Contamination of persistent organochlorines in sediments from Mekong River Delta, South Vietnam

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Introduction

Mekong River is the longest river in southeastern Asia, which flows a distance of almost 4800 km from China through Myanmar, Thailand, Laos, Cambodia and Vietnam. The Mekong River basin with an area of nearly 800 thousand square kilometers is an important habitat for approximately 60 million people. Mekong River delta in South Vietnam, which is inhabited by about 20 million people, is one of the most highly productive agriculture lands in the world. Rice production is major economical sector in Mekong delta contributing half of the rice production in Vietnam - approximately 35 million tons annually. On the other hand, development of agriculture in Mekong delta raised some concern on environmental quality and disturbance on ecosystem. For example, intensive use of organochlorine (OC) insecticides such as DDTs, chlordanes, HCHs may lead to considerable residues in the agriculture land. Moreover, relative persistence of such chemicals together with natural processes like evaporation and run-off, might enhance their ubiquitous distribution in environment, food chains and eventually bio-accumulate in humans.

In Vietnam, despite official ban on the usage of OCs on 1995, there have been evidences of recent uses of such chemicals, particularly DDT, throughout the country[1,2,3]. It can be anticipated that similar situation may occur in Mekong River delta due to high population density and intensive agriculture activities in this region. Despite this fact, no comprehensive study, to evaluate the status of contamination by persistent OCs in this region, has been made in recent years. In this study, we collected sediments from different locations along Mekong River and determined the concentrations of persistent OCs such as DDTs, HCHs, CHLs, HCB and PCBs in order to elucidate the recent contamination status, their usage pattern as well as to evaluate potential pollution sources of these chemicals to the river.

Materials and Methods

Sample collection: Sediment samples were collected in Hau River – one of two biggest branches of Mekong River, which crosses South Vietnam and empty into the East Sea. Sampling points were located along a part of Hau River flowing through Can Tho province. As being shown in Fig. 1, sediments named as *CC* and *NKSE* were collected from canals in Can Tho city and those named as *Hau* were collected along the Hau River. Surface sediments were collected using stainless-steel grab, stored in clean polyethylene bags and transported to our laboratory in boxes with dry-ice. In laboratory, sediments were dried in room temperature, ground and sieved. Fraction of particles less than 2 mm size was used for chemical analysis and those less than 0.05 mm for total organic carbon determination.

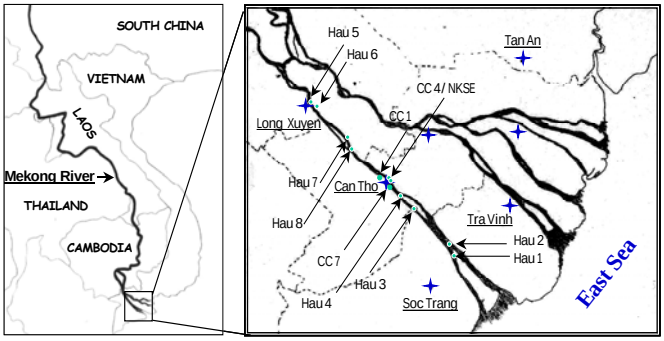

Figure 1: Sampling locations in Mekong River, South Vietnam

Analytical method: Approximately 15g of air-dried sediment samples were placed in a conical flask and 15 ml water was added. The flask was then kept for 30 minutes before adding 100 ml acetone and shaking vigorously for 60 minutes by electric shaker (SR-2W model, Taitec Co. Ltd.) Soil solution was filtered into a separating funnel already containing 600 ml hexane-washed water and 100 ml hexane. The funnel was shaken vigorously for 15 minutes and then kept for at least 8 hours to entirely separate the aqueous and the hexane layers. The aqueous layer was discharged and the hexane layer was washed further three times by 100 ml water. Volume of hexane in the final solution was measured for calculating volume recovery from initial 100 ml. This solution was concentrated to about 10 ml by KD apparatus and further to 5 ml by stream of nitrogen. An equal volume of concentrated H_2SO_4 was added to this solution to remove pigment, humic acids and other organic interferences. This step was repeated several times until the hexane layer became transparent. The solution was further washed by hexane-washed water three times. 4 ml of the remaining solution pipetted and cleaned up by GPC and separated by Florisil chromatography column as described previously[1]. Solution after the separation (5 ml) was treated with activated copper to remove sulfur-containing, interfering substances. For this, several strings of copper wires were activated by HCl and dipped into the solution and kept for an hour until no black sulfur soot appeared on the copper strings. Final solution was further concentrated up to 20 times if necessary prior to analysis by GC/ECD. Good recovery rates (85%-110%) were obtained for all compounds.

Results and Discussion

Residue levels and contamination pattern: Concentrations (ng/g dry wt) of persistent OCs analyzed in this study are given in Table 1. In general, the residue pattern of OCs in the sediment from Hau River followed the order: DDTs > PCBs > CHLs ≥ HCHs ≥ HCB. Concentrations of OCs, however, varied between sampling sites and higher concentrations were mostly observed towards upstream of Mekong River.

Table 1: OCs concentrations (ng/g dry wt.) in sediments from Mekong River, South Vietnam

	CC-1	CC-4	CC-7	NK-SE	HAU-1	HAU-2	HAU-3	HAU-4	HAU-5	HAU-6	HAU-7	HAU-8
PCBs	4.10	2.7	0.26	0.85	0.13	0.19	0.55	0.6	0.18	0.14	0.24	0.45
HCB	0.08	0.02	0.01	0.06	< 0.006	< 0.006	0.01	0.01	0.02	0.02	< 0.006	< 0.006
HCHs	< 0.02	< 0.02	0.11	< 0.02	0.10	0.06	0.05	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
t-nona	0.02	0.04	0.07	0.34	0.01	0.02	0.03	0.03	0.02	0.03	0.02	0.02
t-chlor	0.05	0.06	0.14	0.1	< 0.02	< 0.02	0.06	0.04	< 0.02	< 0.02	< 0.02	< 0.02
c-chlor	0.04	0.06	0.11	0.04	0.02	0.03	0.05	0.04	0.02	0.03	0.02	0.03
CHLs	0.12	0.19	0.36	0.19	0.03	0.05	0.15	0.12	0.04	0.08	0.04	0.05
pp'-DDE	1.9	2.1	0.71	0.81	0.02	0.09	0.52	1.04	0.46	0.90	0.54	0.73
pp'-DDD	0.81	1.2	0.77	0.51	0.01	0.09	0.37	0.26	0.20	0.43	0.33	0.24
pp'-DDT	0.56	1.0	0.44	0.58	0.01	0.02	0.3	0.15	0.52	0.57	0.15	0.03
DDTs	3.3	4.4	1.9	1.9	0.05	0.2	1.2	1.5	1.2	1.9	1.1	1.0
TOC (%)	1.76	1.32	0.55	1.43	0.97	1.35	1.43	1.28	0.82	1.6	0.86	1.54

t-nona: *trans*-nonachlor, *t*-chlor: *trans*-chlordane, *c*-chlor: *cis*-chlordane
DDTs = *p,p'*-DDE + *p,p'*-DDD + *p,p'*-DDT, CHLs = *t*-nona + *t*-chlor + *c*-chlor

The pattern of OCs found in this study was almost similar with those recently observed in human breast milk samples from Hochiminh city[1], suggesting widespread and dominant contamination of DDTs and PCBs in the environment as well as throughout the food chain. Abundance of DDTs and PCBs in Vietnam may be due to their large use, persistency and highly bioaccumulative characteristics over other OC compounds. Interestingly, PCBs concentrations in sediments found in urban areas such as Can Tho city were higher than those in sediments collected from other downstream sites, suggesting urban areas as a pollution source of PCBs to the river. In addition, it is also apparent that PCB levels in the present study were approximately 3 times lower than those in sediments (e.g. from mangroves or paddy fields) collected in the early 1990s from South Vietnam[4] (Table 2). Recent investigation in sediments collected from Hanoi urban areas showed higher PCB residues as compared to those in sediments from rural sites[5]. This observation may again consolidate our assumption that urban areas in Vietnam perhaps still remain as a major pollution source of PCBs to the local environment. Official statistical data showed that approximately 30,000 tons of PCB-contaminated industrial oils were imported to Vietnam during the past years[6]. In addition, electrical equipments like transformer containing PCB were also imported until the mid 1980s[7]. Those materials could be primary sources of PCBs to the environment, besides somewhat release from weapons heavily used during the Indochina War as previously suggested[8].

In global comparison (Table 2), levels of PCBs in Hau River sediment are comparable with those in coastal area of Ukraine or Pearl River in China, etc., and lower than those in the other locations of prominent industrial activities like lake sediments in Canada, harbor sediments in China and Egypt.

Table 2: Comparison of OCs in surface sediments from various locations in the world[a]

Country	Sampling Time	*n*	PCBs	DDTs	HCHs	Reference
A - Vietnam						
Duyen Hai (mangroves)	1990	9	5.2	8.5	0.97	Iwata et al.[4]
Can Tho	2003	10	0.9	1.9	0.08	Present study
Hanoi (Urban)	1997	12	11	30	0.8	Nhan et al.[5]
Hanoi (Outskirt)	1995-1996	2	5.5[b]	10	-	Nhan et al.[2]
North coast	1995-1996	4	1.7[b]	5.5	-	Nhan et al.[2]
B - World						
Brazil (Amazon region)	1997	7	-	24	-	Torres et al.[16]
Canada (6 lakes)	1992-1995	7	15	1.3	0.5	Rawn et al.[17]
China (Pearl River)	1996-1997	20	0.7	2.8	0.7	Hong et al.[11]
China (Minjiang River)	1999	9	35	6.7	8.6	Zhang et al.[13]
China (Daya Bay)	1999	14	8.8	2.7	1.4	Zhou et al.[18]
Egypt (Alexandria harbor)	1998	23	260[c]	87[c]	0.8[c]	Barakat et al.[19]
Korea (Ulsan Bay)	2001	32	-	3.3	0.6	Kim et al.[20]
Korea (Masan Bay)	1997	20	15	13.6	0.3	Hong et al.[12]
Lake Baikal	1992	6	6.1	2.7	0.16	Iwata et al.[15]
Taiwan (Wu-Shi River)	1997-1998	19	-	2.5	3.8	Doong et al.[14]
Taiwan (Da-han River)	1997-1998	20	-	0.9	0.39	Doong et al.[14]
Taiwan (Erh-Jen River)	1997-1999	20	-	0.7	1.03	Doong et al.[21]
Ukraine (Black Sea)	1995	2	5.7-6.8[d]	35-65	1.3-2.3	Fillmann et al.[22]
Ukraine (Coastline)	1995	2	nd-0.4	0.06-0.6	0.02-0.2	Fillmann et al.[22]
Ukraine (Danube River)	1995	2	1.4-2.7	9.2-43	1.3-2	Fillmann et al.[22]

[a]: mean concentration in ng/g dry wt

[b]: as 1254 mixture

[c]: as median value

[d]: range is given when mean value is not available

"-": data is not available

Concentration of DDTs varied several folds among the sampling sites, ranging from 0.05 to 4.4 ng/g dry wt. Similar to the distribution of PCBs, the concentrations of DDTs were higher at sampling sites closer to urban areas and decreased towards the downstream of the river. DDT residue levels from the sites nearby Long Xuyen town and Can Tho city were 10 to 20 folds higher than those in their respective downstream sites. This result indicates that urban areas are major pollution sources for not only PCBs but also DDT. Inputs of DDT residues, therefore, are likely derived from its application for hygienic purposes and malaria vector control in urban areas rather than those used for agricultural purposes.

When compared with previous studies in Vietnam, DDT levels in Hau River's sediment are about 3 to 4 folds lower than those from coastal areas of the North in the mid 1990s or from mangroves of the South in the early 1990s (Table 2), suggesting lesser inputs of DDTs in recent years. In global comparison, DDT residues in sediment from Hau River are comparable to those in several locations of China (e.g. Pearl River, Daya bay, etc.), and higher than those found in some rivers in Taiwan or in lakes of Canada (Table 2). On the other hand, sediments from places like Alexandria harbor, Egypt; Black Sea, Ukraine; etc. contain higher levels of DDTs compared to the present study.

Mean concentrations of HCHs, CHLs and HCB in Hau River sediments were 10 to 20 times lower than those of PCBs and DDTs. Among those contaminants, CHLs were more predominant than HCHs and HCB, even though, their concentration ranged only from 0.05 to 0.35 ng/g dry wt. The present range of CHLs was slightly lower than those found in sediments collected in 1990[6] (0.15 – 0.8 ng/g dry wt.) and comparable with those in sediments recently collected in

Hanoi[7]. However, all studies revealed no clear difference between rural and urban areas. Our results indicate inappreciable contamination of CHLs close to the background levels. Nevertheless, the purpose of CHLs usage in Vietnam as well as other tropical countries remained unclear[6]. Although some samples contained HCHs levels below the limit of quantification (approximately 0.01 ng/g dry wt), it could be recognized that the present HCH levels in Mekong River, South Vietnam were lower compared to those recently found in sediments of Red River, North Vietnam[2] (range: 0.07 – 0.6 ng/g dry wt.). This spatial distribution was also previously observed in human breast milk collected throughout the country[1]. HCB concentrations were generally low (less than 0.1 ng/g dry wt). Similar to CHLs, there was no research documenting usage of HCB as an insecticide in Vietnam and thus the trivial contamination of this chemical might be due to its existence as byproduct in chlorinated solvents and pesticide mixtures[9].

Composition of DDTs: As being shown in Fig. 2, portion of *pp'*-DDT was higher in sediments collected within and nearby urban areas than those in further downstream sediments. This result perhaps indicates more recent DDT input in urban sediments, further strengthening our hypothesis that urban areas are pollution sources of DDT compounds to Mekong River.

Strandberg et al.[10] suggested that DDT/ DDE ratios lower than 0.33 could be the result of the aged mixtures in environment, while those > 0.5 might indicate recent use of DDT. Some sediment samples in the present study such as in Can Tho city (CC-1, CC-4, CC-7, NK-SE) or close to Long Xuyen town (Hau-5, Hau-6) had the ratio higher than 0.5 and thus indicating possible recent input of DDT to the river. However, the question regarding degree of recent use of DDTs compared to other sources such as soil run-off is still not clear because the magnitude of contamination has actually decreased over the last decade and became relatively low at the present.

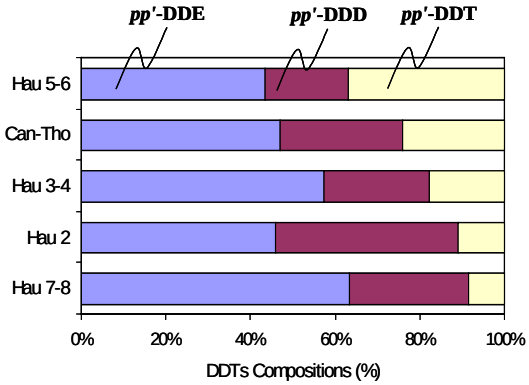

Figure 2: DDTs composition in sediment in Mekong River Delta, South Vietnam

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