



Recent levels of organochlorine pesticides and polychlorinated biphenyls in sediments of the sewer system in Hanoi, Vietnam

Pham Manh Hoai^a, Nguyen Thuy Ngoc^a, Nguyen Hung Minh^b, Pham Hung Viet^a, Michael Berg^c, Alfredo C. Alder^c, Walter Giger^{c,*}

^aCETASD, Research Center for Environmental Technology and Sustainable Development, Hanoi University of Science, 334 Nguyen Trai Street, Hanoi, Vietnam

^bCenter for Environmental Monitoring, Vietnam Environmental Administration, 67 Nguyen Du Street, Hanoi, Vietnam

^cEawag, Swiss Federal Institute of Aquatic Science and Technology, 8600 Dübendorf, Switzerland

Organochlorine pesticides and PCBs were studied in sediments of the sewer system in Hanoi.

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ABSTRACT

The occurrence, temporal trend, sources and toxicity of PCBs and organochlorine pesticides were investigated in sediment samples from the sewer system of Hanoi City, including the rivers Nhue, To Lich, Lu, Set, Kim Nguu and the Yen So Lake. In general, the concentrations of the pollutants followed the order DDTs > PCBs > HCHs (β -HCH) > HCB. However, the pollution pattern was different for the DDTs and PCBs when the sampling locations were individually evaluated. The concentrations of the DDTs, PCBs, HCHs, and HCB ranged from 4.4 to 1100, 1.3 to 384, <0.2 to 36 and <0.2 to 22 ng/g d.w., respectively. These levels are higher than at any other location in Vietnam. Compared to measurements from 1997, the DDTs, PCBs, β -HCH and HCB levels show an increasing trend with DDT/DDE ratios, indicating very recent inputs into the environment although these persistent compounds are banned in Vietnam since 1995.

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1. Introduction

Covering an area of some 1000 km² and having a population of 3.5 million people, Hanoi (the capital and second largest city of Vietnam) and its vicinity is the major industrial and economic region in North Vietnam. During the recent decades, the fast development of industry in conjunction with high population growth have lead to toxic chemicals to enter the rivers of the city as the industrial, medical and domestic wastes are released untreated (Duong et al., 2008; Hoai et al., in preparation). In addition, the deterioration of the rivers and the reduction of streambed have turned these rivers to be open sewers and the principal pollution sources in the city (Hanoi DOSTE, 2003; GHK, 2005; Hanoi Water Discharge Company, 2006), thereby posing a long-term threat to groundwater that is used for drinking water production (Giger et al., 2003; Duong et al., 2003; Berg et al., 2007, 2008; Norrman et al., 2008).

Flowing inside the Hanoi City, mainly to the south and southeast, with a total length of about 70 km, the rivers To Lich, Lu, Set, Kim Nguu, and a part of the Nhue River, serve as important open sewer system for the drainage of rainwater and municipal wastewater, but

are also used for agricultural irrigation in urban and suburban areas. It was reported that 95% of the capital's wastewater effluents are discharged without treatment and an estimated 450 000 m³/day are discharged untreated into the rivers Lu, Set, To Lich and Kim Nguu in Hanoi City (Hanoi Water Discharge Company, 2006).

Persistent organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) were widely used in Vietnam since the 1960s for different purposes in agriculture, industry and public health (Sinh et al., 1999; MONRE, 2006). Since 1995, the use of PCBs and some OCPs such as dichlorodiphenyltrichloroethane (DDTs), hexachlorobenzene (HCB) and hexachlorocyclohexanes (HCHs) are officially banned in Vietnam (Sinh et al., 1999). However, these toxic chemicals are still observed in Vietnam at higher concentrations than in other southeast Asian countries (Minh et al., 2006; Monirith et al., 2003; Müller et al., 2008) and are currently detected at elevated concentrations in various environmental compartments in Hanoi City (Kishida et al., 2007; Toan et al., 2007a,b) and also in human breast milk (Minh et al., 2004) of in Hanoi citizens. Concentrations of PCBs and OCPs in different environmental compartments in Vietnam in general and in Hanoi City in particular were reviewed by Minh et al. (2008). However, knowledge on the contamination levels in sewer systems of medium to large Asian cities like the Hanoi City are still limited.

* Corresponding author.

E-mail address: giger@eawag.ch (W. Giger).

Understanding the contamination status of OCPs and PCBs as well as their potential toxic effects in Hanoi City is very significant in order to provide information for the public and environmental authorities to protect the environment and the ecological systems of the city. Concentrations of these pollutants in sediment may give considerable information on their occurrence, long-term temporal trend, sources, and toxic assessment. Therefore, this study was conducted to investigate the concentrations of a wide spectrum of persistent organic pollutants, including PCBs and 17 OCPs in sediments of the sewer system of Hanoi City. In addition, the temporal trend of the pollution, by comparing with previous measurements, the possible sources, and the potential toxicity to the aquatic environments are discussed in this study.

2. Material and methods

2.1. Sample collection

Twenty-two sediment samples were collected on 18 May 2006 from the sewer system in Hanoi City, including the five rivers Nhue, To Lich, Lu, Set, Kim Nguu and the Yen So Lake (Fig. 1). A fraction of the Set River and the Kim Nguu River is discharged into the Yen So Lake. The samples were collected in urban (TL1, TL2, TL3, TL4, L1, L2, L3, S1, S2, KN1, KN2) and suburban districts (TL5, TL6, TL7, N1, N2, YS1–6). After collection with a stainless steel grab sampler (Van Veen Grab), river and lake sediments were wrapped in aluminum foil and shipped within 1 h to the laboratory (CETASD). Upon arrival at the laboratory, the samples were air-dried, ground, sieved to 1 mm, and stored at -20°C until analysis.

2.2. Chemical analysis

Seven PCB congeners (IUPAC numbers: PCB 28, 52, 101, 118, 138, 153 and 180) and a set of 17 organochlorine pesticides were analyzed. Those 17 pesticides are dichlorodiphenyltrichloroethane compounds (DDTs: *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT, *p,p'*-DDT); hexachlorocyclohexanes (HCHs: α -HCH; β -HCH; γ -HCH); chlordane compounds (CHLs: *trans*-chlordane, *cis*-chlordane, oxychlordane); aldrin; hexachlorobenzene (HCB); heptachlor; *cis*-heptachloroepoxide and mirex. The total

concentration of PCB (PCBs) was calculated based on the sum of seven PCB congeners by multiplication with the value of four, which corresponds to the theoretical contribution of those congeners to Aroclor 1254 (Sauvain et al., 1994; Froeschis et al., 2000).

Sediment samples were analyzed for PCBs and OCPs at CETASD applying the EPA 3620B, EPA 8082, and EPA 8081A methods (EPA, 1996a,b,c) with slight modifications for sample extraction and extract cleanup. Briefly, 20 g of dry sediment was spiked with 10 ng/g surrogate standards (PCB congener 209 and *p,p'*-DDT- ^{13}C), ultrasonically extracted for 5 min, and then shaken for 2 h with 60 ml of acetone/*n*-hexane (1:1, v/v). After completely evaporating the solvents by vacuum and taken up in 2 ml *n*-hexane, the extract was divided into two 1-ml fractions, which were used to determine PCBs and OCPs, respectively. The cleanup step was conducted in the same manner for both fractions. Pigments, humic acids, etc. were removed from the extracts by concentrated H_2SO_4 (98%). This step was repeated several times until the *n*-hexane layer became colorless. The extracts then were concentrated under a gentle N_2 stream to 1 ml and were further purified on a florisil cartridge (1 g, 6 ml). Non-polar compounds such as PCB congeners, HCB, and *p,p'*-DDE were isolated from the first fraction after elution with 4 ml of *n*-hexane. Separately, PCBs and OCPs were isolated from the second fraction after elution with 7 ml of acetone/*n*-hexane (1:9, v/v). The sulfur-containing substances were removed by subsequently adding several activated copper slices to the obtained solutions and were kept 1 h until the black sulfur soot no longer appeared on the copper slices. The purified fractions were then spiked with internal standard (1,1-dibromundecane for PCBs calculation, and phenanthrene- d_{10} and chrysene- d_{12} for OCPs calculation), concentrated under gentle N_2 stream to 0.5 ml, and submitted to GC analysis. A 2- μl volume of the first purified fraction, which mainly contains PCBs, was injected on the GC/ECD system (Shimadzu GC 17A, ECD Ni^{63}) for quantification of PCBs. A 2- μl volume of the second fraction was injected on the GC-EL-MS system (Shimadzu GC/MS QP2010) for quantification of OCPs. A DB-5 capillary column (30 m \times 0.25 mm \times 0.25 μm) with helium as a carrier gas at a flow rate of 1.8 ml/min was applied for the separation of OCPs and PCBs on the GC system. The determination was carried out at injector and detector temperatures of 270 and 300 $^{\circ}\text{C}$, respectively. The GC temperature program for PCBs separation was set to 120 $^{\circ}\text{C}$ before increasing to 200 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$, then to 230 $^{\circ}\text{C}$ at 2 $^{\circ}\text{C}/\text{min}$, and finally to 300 $^{\circ}\text{C}$ at 7 $^{\circ}\text{C}/\text{min}$ where temperature was maintained for 10 min. The oven temperature program for OCPs analysis was 70 $^{\circ}\text{C}$ (1 min); 20 $^{\circ}\text{C}/\text{min}$, 160 $^{\circ}\text{C}$; 2 $^{\circ}\text{C}/\text{min}$, 250 $^{\circ}\text{C}$; 5 $^{\circ}\text{C}/\text{min}$, 300 $^{\circ}\text{C}$ (5 min).

Relative sediment concentrations of PCBs and OCPs in this study are expressed on a dry weight (d.w.) basis (not adjusted to recovery rates). Cluster ions were monitored in the mass spectrometer at m/z 246, 219, 235, 235, 373, 373, 387, 263,

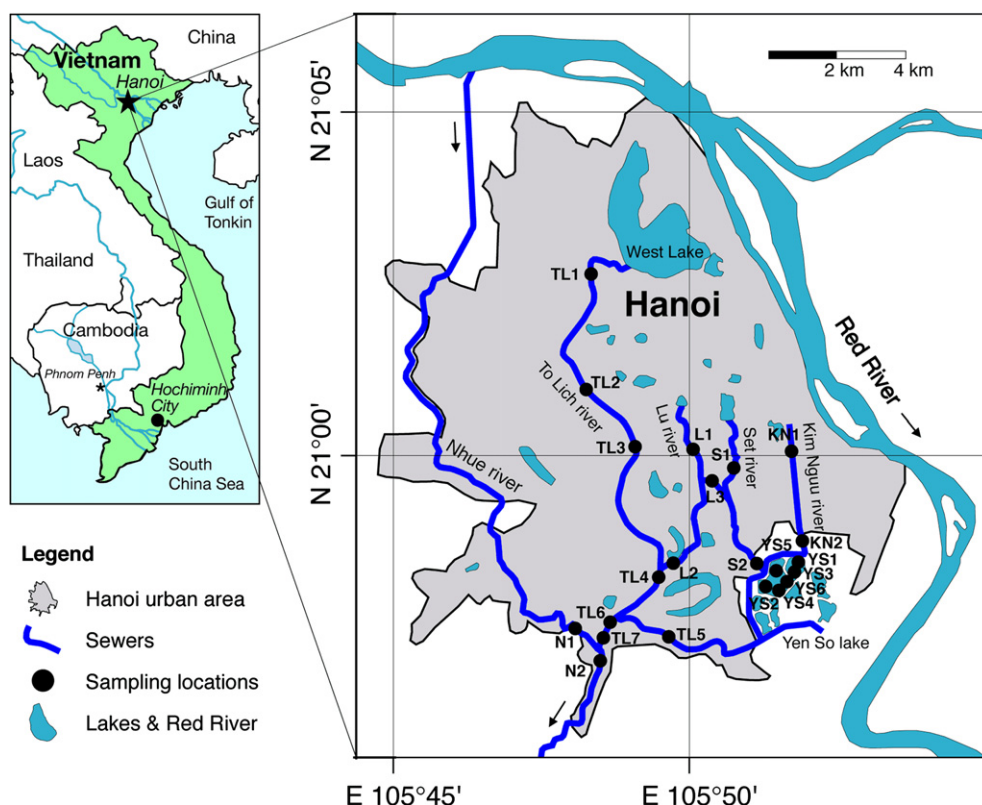


Fig. 1. Map of Hanoi City indicating the sewer system and the locations where sediment samples were collected (N: Nhue River, TL: To Lich River, L: Lu River, S: Set River, KN: Kim Nguu River, and YS: Yen So Lake).

284, 272, 353 and 272 for OCPs: DDE, DDD, DDT, HCH, trans-chlordane, *cis*-chlordane, oxychlordane, aldrin, HCB, heptachlor, *cis*-heptachloroepoxide and mirex, respectively. In addition, mass traces m/z of 247, 188 and 240 were monitored for p,p' -DDT- ^{13}C , phenanthrene- d_{10} and chrysene- d_{12} , respectively. The limits of quantification (LOQs) were 0.6 ng/g for PCBs and 0.1–0.2 ng/g for OCPs. Half of the quantitative limit levels were used to calculate the means, when the measured values were below the limit values.

2.3. Quality assurance

The quality assurance consisted of the analysis of method blanks, reproducibility and repeatability tests, as well as the analysis of certified reference materials. Recovery rates (72–121%) were obtained for all compounds for the spiked samples. The certified reference materials (CRM No. 846-050 for OCPs and CRM-No. 911-050 for PCBs, Resource Technology Corp.-RTC, USA) were used to validate the analytical method. The results of total PCBs from the five tests (1.18 ± 0.06 mg/kg) were in good agreement with the certified value (1.28 mg/kg). Similarly, the results of OCPs from the six tests were in good agreement with the certified values with average relative deviations ranging between 0.6 and 19%.

2.4. Total organic carbon

Total organic carbon (TOC) was measured at CETASD using a Total Organic Carbon Analyzer (Shimadzu TOC-V_{CSH}), which was equipped with a Solid Sample Module (Shimadzu SSM-5000A) following the manufacturer's method (Shimadzu, 2001). The TOC value was calculated by the difference of the results of the combustion–oxidation reaction (total carbon analysis) and carbonate acidification reaction (inorganic carbon analysis).

3. Results and discussion

3.1. Pollution status and pattern

The concentrations of PCBs and OCPs in sediments of the Hanoi sewer system are listed in Table 1. Eight of the 17 OCPs (β -HCH; HCB; o,p' -DDE; p,p' -DDE; o,p' -DDD; p,p' -DDD; o,p' -DDT; p,p' -DDT) were detected. Although other pesticides such as aldrin, heptachlor, oxychlordane, *trans*-chlordane, *cis*-chlordane were previously detected in different environmental samples in Hanoi City (Kishida et al., 2007; Minh et al., 2004; Nhan et al., 2001) and in Ha Long Bay,

Hai Phong Harbor and Ba Lat Estuary (Hong et al., 2008), the somewhat higher limits of quantification might have limited their detection in this study. Because α - and γ -HCH isomers were all below the limit of quantification (0.2 ng/g), the HCHs represent the concentrations of β -HCH in this report. Finally, the PCB congener 28 was not detectable in any of the sediment samples.

In general, the concentrations followed the order DDTs (mean 135 ng/g) > PCBs (mean 104 ng/g) > HCHs (mean 3.8 ng/g) > HCB (mean 3.5 ng/g). This pollution pattern agrees well with observations in sediments of the Hanoi rivers in 1997 (Nhan et al., 2001). Besides, Minh et al. (2004) revealed a similar pollution pattern (DDTs > PCBs >> HCHs, HCB) in human breast milk of Hanoi citizens in 2000. These facts demonstrate that DDTs and PCBs are the two dominant pollutants in the environment of Vietnam. The pollution pattern of DDTs and PCBs in this study varied depending on the sampling locations (comprising the rivers Nhue, To Lich, Lu, Set, Kim Nguu and the lake Yen So). The mean concentration of PCBs was higher than DDTs in sediments of the Nhue River, the Lu River, and the Yen So Lake (PCBs level was around 1.5 time to one order of magnitude higher than DDTs). In contrast, the mean concentrations of DDTs were higher than PCBs at the rivers To Lich, Set, and Kim Nguu (Fig. 2). The possible sources for such a pollution pattern are difficult to evaluate since the environment of Hanoi City is impacted by a variety of local activities such as suburban agriculture and industry services in the urban districts.

The spatial distribution shows significantly higher concentrations of DDTs, PCBs, and HCB in the rivers Kim Nguu and Set (Fig. 2). As a result, the Yen So Lake, a reservoir receiving water from these two rivers, is polluted with relatively high levels of PCBs (20–384 ng/g) and OCPs (17–109 ng/g DDTs, up to 12 ng/g HCB). The sediment concentrations of OCPs in the Yen So Lake were even higher than in the rivers Nhue, To Lich, and Lu. In conjunction with the rivers Lu and Set, the higher levels of PCBs and OCPs at the upper streams (sites TL1, TL2, TL3, and KN1) compared to those at the lower streams (TL4, TL5, TL6, TL7, and KN2) of the rivers To Lich

Table 1
Concentrations of detectable OCPs and PCBs in sediment.

Sample	Location		TOC (%)	PCBs ^a	DDTs ^b	β -HCH	HCB	
	Latitude	Longitude						
Nhue River	N1	N 20° 57' 263"	E 105° 48' 444"	3.1	153	12	<0.2	1.1
	N2	N 20° 57' 144"	E 105° 48' 472"	2.3	22	14	<0.2	1.3
To Lich River	TL1	N 21° 02' 403"	E 105° 48' 364"	7.5	50	50	12	<0.2
	TL2	N 21° 00' 923"	E 105° 48' 270"	2.7	44	47	<0.2	<0.2
	TL3	N 21° 00' 106"	E 105° 49' 083"	6.0	26	26	<0.2	0.87
	TL4	N 20° 58' 237"	E 105° 49' 501"	2.0	9.2	61	0.8	3.3
	TL5	N 20° 57' 577"	E 105° 48' 795"	5.5	70	24	<0.2	2.4
	TL6	N 20° 57' 615"	E 105° 48' 752"	4.7	14	6.4	<0.2	<0.2
	TL7	N 20° 57' 166"	E 105° 48' 466"	1.0	1.3	11	<0.2	<0.2
Lu River	L1	N 21° 00' 072"	E 105° 50' 090"	5.3	42	11	<0.2	3.2
	L2	N 20° 59' 486"	E 105° 50' 462"	9.9	122	103	17	<0.2
	L3	N 20° 58' 409"	E 105° 49' 707"	7.6	78	73	<0.2	<0.2
Set River	S1	N 20° 59' 587"	E 105° 50' 594"	4.1	36	680	<0.2	5.3
	S2	N 20° 58' 313"	E 105° 51' 228"	5.6	139	215	<0.2	11
Kim Nguu River	KN1	N 21° 00' 028"	E 105° 51' 717"	11	328	1100	<0.2	1.4
	KN2	N 20° 58' 560"	E 105° 51' 923"	10	237	82	<0.2	22
Yen So Lake	YS1	N 20° 58' 471"	E 105° 51' 881"	6.4	210	79	<0.2	<0.2
	YS2	N 20° 58' 201"	E 105° 51' 266"	9.1	24	17	13	8.0
	YS3	N 20° 58' 395"	E 105° 51' 793"	9.0	384	67	<0.2	<0.2
	YS4	N 20° 58' 130"	E 105° 51' 406"	8.3	98	109	<0.2	12
	YS5	N 20° 58' 299"	E 105° 51' 418"	7.5	20	27	<0.2	<0.2
	YS6	N 20° 58' 308"	E 105° 51' 659"	6.7	80	33	36	<0.2

^a PCBs: Sum of seven PCB congeners (PCB 28, 52, 101, 118, 138, 153, and 180) by multiplication with the value of four according to Froescheis et al. (2000).

^b DDTs: Sum of o,p' -DDE, p,p' -DDE, o,p' -DDD, p,p' -DDD, o,p' -DDT, and p,p' -DDT.

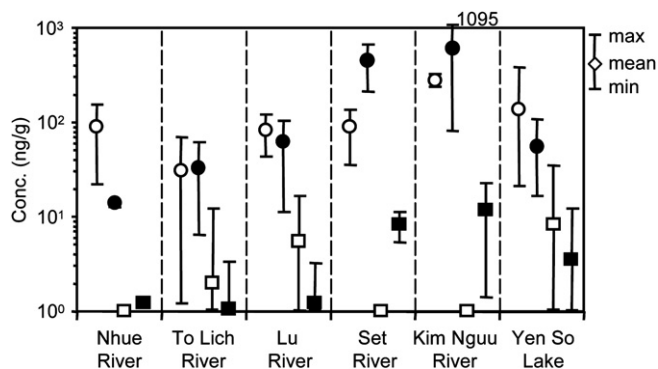


Fig. 2. Concentration ranges of PCBs (○), DDTs (●), β -HCH (□), and HCB (■) in sediments of the sewer system in Hanoi.

and Kim Nguu (Table 1) point to input sources within the highly populated center of Hanoi. In addition, pollution sources from industrial and agricultural activities along the course of the rivers must be taken into account since some pollutants showed increased concentrations down stream, e.g. PCBs (in the rivers Set and Lu) and DDTs (in the rivers Lu and Nhue).

3.2. Temporal trend and composition of pollutants in sediments

3.2.1. HCB

HCB was detected in 55% of the sediment samples with concentrations ranging from <0.2 to 22 ng/g. In general, HCB was scarcely investigated in Vietnam compared to PCBs, DDTs, and HCHs. The HCB levels were reported to be higher in human breast milk of women living in Hanoi City than in Hochiminh City (Minh et al., 2004) and in sediment along the coast of Northern Vietnam (Nhan et al., 1999). In the survey conducted in 1997, Nhan et al. (2001) reported HCB concentrations in the sediments of the Hanoi rivers ranging from n.d. to 0.13 ng/g. The HCB levels of the present study are about one to two orders of magnitude higher than those in 1997, but comparable to the levels in Hochiminh City canals in 2004 (Minh et al., 2007a). HCB was used as a fungicide in Vietnam. Recent sources of HCB are attributed to waste incineration (World Health Organization, 1997) but they may also originate from the production and use of agrochemicals and industrial chemicals containing HCB as a byproduct (Monirith et al., 2003).

3.2.2. HCHs

β -HCH was the only isomer (among three investigated HCH isomers) detected in quantifiable amounts in five of the 22 samples. The sediment concentrations of β -HCH determined in this study (<0.2 –36 ng/g, mean 3.8 ng/g) were higher than those measured in Hanoi rivers in 1997 (Nhan et al., 2001), in Hochiminh canals and in the Mekong River in 2004 (Minh et al., 2007a,b). The typical technical HCH mixture generally applied in Northern Vietnam contained 55–80% α -HCH, 5–14% β -HCH, 8–15% γ -HCH, and 2–16% δ -HCH, and a similar pattern of HCH isomers was actually detected by Nhan et al. (2001). However, the predominant presence of the β -HCH isomer found in this study can be explained by the relatively distant time between the use of HCH and the sampling time, and by the lowest water solubility, lowest vapour pressure, highest chemical stability, and the resistance to microbial transformation of β -HCH compared to other isomers (Ramesh et al., 1991). In addition, α -HCH can be transformed to β -HCH in the environment (Wu et al., 1997). Relatively high levels of β -HCH as the only isomer were also reported in human breast milk in Hanoi City (Minh et al., 2004).

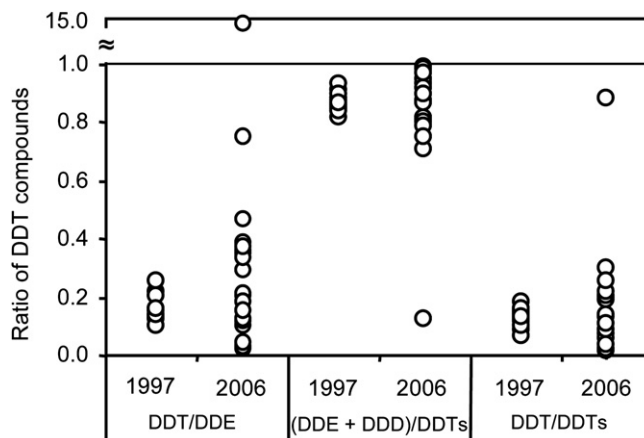


Fig. 3. Ratios of DDT compounds in sediments of the Hanoi sewer system in 1997 (Nhan et al., 2001) and 2006 (present study).

3.2.3. DDTs

In conformity with previous studies conducted by Nhan et al. (2001) and Kishida et al. (2007), we report the total DDTs concentration as the sum of *o,p'*-, *p,p'*-DDD, *o,p'*-, *p,p'*-DDE, *o,p'*-, *p,p'*-DDT. The sediment concentrations of DDTs varied from 12 to 14 ng/g in the Nhue River, 6.4–61 ng/g in the To Lich River, 11–103 ng/g in the Lu River, 215–680 ng/g in the Set River, 82–1100 ng/g in the Kim Nguu River, and 17–109 ng/g in the Yen So Lake. All the collected sediment samples contained DDTs and the highest concentration was observed at site KN1 (1100 ng/g), which is located in the highly populated center of Hanoi City. Nhan et al. (2001) and Kishida et al. (2007) reported sediment concentrations of DDTs in the Hanoi rivers ranging from 7.4 to 81 ng/g (mean 31 ng/g) in 1997 and 42–44 ng/g (mean 43 ng/g) in 2002, respectively. The results of this study (4.4–1100 ng/g, mean 135 ng/g) clearly reveal higher concentrations, indicating recent input of DDTs to the aquatic environment, although the use of DDT is banned in Vietnam since 1995.

The hypothesis of recent input of DDT to the environment in South Vietnam was elucidated by evaluating the pattern of individual DDTs (Phuong et al., 1998; Minh et al., 2007a,b). Similarly, three major compounds, including DDT, DDD, and DDE, can be used for assessing the chronology of DDT input in the Hanoi sewers in North Vietnam. Hong et al. (1999) suggested that a ratio of (DDE + DDD)/DDTs of more than 0.5 is indicative for a long-term biotransformation of DDT to DDD and DDE, while a ratio of less than 0.5 may imply recent input. In addition, a ratio of DDT/DDE >0.5 may indicate recent input of DDT, and, in contrast, of <0.3 may imply past input of DDT (Strandberg et al., 1998). Fig. 3 illustrates the patterns of DDT compounds detected in sediments from this study and those calculated for sediments in 1997 (Nhan et al., 2001). The DDT/DDE ratios being <0.3 and the (DDE + DDD)/DDTs ratios >0.5 in sediments of 1997 (Nhan et al., 2001) revealed that biotransformation was significant in the period of 1997–2006. However, a decreasing trend of the (DDE + DDD)/DDTs ratios and an increasing trend of DDT/DDE ratios as well as DDT/DDTs ratios among sediments collected in 1997 and 2006 were recognized, revealing additional recent input of DDT to the environment. Particularly, a ratio of DDT/DDE up to 14 (DDT occupied 88% among DDTs) in a sediment sample collected at site KN1 signified a very recent input of DDT to the Hanoi sewer system. DDT might originate from illegal usage of DDT in suburban agriculture, leakage from remaining stockpiles and unsecured landfills, or vector control and hygienic purposes (Minh et al., 2004, 2006; Nhan et al., 2001). Minh et al. (2006) suggested a further source of DDTs might be the insecticide Dicofof, which contains DDT as a byproduct. For example, Dicofof was

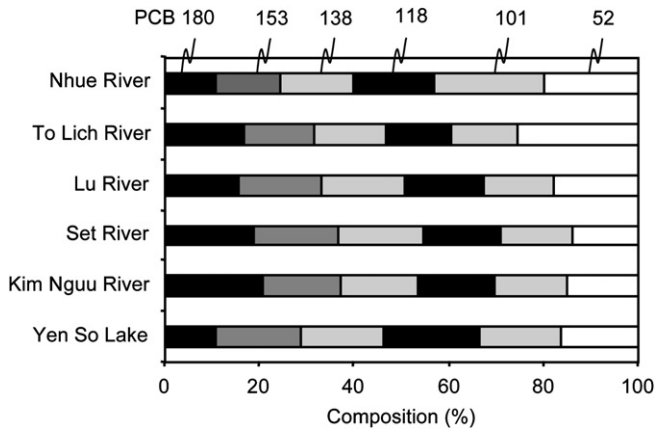


Fig. 4. Mean composition of PCB congeners in Hanoi river sediments.

used in China from 1988 to 2002, thereby, spreading an estimated 8800 tons of DDT to the environment (Qiu et al., 2005).

3.2.4. PCBs

Similar to DDTs, the PCBs spanned a relatively wide range. The sediment concentrations of PCBs varied from 22 to 153 ng/g in the Nhue River, 1.3–70 ng/g in the To Lich River, 42–122 ng/g in the Lu River, 36–139 ng/g in the Set River, 237–328 ng/g in the Kim Nguu River, and 20–384 ng/g in the Yen So Lake (Fig. 2). In the SaiGon-Dong Nai River Basin, Hochiminh City, Minh et al. (2007a) reported PCB levels to decline 3–6 times lower than those in the early 1990s. However, PCB levels in sediment of Hanoi showed an opposite trend. Ranging from 1.3 to 384 ng/g (mean 104 ng/g), the sediment levels of PCBs measured in this study revealed a clear increase compared to 0.79–40 ng/g (mean 13 ng/g) in 1997 (Nhan et al., 2001, quantification using Aroclor 1254) and 15–120 ng/g (mean 45 ng/g) in 1999 (Viet et al., 2000). Since sediment samples were collected in the dry season in this study and at the onset of the

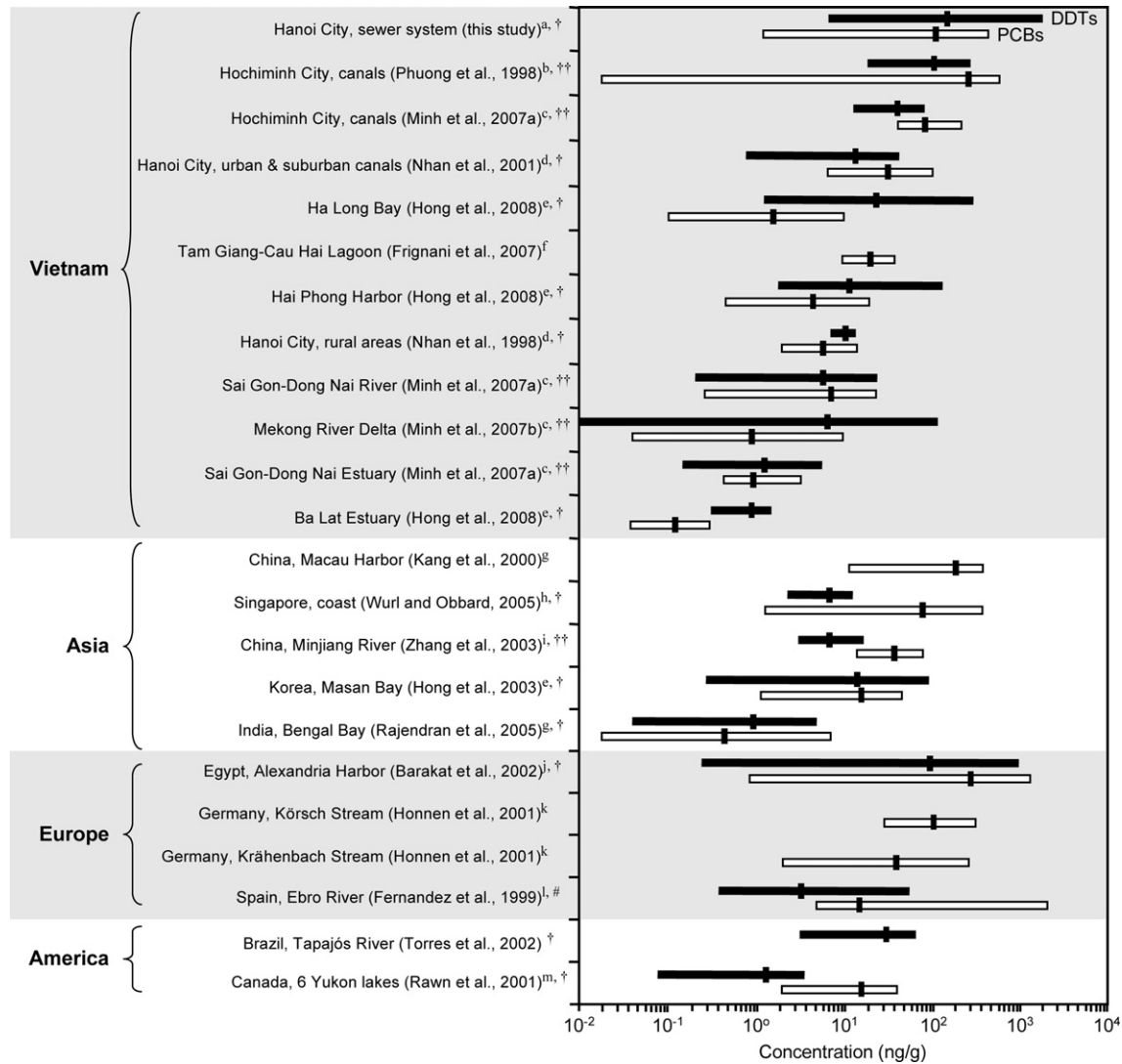


Fig. 5. Concentration ranges and mean values of DDTs (◄) and PCBs (◄) in recently collected sediments from various locations in the world. ^a Sum of PCB congeners 28, 52, 101, 118, 138, 153, 180 multiplied by a value of four; ^b Sum of PCB congeners 28, 52, 101, 138, 153, 180 multiplied by a value of 4.81; ^c Sum of Kanechlor KC300–KC600; ^d As Aroclor 1254; ^e Sum of PCB congeners 8, 18, 28, 29, 44, 52, 66, 87, 101, 105, 110, 118, 128, 138, 153/132, 170/190, 180, 187, 195, 200, 206, 209; ^f Sum of 53 PCB congeners; ^g sum of Aroclor 1242, 1248, 1254, 1260; ^h Sum of PCB congeners 28, 31, 33, 44, 49, 53, 70, 74, 87, 118, 128, 138, 153, 206, 208; ⁱ Sum of PCB congeners 1, 5, 28, 29, 47, 49, 52, 77, 97, 101, 105, 118, 138, 153, 154, 169, 171, 180, 187, 200, 204; ^j Sum of 99 PCB congeners; ^k Sum of PCB congeners 28, 52, 101, 138, 153, 180; ^l Sum of PCB congeners 77, 101, 105, 118, 126, 138, 153, 156, 167, 169, 170, 180, 194; ^m Sum of 104 PCB congeners. [†] Sum of o,p'- and p,p'-DDT, DDD, DDE; ^{††} Sum of p,p'-DDT, DDD, DDE; [#]: Sum of dichlorobenzophenone and p,p'-DDT, DDD, DDE.

rainy season in 1997, the different amount of water drained through the sewer system might affect the washout of suspended particle containing PCBs. However, by evaluating the temporal trend of PCBs in soils collected in Hanoi City in 2006, Toan et al. (2007b) reported clearly increasing concentrations of PCBs compared to levels in 1990s. In addition, in a sediment survey conducted in 1995, Nhan et al. (1998) reported a relatively low PCB concentration of 5.64 ng/g in the dry season in an irrigation canal close to the Nhue River. Hence, the observation made in this study raises serious concern on the increase of PCB levels in Hanoi City.

Concerning the PCB congeners, Toan et al. (2007b) reported that until 1998, about 48% of the total imported quantity of likely PCBs-containing oil originated from the Soviet Union. This oil contained 11.7, 7.0, 6.5, 3.6, 0.4, and 0.8% of PCB congeners 138, 153, 101, 52, 180, and 28, respectively, which were coincident with those in soil samples collected in Hanoi City. However, a similar composition of PCB congeners in different categories of sediments was observed in this study, except the less persistent congener 28 was not detected (Fig. 4). This result indicates significant recent sources of PCBs to the sediments of the Hanoi sewer system, such as from the industry, atmospheric deposition, and domestic wastewater. The leakages of PCBs from the PCBs-containing oils in old transformers and capacitors, which are widely installed in Hanoi City, and especially from recent PCBs-containing wastes, are thinkable sources of the PCBs pollution. Initial inventory results show that there are more than 11 800 likely PCB-containing electrical equipments in Vietnam, containing some 7000 tones of likely PCB-containing oils (MONRE, 2006). In addition, the rapid development of Hanoi City without adequate measures for safe handling of PCBs-containing oils and other materials are likely to have led to the increase of PCBs pollution in the city. As cited in Toan et al. (2007b), PCBs could currently be used as a component of lubricating oils for motor vehicles. This fact suggests that the assessment of the sources of PCBs should be given utmost attention.

3.3. Comparison of PCB and OCP levels in Vietnam with other regions of the world

A comprehensive comparison of PCB and DDT levels in recently collected sediments from various locations in Vietnam and in the world is presented in Fig. 5. It can be recognized that among the reported locations in Vietnam, the levels of PCBs (mean 104 ng/g) and DDTs (mean 135 ng/g) in sediments of the Hanoi sewer system are highest followed by the Hochiminh City canals. The result indicates Hanoi City itself is likely comprising sources of PCB and DDT pollution. Furthermore, the sediment levels of PCBs and DDTs in the Hanoi sewer system are comparable to those found in the highly polluted Alexandria Harbor (Egypt) and Macau Harbor (China).

The total organic carbon content (TOC) has a significant influence on the sediment concentration of PCBs and OCPs as these compounds are highly sorptive with high K_{OC} values (Ding and Wu, 1995; Lu et al., 2006). By evaluating the correlation between TOC and the concentration of PCBs, DDTs, and CHLs in sediments of the Hochiminh City canals, the Saigon-Dong Nai River and the estuary in South Vietnam, Minh et al. (2007a) demonstrated that higher amounts of these pollutants mainly occurred in sediments with high TOC. In general, the TOC values in sewers and lake in Hanoi City (1.0–11%, mean 6.2%; see Table 1) are higher than those in Hochiminh City canals (3.2–4.9%), the Saigon-Dong Nai River and the estuary (0.44–4.8%). This could explain the higher concentrations of DDTs and PCBs in Hanoi sewer system in comparison with those in the South of Vietnam in the recent study of Minh et al. (2007a,b). The TOC values in sediments of other reported locations, including the Tam Giang-Cau Hai Lagoons (Frignani et al., 2007), the Ba Lat Estuary, the Ha Long Bay, and the Hai Phong Harbor (Hong et al., 2008) were also reported lower than those in Hanoi sewer system.

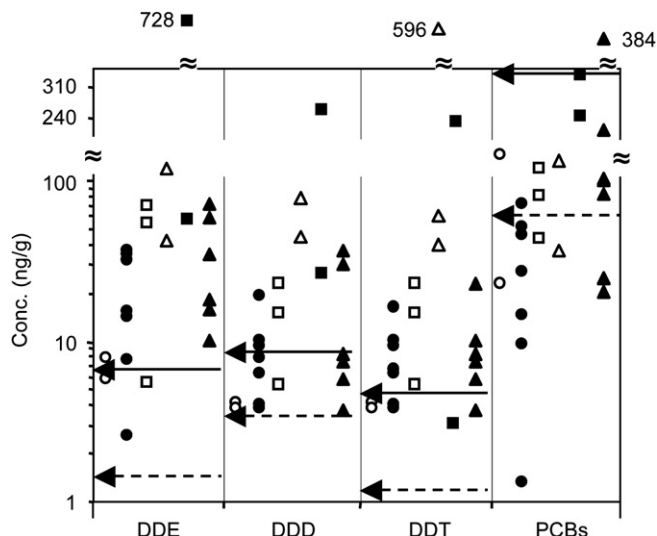


Fig. 6. Comparison of measured DDT and PCB concentrations with the Canadian Environmental Quality Guideline for Sediment. (○) Nhue River, (●) To Lich River, (□) Lu River, (△) Set River, (■) Kim Nguu River, (▲) Yen So Lake. (←) interim sediment quality guideline, (←) probable effect level.

3.4. Hazard assessment

In order to obtain an overall view on the possible toxic effects to the benthic and epibenthic organisms in the Hanoi sewer system (Fig. 6), the sediment concentration of DDTs and PCBs were compared with the interim sediment quality guideline (ISQG) and the probable effective level (PEL), issued by the Canadian Council of Ministers of Environment (CCME, 2002). The concentrations of DDE, DDD, and DDT (sum of *o,p'*- and *p,p'*-isomers) in all the Hanoi sediment samples were higher than the ISQG values (1.42, 3.54, and 1.19 ng/g, respectively). The DDE, DDD, and DDT generally exceed the PEL values (6.75 ng/g for DDE, 8.51 ng/g for DDD, and 4.77 ng/g for DDT) but vary among the sediment samples. Most of the sediments from the rivers To Lich, Lu, Set and the Yen So Lake contained DDTs above the PEL values, while they were below at the Nhue River. In contrast, the PCBs concentrations (except for sample YS3, 384 ng/g) were lower than the PEL value (340 ng/g as for Aroclor 1254), and only half of them exceed the ISQG value (60 ng/g as for Aroclor 1254).

4. Conclusions

Occurrence, patterns, temporal trend, sources, and the potential toxicity of PCBs and OCPs were assessed in sediments of the Hanoi sewer system. Although pollution patterns are different among the various rivers and lake investigated, the relatively high concentrations of PCBs, DDTs, HCB and β -HCH indicate that pollution by persistent organochlorines is still an important environmental issue in Hanoi City. The increasing trend of these pollutants documented over the last decade in conjunction with increasing DDT/DDE ratios indicates very recent inputs to the environment. The levels of PCBs and DDTs in sediments of the Hanoi sewer system are the highest recorded in Vietnam so far, indicating that the pollution originates from sources within the city itself. DDE, DDD, DDT and about half of the PCBs exceed the interim sediment quality guidelines established in Canada. Furthermore, DDE, DDD and DDT exceeded the probable effect levels in most of the sediment samples originating from the Hanoi rivers To Lich, Lu, Set and the lake Yen So.

The findings of this study provide valuable information for the public and environmental authorities of Vietnam to mitigate the discharge of toxic chemicals into the aquatic environment via

the sewer system (Hoai et al., in preparation). In addition, the assessment of the sources of DDTs and PCBs should be given adequate attention, particularly in light of the fact that water of the sewer rivers is used for agricultural irrigation and therefore pose a threat to accumulate in food.

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