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

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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.

1. Introduction

Covering an area of some 1000 km^2 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 m^3/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.

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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 arrived 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; Froescheis 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-EI-MS system (Shimadzu GC/MS QP2010) for quantification of OCPs. A DB-5 capillary column (30 m × 0.25 mm × 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 °C, respectively. The GC temperature program for PCBs separation was set to 120 °C before increasing to 200 °C at 10 °C/min, then to 230 °C at 2 °C/min, and finally to 300 °C at 7 °C/min where temperature was maintained for 10 min. The oven temperature program for OCPs analysis was 70 °C (1 min); 20 °C/min, 160 °C; 2 °C/min, 250 °C; 5 °C/min, 300 °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,

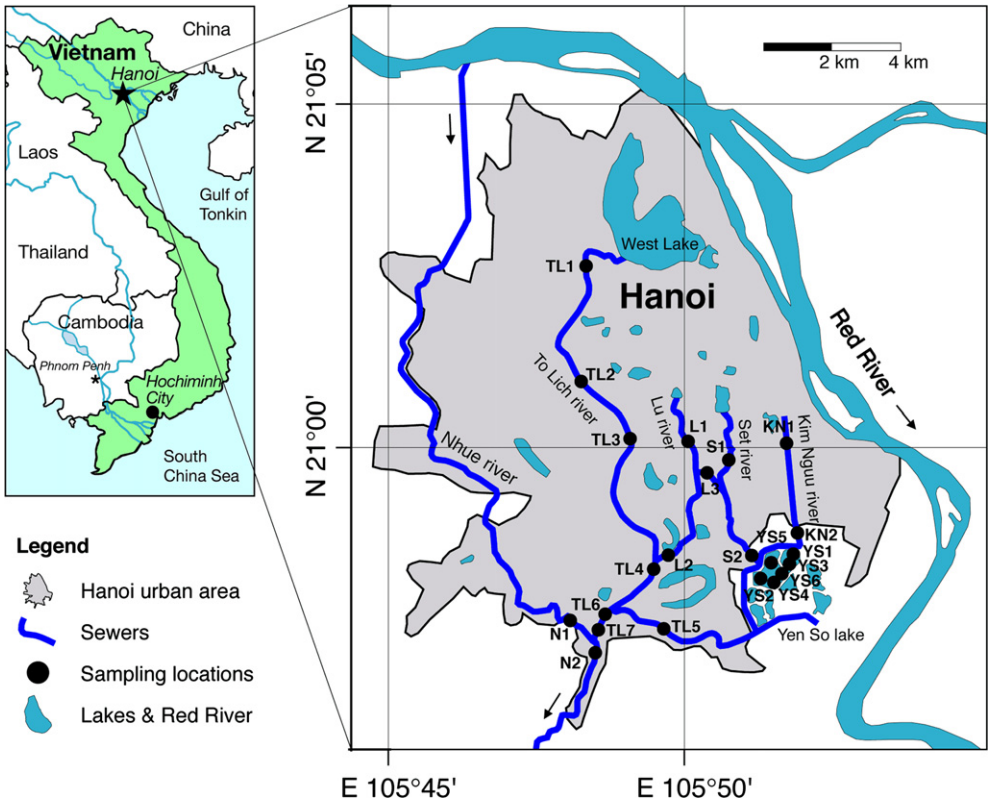

Fig. 1. Map of Hanoi City indicating the sewer system and the locations where sediment samples were collected (N: Nhue River, TL: To Lich River, L: Lu River, S: Set River, KN: Kim Nguu River, and YS: Yen So Lake).