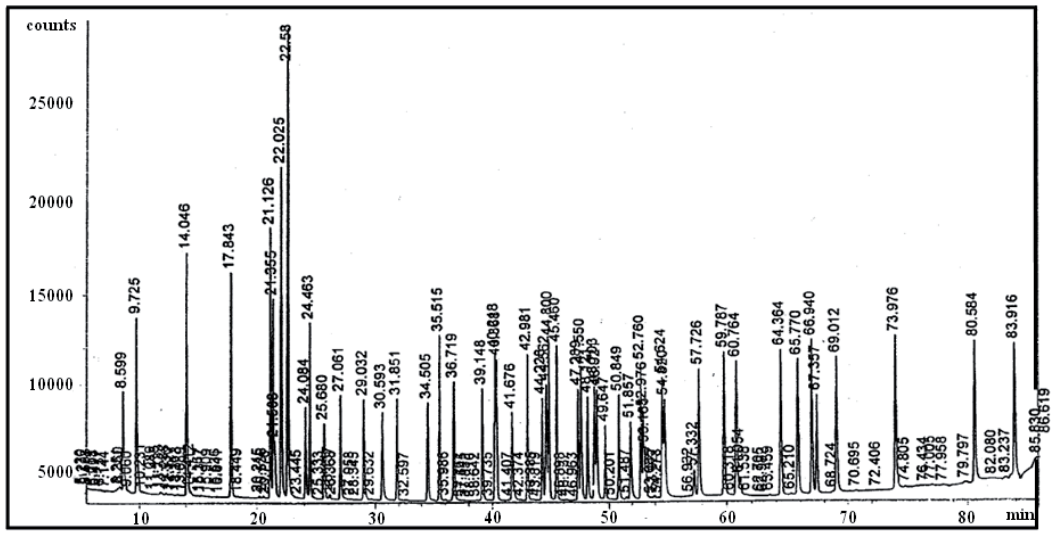

Figure 2. Chromatogram of organochlorine pesticide and PCB standards

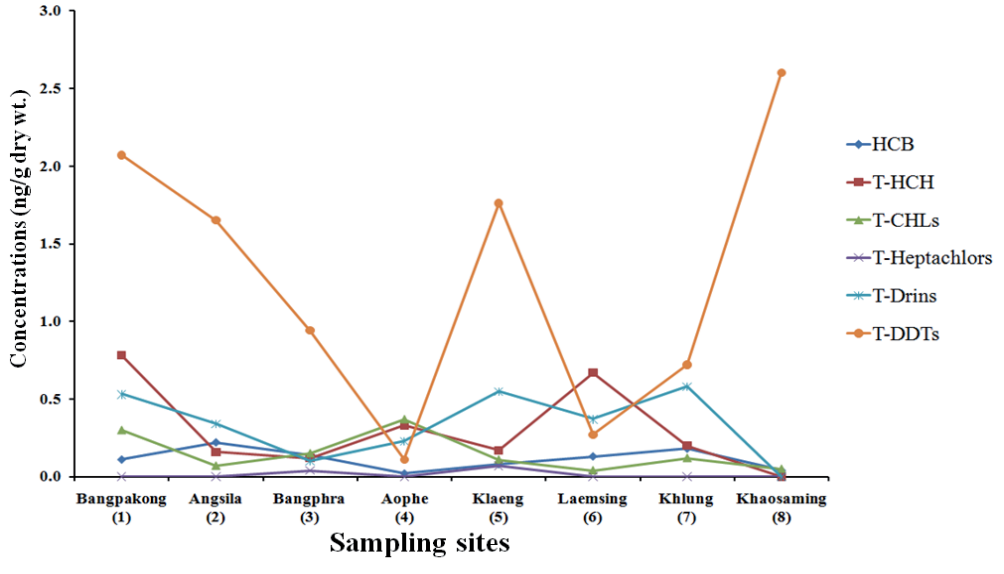

Figure 3. Organochlorine pesticide concentrations (ng/g dry wt.) in sediment from the east coast of Thailand

detected in every stations, ranging from 0.04-0.37 ng/g while earlier study by Guruge and Tanabe (2001) showed a range of 0.07-0.45 ng/g, Iwata *et al*. (1994) showed a range of 0.66-2.1 ng/g and Hong *et al*. (2003) showed a range of nd-2.22 ng/g.

Total HCH-concentrations (ΣHCH; sum of α-, β-, and γ-HCH) in sediments are in the range of nd-0.78 ng/g (Table 2). Concentrations of HCHs were relatively low in comparison to overseas data. The usage of technical-grade HCH and lindane (purified -HCH), which has been used as broad spectrum insecticide for fruit, grain and seed, has been banned and/or has been restricted in many countries (including Thailand) since 1970s. However, lindane is still used in several countries, including Canada and US, as seed dressing and a medical purpose reagent (Willett *et al*., 1998). The application of γ-HCH (lindane) still appears to be continuing in Thailand (Siriwong *et al*., 1991). The detection of γ-HCH as a prevalent isomer in some locations may suggest the usage of lindane in Thailand (Ruangwises *et al*., 1994; Kannan *et al*., 1995). However, the quantity of HCH usage in Thailand seems to be quite small, because of its reside levels in the present study were lower than in other Asian countries such as Vietnam and India (Table 2). Between 1948 and 1997 total global usage of technical HCH was estimated to be approximately 10 million tons (Li, 1999).

Table 2. Comparison of organochlorine concentrations in sediments from coastal areas in the world (ng/g dry wt.)

Location	Year	PCBs	DDTs	HCB	HCHs	CHLs	Reference
Spain	1995-1996	5.29-1772	0.413-51.8		0.001-0.038		Fernandez *et al*. (1999)
Northern part of the Baltic Sea	1991-1992	9-9.3	1.9-6.9	0.79-0.94	5-7		Strandberg *et al*. (1998)
West and east coast of India	1995-1997		nd-364		1.5-1053		Pandit *et al*. (2001)
North Coast of Vietnam	1997	1.1-66.4	6.2-10.4	0.1-6.5	1.2-33.7		Nhan *et al*. (1999)
West coast of Sri Lanka	1996-1997	0.45-4.4	0.09-1.6	<0.01-0.021	0.086-0.33	0.07-0.45	Guruge and Tanabe (2001)
Vladivostok, Russia	1998		<0.01-4.78		<0.2-4.47		Tkalin *et al*. (2000)
Osaka Bay, Japan	1989-1991	63-240	2.5-12		4.5-6.2	0.66-2.1	Iwata *et al*. (1994)
Daya Bay, China	1999	2-110	1.12-20.3		0.32-4.16		Zhou *et al*. (2001)
Coast of Bohai and the Yellow Sea	1997		0.37-1273				Ma *et al*. (2001)
Masan Bay, Korea	1997	2.48-75.0	0.27-89.2	0.02-0.59	nd-1.33	nd-2.22	Hong *et al*. (2003)
East coast of Thailand	2013	0.04-3.03	0.11-2.6	0.02-0.22	nd-0.78	0.04-0.37	This study

nd = not detectable

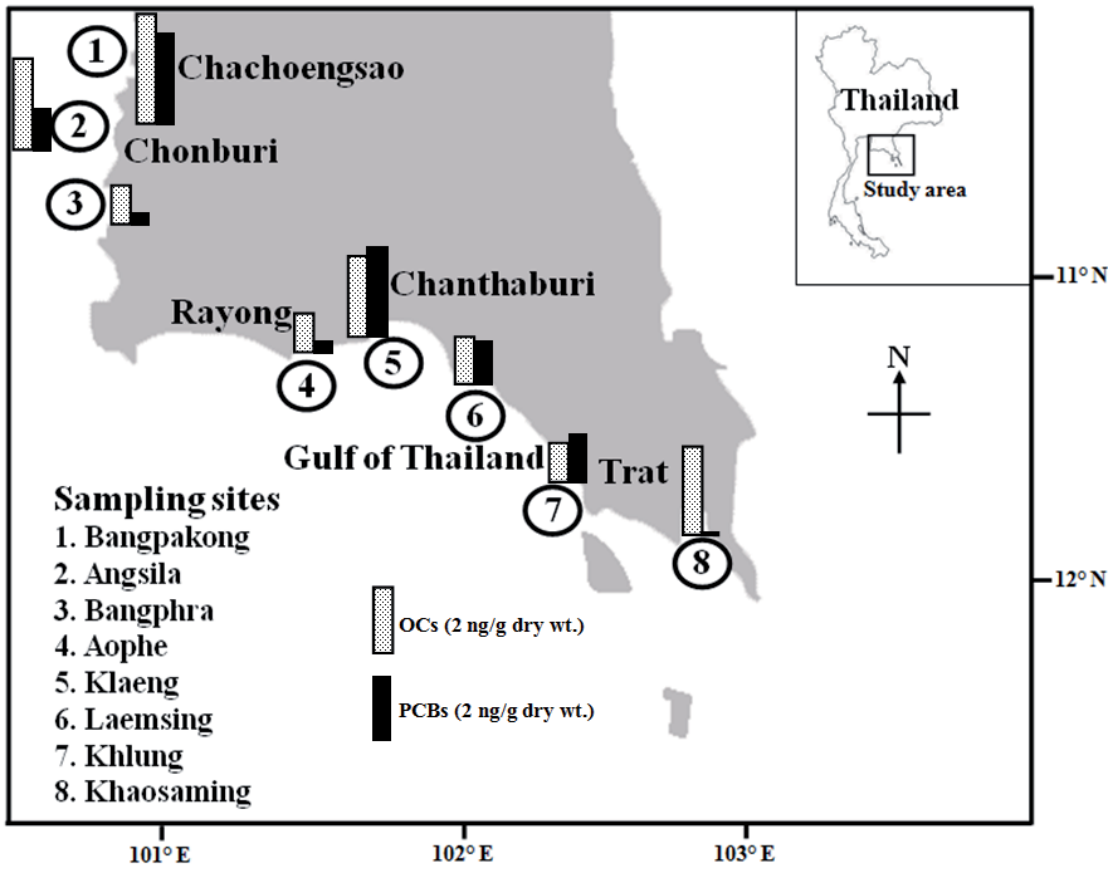

Figure 4. Distribution of OC and PCB concentrations (ng/g dry wt.) in sediment from the east coast of Thailand

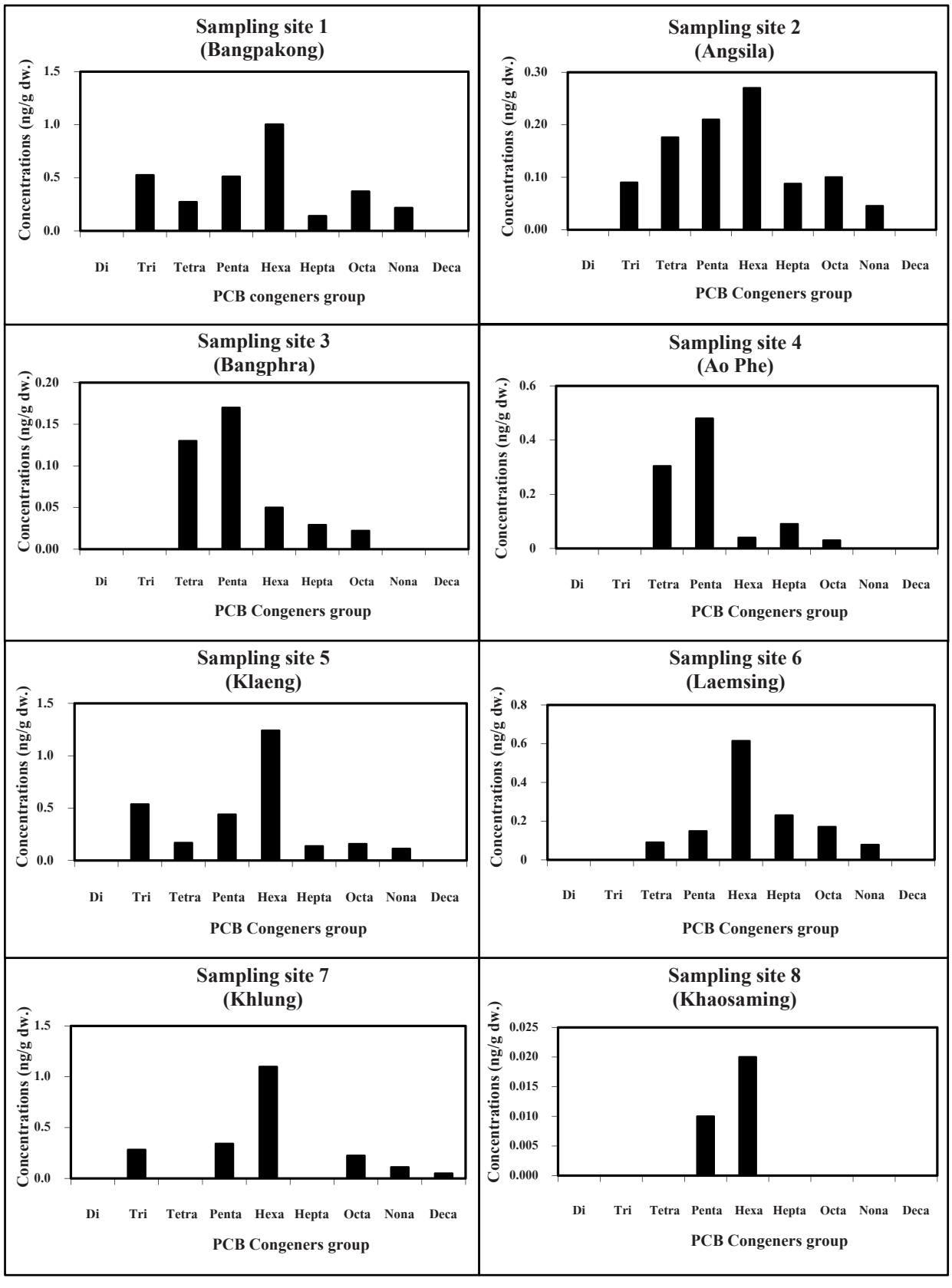

Figure 5. The PCB congeners group in sedment from the east coast of Thailand

HCB contamination seems to have originated from the usage of fungisides or as an impurity in pesticide formations, a byproduct of various chlorination processes and the combustion of industrial and municipal wastes (Kannan *et al*., 1995). HCB was detected in every stations. The concentrations of HCB found in the present study ranged from 0.02-0.22 ng/g, which is slightly lower than the earlier reported, such as 0.79-0.94 ng/g (Strandberg *et al*., 1998), 0.1-6.5 ng/g (Nhan *et al*., 1999) and 0.02-0.59 ng/g (Hong *et al*., 2003).

Total Drins-concentrations (Sum of Aldrin, Dieldrin and Endrin) are in the range of nd-0.58 ng/g. It is known that Aldrin is quickly transformed to the much more toxic and persistent dieldrin (Falandysz *et al*., 1998).

The spatial differences in organochlorine residue levels in sediments collected from the east coastal waters of Thailand suggested that these compounds were widely used in Thailand. Although the agricultural usage of organochloride pesticides, such as DDT and HCH, was banned in Thailand, their current sources still remain in the aquatic environment. When compared to the international data, residue levels of organochlorine pesticides in Thailand's marine environment was lower. Considering the data on an international basis (Table 2), contamination by organochlorine pesticides is not of serious concern. Distribution of OC and PCB concentrations (ng/g dry wt.) in sediment from the east coast of Thailand are given in Fig. 4.

3.2. PCB concentrations

Total PCB concentrations (PCB; sum of 22 congeners) from 8 sediment samples range from 0.04–3.03 ng/g dry wt. Concentrations of PCBs in this study were generally very low (Table 2). Concentrations of PCB in sediments from the east coast of Thailand exhibited a smaller variation among locations. An earlier study in Sri Lanka by Guruge and Tanabe (2001) also give the similar results with a range of 0.45-4.4 ng/g and much lower than in more industrialized countries such as Japan, China and Korea. The higher concentrations, with a maximum at station 1 (3.03 ng/g), could be due to the waste drainage from the industrialized city and the power plant. The possible sources may be from transformer fluids and hydraulic additives. One of the major source of PCBs in Thailand is considered to be transformers and capacitors imported by Electricity Authority of Thailand (Watanabe *et al.*, 1996). Watanabe *et al*. (1996) recorded the PCB pollution in the dumping site of transformers and capacitors located at suburb Bangkok near by the estuary of Chao Phraya river. Although the studies suggests the contamination by PCBs in the coastal waters of Thailand is not a serious concern at present, but need to be monitored continuously due to the increasing industrial and related polluting activities. The PCB congeners group concentrations (ng/g dry wt.) in sediment from the east coast of Thailand are given in Fig. 5.

4. Conclusions

The international comparison of organochloride residues and PCBs in sediments from Thailand (this study) and various other countries is summarized in Table 2. The levels of OCs residues in sediments found in the present study were comparable with the levels found in other developing countries, but relatively less than those of developed nations. This could be explained by the flux modeling study in the tropics, which suggest that OCs budget to the aquatic ecosystem was less significant and its residence time was quite short, whereas transfer to the atmosphere was much larger due to the high temperature (Watanabe *et al*., 1996). Concentrations of DDTs and PCBs in sediment in this study were the highest among all of the chlorinated hydrocarbons detected here. The results were shown a smaller variation and not of serious concern. Most of these PCB pollutions in Thailand are probably from the transformers and capacitors. The major parameters that determine the PCB concentration levels are likely to be the distance from the factory district, characteristics of the sediment, and transportability of the sediment by the flowing of river water (Jeong *et al*., 2001).

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Correspondence to
Jakkapan Potipat
Department of Environmental Science,
Faculty of Science and Technology,
Rambhai Barni Rajabhat University,
Chanthaburi, 22000
Thailand
Tel: +668 3068 0800
Fax: +66 3947 1060
Email: bomb1112@yahoo.com