ORGANOCHLORINE PESTICIDES IN SEDIMENT CORES FROM BALAT – A MAJOR ESTUARY OF RED RIVER, NORTHERN VIETNAM: SPATIAL DISTRIBUTION AND DEPTH PROFILES

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Abstract

We investigated spatial and vertical distributions of organochlorine pesticides (OCPs) in surface sediment and sediment cores from Ba Lat estuary, a major estuary of Red River, the biggest river in Northern Vietnam. Concentrations of dichlorodiphenyltricloroethanes (DDTs), hexachlorobenzene (HCB) and hexachlorohexanes (HCHs) were in range of 0.68 – 3.46, <0.05 – 0.69, <0.06 – 2.87 ng/g, respectively. Concentrations of DDTs were higher at station near the mouth of Red River. Vertical depth profile of DDTs in sediment cores reasonably reflects the history of DDT usage in Vietnam.

Introduction

Organochlorine pesticides (OCPs) are ubiquitous pollutants in the environment. For several decades, the compounds have been produced and also extensively used for various purposes in the world. Since 1970 in most developed countries, the use of these pollutants has been restricted. However, many developing countries are still using them for agricultural and public health purposes. These organic pollutants released into water system readily adsorb to particles, and then incorporated into sediments. Thus the concentrations of OCPs in surface sediments provide information on recent contamination, whereas levels in sediment cores may help trace the history of contamination.

Vietnam is a developing country in tropical region. In Vietnam, by virtue of their low cost and high insecticidal efficacy, OCPs such as DDTs have been used extensively in agriculture. Additionally, a considerable quantity of insecticides has been widely sprayed for malaria vector control. Ba Lat estuary is the main estuary of the Red River system in the North Vietnam. Therefore, persistent organochlorine pollutants tend to accumulate in sediments in Ba Lat estuary. However, contamination of OCPs, especially in sediment cores in the estuary is still limited. In this study, we collected sediment cores to investigate the distributions of OCPs in both spatial and vertical terms.

Materials and method

Study area and sampling

Ba Lat estuary (Red River mouth) is one of the biggest river estuaries in Vietnam. Samples were collected from Ba Lat estuary in October 2008. Surface sediment samples were collected from 4 stations. Sediment core samples were also collected from 4 stations. A gravity corer consisting of an acrylic pipe was used. The corer was pushed into sediment to obtain 20-35 cm cores. Sediment cores were sliced into 5 cm intervals. Samples were covered in aluminium foil and kept in clean polyethylene bags, then transported to the laboratory in boxes packed with dry ice. In the laboratory, sediment samples were freeze-dried then kept at -20^{0}C until chemical analysis.

Table 1. Geographic coordinates of sampling locations

Sampling location	Coordinate		Length of core
	Longitude (E)	Latitude (N)	
Point 18	106°39’16”	20°10’43”	25 cm
Point 19	106°35’28”	20°06’05”	20 cm

Point 25	106°27'10"	20°00'07"	30 cm
Point 26	106°33'15"	20°01' 26"	35 cm

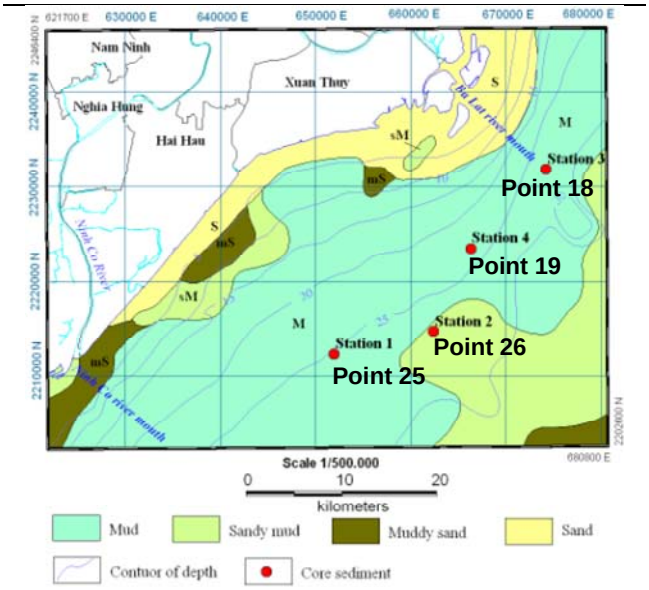

Fig 1. Sampling locations in Ba Lat estuary

Analytical procedure

Sediment samples were prepared for OCPs analysis. Briefly, freeze-dried sediment sample (10 g) after adding surrogates (1,3,5–tribromobenzene and endrineketone) was homogenized with anhydrous sodium sulfate, extracted by ultrasonic and shaked with 60 ml hexane/acetone (1:1, v/v) two times. Following extraction, extracts were mixed with activated copper granules to remove elemental sulfur. Extracts were then fractionated using an 8 g fully activated silica gel column. The first hexane fraction (65 ml) contained PCBs, HCB and DDE. HCH, chlordane related compounds, DDT, DDD and other moderately polar OCPs were eluted in the second fraction with 130 ml hexan/DCM (1:1, v/v). A procedure blank was run for every batch of five samples.

Quantification of OCPs were carried out using GCMS-QP2010 (Shimadzu). The column used for analysis OCPs was DB-5 (30 m x 0.32 mm i.d x 0.25 μm thickness).

OCPs were quantified using internal standard method. Chrysense – d12 and phenanthrene – d10 were used as the internal standards. The calibration standard consisted of DDT compounds, HCH compounds, aldrin, dieldrin, endrin, chlordane compounds, nonachlor compounds, endosulfane compounds, heptachlor, heptachlor epoxide, nonachlor, 3,4,5-trichloroveratrole, pentachloroanisole, endosulfane compounds (endosulfane I, II and endosulfane sulfate).

Method detection limit of OCPs is in range of 0.05-0.1 ng/g. Surrogate recoveries were in range of 60-150%. All concentration data were reported as dry weight basis. DDTs concentrations were calculated by summing o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT, and p,p'-DDT. HCHs concentrations were calculated by summing α-HCH, β-HCH and γ-HCH.

Results and discussion

Distributions of organochlorines in surface sediment samples

Mean concentration of OCPs in 4 surface sediment samples followed the order: DDTs > HCHs > HCB. Concentrations of DDTs and HCHs were 5 to 6 times higher than those of HCB. Concentrations of HCB from 4 surface sediment samples were in range of <0.05-0.49 ng/g. Aldrin, dieldrin, endrin, chlordane compounds, nonachlor compounds, and endosulfane compounds were not present in all surface samples and rarely detected in core samples. In contrast, DDT and metabolites were present in all surface and core samples. HCHs were determined in most of samples in Ba Lat estuary. Concentrations of OCPs surface sediments were summarized in Table 2.

Table 2. Concentrations of organochlorines (ng/g dry wt.) in surface sediments from Ba Lat estuary

Station	HCB	HCHs	DDD	DDE	DDTs*	DDTs
Point 18 M1	0.42	2.87	0.47	0.45	0.89	1.03
Point 18 M2	0.49	1.85	0.63	1.32	2.06	2.87
Point 19 M	0.42	0.47	0.59	1.01	1.63	2.17
Point 25 M	<0.05	1.09	0.58	0.53	0.65	1.26
Mean	0.33	1.57	0.57	0.83	1.31	1.83

DDTs*: sum of p,p'-DDE, p,p' –DDD and p,p'-DDT.

Table 3. Comparison of organochlorines in surface sediments from various countries (ng/g dry wt.)

Country	Year	HCB	HCHs	DDTs	Reference
A - Vietnam					
Hanoi, Canals	1995	-	0.28[a]	7.21	1
Thai Binh, Estuaries	1995	-	0.49	6.59	1
Ba Lat estuary	2008	0.33	1.57	1.31	This study
Coast of the North	1997	1.56	8.53	7.74	2
Can Tho, Canals, Mekong River – In Can Tho city	2003- 04	-	-	2.8 (1.8-4.3)[b]	3
Hau River, Mekong River delta	2003-04	0.016 (<0.006-0.08)	0.1 (<0.02-1.3)	6.5 (<0.01-110)	4
Hochiminh city, Canals, Saigon River – densly populated areas	2004	6.6 (<0.1-18)	<0.02-0.044	37 (12-72)	5
Saigon-Dongnai River	2004	0.24 (0.001-0.61)	0.011 (<0.01 – 0.03)	5.6 (0.21-23)	5
Saigon-Dongnai River estuary	2004	0.031 (<0.001-0.11)	0.012 (<0.005-0.022)	1.2 (0.15-5.4)	5
B - Other countries					
China, Pearl Estuary	1996-97	-	0.68	2.84	6
Hongkong, Victoria Habour	1992-94		nd-0.94	1.38-25.4	7
Hongkong, Xiamen Western Bay	1992-94		0.14-1.12	4.45-311	7
Korea, Masan Bay	1997	-	0.24	16	8
Korea, Korean coast	1997-2002	-	0.32 (nd-5.46)	0.68[d] (0.01-135)	9
Sweden, Baltic Sea - Coastal stations in basin	1991-92	0.79-0.94[c]	5.0-7.0	1.9-6.9[d]	10

HCHs: sum of α-HCH, β-HCH and γ-HCH.
DDTs: sum of p,p'-DDE, p,p'-DDD and p,p'-DDT
[a]: Mean; [b]: Mean (range); [c]: Range.
[d]: sum of o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p' -DDD, p,p'-DDT and p,p'-DDT

Compared with DDTs levels in sediment from various locations in Vietnam, DDTs levels in Ba Lat estuary were similar to the level in Saigon-Dongnai estuary in the South Vietnam (Table 3, Fig. 2). DDTs accumulate more in

sediment of rivers and canals than in estuaries because rivers and canals are near the populated and agricultural areas. Fig 2. showed DDTs levels in canals and rivers were about 2 to 30 times higher than in estuary.

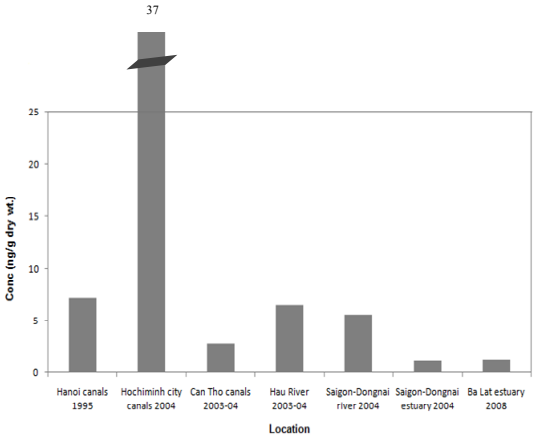

Fig 2. Comparision of DDTs (ng/g dry wt.) in surface sediments from various locations in Vietnam [1,3,4,5,this study]

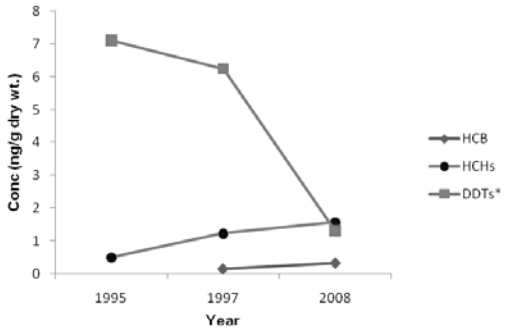

Fig 3. Temporal trend of DDTs, HCHs and HCB in surface sediments from Ba Lat estuary [1,2,this study]

In previous studies carried out by Dang Duc Nhan, HCB, HCHs and DDTs were determined in Ba Lat estuary in dry season of 1995 and 1997[1,2]. In comparison to previous studies, concentrations of HCB and HCHs in the sediment were slightly higher whilst DDTs levels in this study were about 3 to 4 to 6 times lower (Fig. 3). In fact, the prohibition of DDTs has been implemented in Vietnam since 1995. Our result suggest relatively rapid decline of DDTs in estuary of Red River delta over the last decade.

The data of this study was compared with those reported from other countries in East and South Asia. In general, the DDTs levels were lower than those in Pearl River estuary-China, Victoria Habour and Xiamen Western Bay-Hongkong and Masan Bay, Korea[6,7,8]. However, these levels were higher than those in Korean coasts[9].

In Vietnam, total quantity of DDT imported into Vietnam for malaria control from 1957 to 1990 was 24,042 tons Besides, a huge quantity of DDT was used in agriculture. Technical DDT contains 75% p,p'-DDT, 15% o,p'-DDT, 5% p,p'-DDE, and less than 5% other compounds In the environment, DDT is degraded to DDE and DDD. Relatively high proportions of p,p'-DDT in surface sediment samples from station P-18 and P19 indicate recent usage of DDT in the Red River delta. The order of p,p'-DDT in this study follows: Point 18 M2, Point 19 M, Point 25 M. This order agrees well with distance from station to the mouth of Red River.

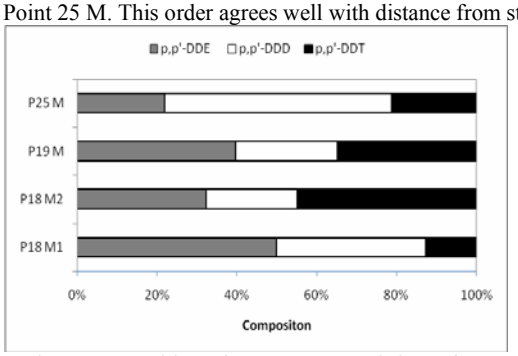

Fig 4. Composition of DDT compounds in surface sediments from Ba Lat estuary

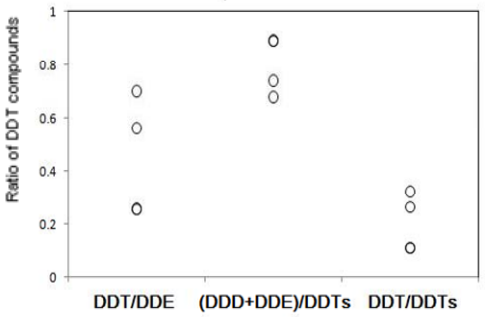

Fig 5. Ratios of DDT compounds in surface sediments from Ba Lat estuary

Ratios of DDT and metabolites, DDD and DDE, can be assessed in order to understand of usage DDT. Bo Strandberg suggested that ratios of DDT/DDE in sediments higher than 0.5 may indicate recent input of DDT and the ratios lower than 0.3 may indicate past input of DDT[10]. Huasheng Hong suggested that ratios of (DDD+DDE)/DDTs higher than 0.5 may indicate old DDTs residue while those less than 0.5 imply recent input[6]. In this study, DDT/DDE ratios were in range 0.25 - 0.7, which may indicate recent usage. The ratio (DDD+DDE)/DDTs in Ba Lat estuary sediment show no clear trend of DDT usage. Although DDTs concentrations in surface sediments of Ba Lat estuary in this study were lower than those previous reported, our result may suggest a sign of recent input of DDT. In this regard, the possibility of illegal use of DDT after official ban in 1995 can not be ruled out. This may be consistent with monitoring result by using plastic resin pellets (International Pellet Watch) where higher concentrations of DDTs with predominance of DDT over the metabolites were observed in northern Vietnam[11] (Ogata et al., in press).

Vertical distributions of organochlorines in sediment cores

In each station, HCB, HCHs and DDTs levels in surface samples were higher than those in core samples. Concentrations of OCPs at station Point 18 were slightly higher than those in other stations. This station is close to the mouth of Red River than others. Previous studies in Sai gon – Dong Nai River, southern Vietnam also demonstrated an decreasing trends of DDTs and PCBs from estuary towards the coast[5]. Concentration of DDTs in sediment cores were in range of 0.68-3.46 ng/g. Sediment accumulation rates at sampling stations were cited from Van der Bregh[12]. On this basis, age of sediment core samples in Ba Lat estuary was estimated. In cores from station Point 18 and 25, the DDTs levels peak in sediment deposited from 1992 – 1995 (Fig. 6). In sediment deposited before 1990 and after 2000, DDTs residues were lower. However, vertical profile of sediment from station Point 19 suggests a sign of increase in DDT concentrations after 1995. This depth profile reasonably reflects the history of DDT usage in Vietnam. DDT usage was officially banned in 1995. DDT had been replaced by other chemicals in agriculture and public health control since 1995. Results in sediment core from station Point 19 also agree with those observed in surface sediment samples, which may suggest recent usage of DDT in the estuary.

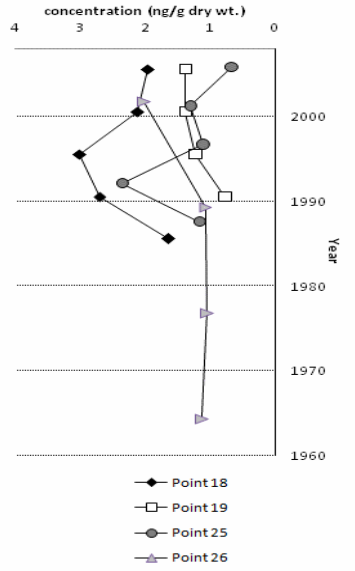

Fig 6. Concentrations of DDT and metabolites (ng/g dry wt.) in sediment cores from Ba Lat estuary

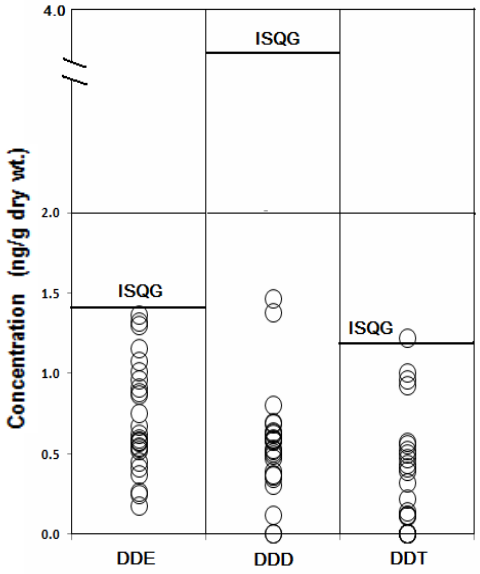

Fig 7. Comparison of DDTs with the Canadian Environment Quality Guideline for sediment (ISQG)

Comparison to the Canadian Environment Quality Guideline for sediment

In order to provide an overall view about the DDTs levels in Ba Lat estuary, these were compared with guidelines issued by The Candian Council of Ministers of Environment (CCME 2003) and the Florida Department of Environmental Protection (FDEP 1994), (Fig. 7)[13].

According to CCME, the Interim Fresh Water Sediment Quality Guidelines (ISQGs) for DDE, DDD and DDT in sediment are 1.42, 3.54 and 1.19 ng/g dry wt. According to FDEP, the Probable Effect Levels (PELs) for DDE, DDD and DDT in sediment are 6.75, 8.51 and 4.77 ng/g dry wt., respectively. The maximums of p,p'-DDE, p,p'-DDD and p,p'-DDT of all samples in Ba Lat estuary were 1.37, 1.47 and 1.22 ng/g, respectively. Only one sample showed value > ISQGs and few samples contained p,p'-DDE and p,p'-DDT concentrations approaching the ISQG values. Moreover, residue levels of DDT compounds were lower than the PELs values in all sediment samples. Overall, possible risk posed by present DDTs residues in sediments seems less pronounced.

Conclusions

This study was the initial result about the organochlorine pollutants in sediments in Ba Lat estuary. The horizontal and vertical distribution, temporal trend of organochlorines in Ba Lat estuary were investigated. Despite DDTs levels have declined during the last decade, our results suggest an evidence of recent DDT input to the Red River estuary watershed. Control measures towards management of usage and handling of DDT and other insecticides are needed to mitigate their release into the environment.

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