OCCURRENCE OF 185 ORGANIC MICRO-POLLUTANTS IN RIVER SEDIMENTS FROM VIETNAM

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Introduction

The four biggest cities (Hanoi (HN), Haiphong (HP), Danang (DN) and Hociminh (HCM)) are considered to be the most highly industrialized and urbanized in Vietnam. The fast development of industry and high population growth in conjunction with lack of proper wastewater treatment facilities have lead to toxic chemicals inputs to the environment via wastewater discharge[1]. An earlier study of ours[1] dealing with water pollution in these cities revealed that a wide range of organic micro-pollutants in the aquatic environment, and greater attention has been focused on man-made chemicals originating from household activities such as steroids and other endocrine disrupting substances, PPCPs, and pesticides, due to their elevated concentrations. In addition, the existent of persistent organic pollutants, such as organochlorine pesticides and PCBs in the water column has raised great concern about sediment contamination.

The aim of this study was: (1) to examine the concentrations of a thousand organic micro-pollutants and their distribution in river sediments, (2) to find chemicals that pose adverse biological effects to aquatic organisms, (3) to clarify the pollution characteristics of contaminants at each river, (4) to determine the emission sources of main detected chemicals.

Materials and methods

Sample collection

In the rainy season (October 2011), surface river sediment samples (5 cm depth) were collected at 17 sites (Fig.1) and were kept at -20°C until analysis. Moisture contents of sediment were determined by measuring the weight loss in 10g subsamples after oven-drying at 105°C for 2 hours. Volatile solid was analyzed by igniting the dry residue obtained after removing moisture in a muffle furnace at a temperature of 550°C.

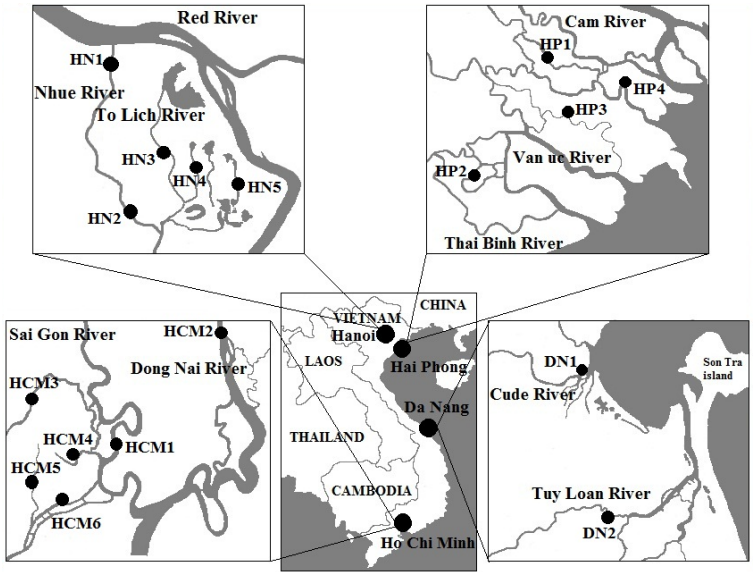

Fig.1. Sampling sites in Hanoi, Haiphong, Danang and Hochiminh [urban sites: HN2-5, HCM3-6; suburban sites: HN1, HP4, DN1, HCM1-2; rural sites: HP1-3, DN2]

Chemical analysis

Semi-volatile organic compounds in sediment were analyzed following the method of Kadokami et al. (2012)[2]. Briefly, approximately 10g of wet sediment sample was extracted with dichloromethane/acetone (1:1) using an accelerated solvent extractor. Liquid-liquid extraction with dichloromethane was further performed on the extracts before SPE cleanup step. The concentrated was applied to silica-gel cartridge and separated into 3 fractions by sequential elution of hexane (Fr-1), 5% acetone–hexane (Fr-2), and 30% acetone–hexane (Fr-3). The elute of Fr-1 was treated with activated copper to remove sulfur-containing substances. The elute of Fr-3 was treated activated carbon column to remove colored substances. Final solution (about 1ml) of each fraction was spiked with internal standards before quantification by GC-MS and GC-MS-MS instrument.

Quality control

Quality assurance and quality controls were performed by blank analysis, reproducibility and repeatability tests and the analysis of a certified reference material (SRM 1941b). Surrogate compounds (38) spiked into sediment samples showed good recovery rates (73-126%) except for some highly polar compounds. Relative standard deviations were below 20%. Results of determined substances in SRM 1941b were in good agreement with the certified values. The relative average deviations of 152 out of the 185 detected substances were below 20% for duplicate analysis, which indicating that the method produced the results in a good reproducibility and repeatability and sufficient for environmental surveys.

Results and discussion

Overview

One hundred and eighty-five of the 940 analytes, belonging to 26 different chemical groups were detected in at least one sample. Contamination levels in sediments from highly populated urban areas (such as HN3-5, HCM3-4, and HCM6) were over 5 times higher than those in suburban and rural areas (Fig.2). Chemicals originating from domestic sources and sterols compounds were the most dominant, contributing over 90% of total concentration in sediment samples (Fig.2). This observation clearly demonstrates the sewage contamination of the rivers. Although there is a large latitudinal gap between Hanoi and Hochiminh City, a similar pollution profile was still observed in sediments of the two cities, perhaps as a result of their similar social features.

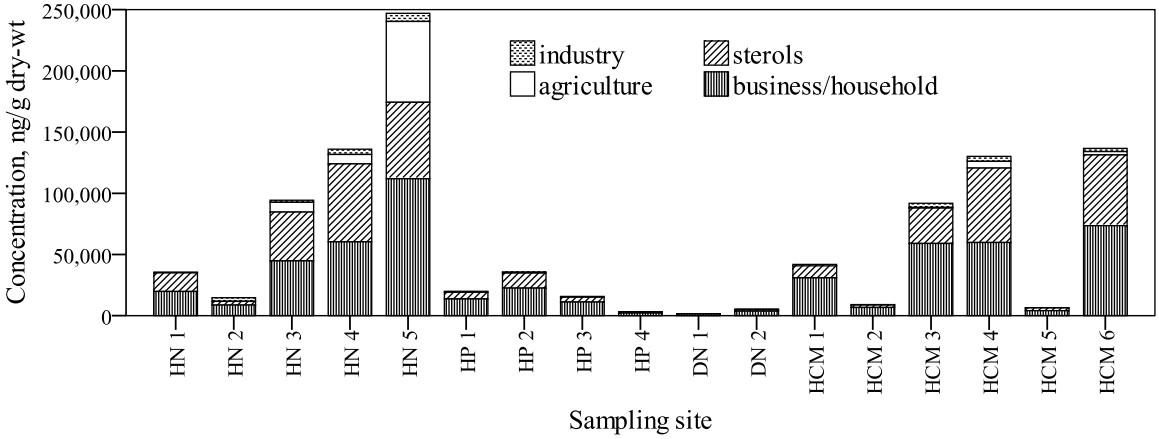

Fig.2. Concentrations (ng/g dry-wt) and compounds categorized by origin at each site

Sterols

Eight out of the 10 sterols analyzed were observed in all sediment samples. Coprostanol, cholestanol and cholesterol were sterols quantified for evaluating sewage effects, appearing at highest mean concentration values (7,100; 4.700; 4,300 ng/g dry-wt, respectively). Elevated total concentrations of sterols were observed in the metropolitan area of Hanoi (HN3-5) and Hochiminh City (HCM3-4, HCM6) (Fig.2); these levels are about 2 times higher than those in other Asian developing countries[3], clearly indicating their deriviation from untreated domestic wastewater . Coprostanol is an indicator of fecal pollution[4] and that a ratio of coprostanol to cholesterol (>0.2) indicates sewage[5] or human feces[6] (>0.3). In this study, values >0.4 were seen at all sampling sites, and values greater than 1 were observed in 10 out of 17 sites in urban areas, suggesting all of study rivers were seriously contaminated by sewage. A higher percentage of coprostanol relative to total sterols (%Cop) indicates greater contributions of fecal matter of human origin to fecal pollution[7]. The %Cop (> 20%) were higher in sediments from urban canals (HN1-5 and HCM4-6) than those in rural and suburban areas, which suggests the direct inputs of human feces to urban canals.

Organochlorine pesticides and current usage pesticides

Twenty five out of the 457 pesticides in the database were detected: 5 current usage insecticides (chlorpyrifos, deltamethrin, permethrin-1, permethrin-2, piperonylbutoxide), 19 banned insecticides and one fungicide. The most frequenly detected pesticides were DDTs metabolites (above 80%), followed by lindane (γ-HCH) (60%). Permethrin-1, and -2 were the most abundant (contributing over 98% of total detected pesticides) and only found

in sediments from urban areas (HN3-4, HCM3-4, HCM6), which clearly demonstrated that pemethrins were used for health services rather than crop protection. Elevated concentration of deltamethrin was found only in HN5 (60,000 ng/g dry-wt) and contributing over 90% of total pesticides in the sample. However, the emission sources of deltamethrin is currently unknown, and requires further research.

DDTs residue levels were highly variable among sampling sites, ranging from nil (HCM5, DN1) to 127 ng/g dry-wt (HCM4). ΣDDTs concentrations in urban areas were around 5 times higher than those in the city outskirts. The concentrations of DDDs and DDEs in 4 sediments exceeded Canadian Environmental Quality Guideline for freshwater sediments (CCME, 2002)[8], implying the potential hazard effects of DDTs to aquatic organism in the rivers. The high proportion (>80%) of DDE + DDD to ΣDDTs (Fig.3) in conjunction with the ratio of DDT/DDE (<0.3) suggest the past use of DDT and no recent inputs of DDT in the study areas[9].

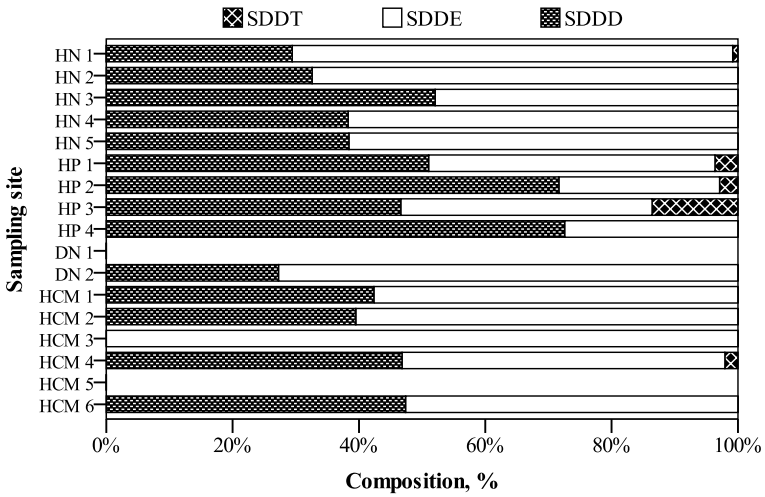

Fig.3. DDTs composition in sediments in 17 studied stations [SDDT = o,p'-DDT + p,p'-DDT; SDDD = o,p'-DDD + p,p'-DDD; SDDE = o,p'-DDE + p,p'-DDE]

Polychlorinated biphenyls

PCBs were detected in most of the sediment samples, ranged from 0.13 ng/g dry-wt (HN2) to 121 ng/g dry-wt (HCM4). PCBs levels in urban areas of Hanoi (HN3-5) and Hociminh City (HCM3-4, HCM6) were almost 100 times higher than those from rural areas (HP2-4), which suggests that the metropolitan areas are the sources of PCBs pollution to the river.

Table 1: Comparision of organochlorines in Vietnamese sediments with that reported elsewhere in Asia[a]

Country	Year	n	PCBs[b]	DDTs[c]	HCHs[d]	HCB[e]	CHLs[f]	Reference
A - Vietnam								
Hochiminh (urban areas)	1990	5	7.6-630	47-790	0.97-12	-	0.46-20	Iwata et al. (1994)
	2004	6	46-150	12-72	<0.05	<0.1-18	0.6-4.5	Minh el al. (2007[a])
	2012	4	1.5-121	0-127	0.12-3.14	0-1.6	0.03-2.0	Present study
Hochiminh (outskirt)	2003-2004	22	0.04-9.2	<0.01-110	<0.02-1.3	-	-	Minh et al. (2007[b])
	2004	9	0.33-22	0.21-23	<0.01-0.03	<0.001-0.6	0.016-1.0	Minh el al. (2007[a])
	2012	2	0.9-5.5	0.3-3.8	0-0.2	0	0	Present study
Hanoi (urban areas)	1997	12	0.67-40[g]	7.3-73	0.07-3.1	-	-	Nhan et al. (2001)
	2006	16	1.3-328[h]	6.4-1100	-	<0.2-22	-	Hoai et al. (2010)
	2012	4	0.13-55	0.4-45	0-2.8	0-3.82	0.05-0.1	Present study
Hanoi (outskirt)	1995-1996	2	2.2-11[g]	7.0-14	-	-	-	Nhan et al. (1998)
	2012	1	1.7	6	0.1	0.05	0	Present study
B - World								
China (Pearl River Estuary)	1996-1997	20	0.18-1.82	1.36-8.99	0.28-1.23	-	-	Hong et al. (1999)
China (Minjiang River)	1999	9	15.1-57.9	1.5-13	2.9-16	-	-	Zhang et al. (2003)
Taiwan (Wu-Shi River)	1997-1998	19	-	0.53-11.4	0.99-14.5	-	-	Doong et al. (2002)
India (urban and sub-urban area)	1989	6	4.8-1000	8-450	0.58-38	-	0.47-130	Iwata et al. (1994)
Thailand (urban and industrial area)	1990	4	11-520	4.8-170	0.48-3.1	-	1.4-210	Iwata et al. (1994)
Indonesia (urban and residential area)	1991	4	5.9-220	3.4-42	0.035-0.1	-	0.16-38	Iwata et al. (1994)
Japan (urban area)	1990	3	63-240	2.5-12	4.5-6.2	-	0.66-2.1	Iwata et al. (1994)
Taiwan (urban and suburban area)	1990	3	2.3-230	0.39-11	0.29-0.79	-	0.14-5.6	Iwata et al. (1994)

"-": Data is not available; [a]concentration in ng/g dry-wt; [b]As Kanechlor (KC-Mix); [c]Sum of o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p' DDD, o,p'- DDT, p,p'-DDT; [d]Sum of α-HCH, β-HCH, γ-HCH; [e]Hexachlorobenzene; [f]Sum of trans-Chlordane, cis-Chlordane, trans-Nonachlor, cis-Nonachlor, ; [g]As alochlor 1254 mixture; [h]Sum of 7 PCB (28,52,101,118, 138, 153, 180)

In urban areas of Hanoi city, PCBs levels were comparable to those in previous study in 1997[10], but lower than observed in 2006[11] (Table.1). This probably due to intense rainfall, which might affect the washout of suspended

particle containing PCBs. PCBs values in urban areas and outskirts of Hochiminh city were around 2 times lower than those reported in 2004[12], whilst over 5 times lower compared to early 1990s[13] (Table.1), which implies a decreasing trend of PCBs in the river system in Hochiminh city. In global scale, PCBs levels in the city's canals of Hanoi and Ho Chi Minh City were similar to those reported in Minjiang River, but more than 20 times higher than those reported in the Pearl River estuary (China) (Table.1). However, the present range of PCBs in Vietnamese sediments was several times lower than sediments collected in other Asian countries in 1990s[13] (Table.1). This trend implying the local source of PCBs in Vietnam is less than the other above countries. However, greater residues were occasionally found in some places (HN4-5, HCM4) indicating that point sources of PCBs in Vietnam are still remaining.

Polycyclic aromatic hydrocarbons

Twenty-eight PAHs were detected, with means ΣPAHs (except for perylene which naturally occurring) in Hanoi, Haiphong, Danang and Hochiminh City being 2700, 500, 100 and 1700 ng/g dry-wt, respectively. ΣPAHs in urban areas (median 3000 ng/g dry-wt) were higher than those in outskirt areas (420 ng/g dry-wt). The concentrations of naphthalene, pyrene, acenaphthene, fluorene, fluoranthene, chrysene and triphenylene benzo(a)anthracene, benzo(a)pyrene and phenanthrene in some urban sites exceeded the ISQG values (CCME, 2002)[8], suggesting the toxicological stress of these compounds on aquatic biota in the rivers. The compositions profiles of 2- to 6- aromatic ring PAHs (except for perylene) in the 17 sediment samples were similar (Fig.4). The ratios of methylphenanthrenes to phenanthrene were above 1.6 in urban areas (HN2-5, HCM3-4 and HCM6), indicating that PAHs pollution was mainly caused by petroleum spills (petrogenic origin)[14]. This is a common phenomenon in Southest Asia countries[14]. However PAHs in the suburban and rural areas were predominantly of pyrogenic origin, such as the combussion of fossil fuels and biomass (burning of rice straw after harvest).

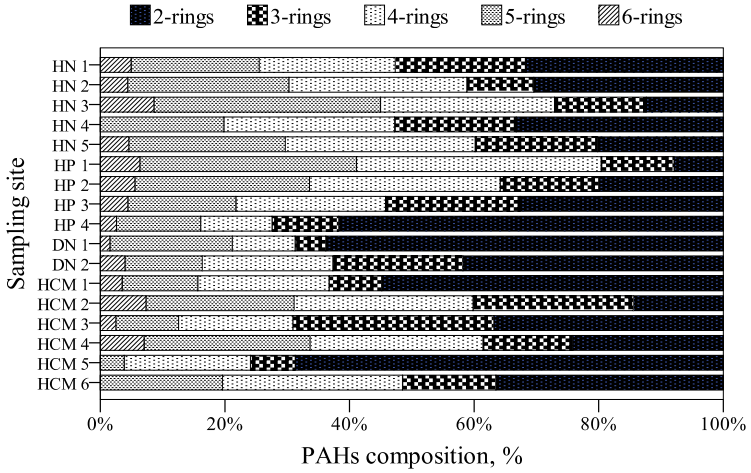

Fig.4. Profiles of 2- to 6- aromatic rings of PAHs (except perylene) in sediment samples in seventeen studied stations

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