Screening and analysis of 940 organic micro-pollutants in river sediments in Vietnam using an automated identification and quantification database system for GC–MS

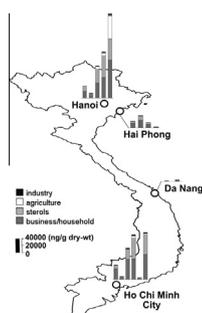Hanh Thi Duong [a], Kiwao Kadokami [a,*], Shuangye Pan [a], Naoki Matsuura [a], Trung Quang Nguyen [b]

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HIGHLIGHTS

- 185 out of 940 organic chemicals were found in river sediments in Vietnam.
- Rivers were mainly polluted with chemicals originating from domestic sources.
- Urban canals were heavily polluted with pyrethroid insecticides.
- PAHs and OCPs compounds had concentrations exceed sediment quality guidelines.
- This comprehensive analytical method is a useful tool for environmental surveys.

GRAPHICAL ABSTRACT

ABSTRACT

In order to obtain a detailed picture of pollution by organic micro-pollutants in Vietnamese rivers, 940 semi-volatile organic compounds in river sediments collected from four major cities were examined by a comprehensive gas chromatography–mass spectrometry-database. The number of detected chemicals at each site ranged from 49 to 158 (median 96 out of 940) with 185 analytes detected at least once in the survey. The substances detected with high frequency (over 80%) and high concentrations were n-alkanes, phthalates, sterols and PAHs. For most substances, sediments from metropolitan areas (Hanoi and Ho Chi Minh City) were more heavily contaminated than those in rural and suburban areas. Sterols were observed in nearly 100% of sediments at extremely high concentrations, suggesting that the studied rivers were contaminated by sewage. Pyrethroids (permethrin-1 and -2) were the most dominant insecticides found in inner canals of Hanoi and Ho Chi Minh City. Deltamethrin was only detected at a site in Hanoi at an elevated concentration. This reflects that pyrethroids are used for the protection of private and public health rather than for agriculture. p,p′-DDE and p,p′-DDD were the dominant members of the DDT family of chemicals detected, indicating no recent inputs of DDTs in the study areas. PCBs residues were lower than those in other Asian countries, which suggest historically much lower use of PCBs in Vietnam. PAHs pollution in urban areas is caused by the runoff of petroleum products and vehicle exhaust gases, whereas in rural and suburban areas, the combustion of fossil fuels and biomass is major sources of PAHs. Overall, the study confirmed that rivers in Vietnam were heavily polluted mainly by domestic wastewater.

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1. Introduction

Four large cities (Hanoi (HN), Hai Phong (HP), Da Nang (DN) and Ho Chi Minh City (HCM)) are considered to be the most highly industrialized and urbanized in Vietnam. The rapid development of industry and high population growth in conjunction with lack of proper wastewater treatment facilities have led to toxic chemicals entering the rivers of the cities via industrial, medical, and domestic wastes in wastewater discharge (Duong et al., 2008). For instance, Hoai et al. (2010) reported that 95% of the Hanoi's wastewater effluents, which is estimated to be 450000 m³/day, are discharged into its inner rivers without treatment. Three types of systems for domestic wastewater disposal exist in Hanoi; about 32% of Hanoi's population is served by septic tank, 21% by double vault latrines, and 23% by on-site systems. The remaining 24% are not served by any system at all (World Bank, 1996). Currently only a fraction of the wastewater produced in the city is treated in any way. Although construction of modern wastewater treatment facilities is under consideration, financial and infrastructure constraints make matters difficult (Wnukowska, 2004).

Since our previous study dealing with water pollution in Vietnam (Hanh et al., 2012) revealed that a wide range of organic micro-pollutants contaminates the Vietnamese aquatic environment, greater attention has been focused on man-made chemicals originating from households, such as sterols, endocrine disrupting chemicals (EDCs), pharmaceuticals and personal care products (PPCPs). Sterols (coprostanol and cholesterol) and PPCPs (caffeine and L-menthol) were found in nearly 100% of samples, indicating that rivers are heavily polluted by untreated domestic wastewater. EDCs (bisphenol A and nonylphenol) were found at elevated concentrations in river water in metropolitan areas, and some sites have values exceeding the predicted no-effect concentration for aquatic organisms (MOE, 2001). The existence of legacy persistent organic pollutants, such as organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in sediments in Vietnam, is still of concern because of their persistence, accumulation in sediments, high bioaccumulation potential and harmful biological effects (Iwata et al., 1994). Our previous study (Hanh et al., 2012) has revealed that some OCPs still remain in the aquatic environment although they were banned 20 years ago. In addition, most of the banned OCPs can still be found in relatively high concentrations in the environment throughout Vietnam (e.g. see Viet et al., 2000; Kishida et al., 2007; Minh et al., 2007a,b; Hoai et al., 2010) and their concentrations are higher than those in other Southeast Asian countries (Monirith et al., 2003; Minh et al., 2006). Although a number of studies have indicated that sediment contamination by banned OCPs in Vietnam has continued until recently (Nhan et al., 2001; Minh et al., 2007a,b) and while some researchers on PCB contamination have been conducted in several regions in Vietnam, a complete picture of their contamination in Vietnam has not yet to be compiled.

Managing the effects of such contaminants ultimately requires information on chemical concentrations. For metals, methods using inductively coupled plasma mass spectrometry (ICP-MS) have become useful tools in sediment monitoring because ICP-MS can measure almost all of the most harmful metals simultaneously. When assessing organic substances, many analytical methods have historically had to be used to cover a large number of known compounds (Camino-Sánchez et al., 2011; Gómez et al., 2012), with concomitant financial implications associated with operating multiple definitive tests. Preliminary screening of samples using rapid assessment tools is thus an increasingly attractive prospect for waterways managers. Consequently, we developed an Automated Identification and Quantification System with a GC–MS Database (AIQS-DB) (Kadokami et al., 2004, 2005)

that can determine the concentrations of 940 semi-volatile organic compounds, and comprehensive analytical methods for various environmental substrates by making full use of the AIQS-DB. The AIQS-DB was successfully applied to samples from 11 Japanese rivers (Kadokami et al., 2009), highlighting that (1) the rivers were not seriously polluted, and (2) the chemicals detected most often appeared to be mainly being discharged from domestic sources.

An understanding of the contamination status of chemicals, as well as their sources and potential toxic effects on aquatic organisms in Vietnam, is required to provide information for the public and environmental authorities to protect the environment and ecological system. Therefore, this research on a wide variety of organic micro-pollutants (940) in 17 river and canal bed sediments collected from urban, suburban and rural areas of the four biggest cities in Vietnam was conducted in order: (1) to produce a more complete picture of pollution in Vietnamese rivers, (2) to clarify the main emission sources, (3) to clarify the pollution characteristics of contaminants at each river, (4) to identify chemicals having the potential to pose adverse effects on aquatic organisms, and (5) to assess the long-term temporal trends of pollutants by comparing data with previous studies.

2. Materials and methods

2.1. Sample collection

In the rainy season of 2011 (October), surficial river sediment samples (5 cm depth) were collected from 17 sites from 16 rivers in four cities: HN, HP, DN and HCM (Fig. 1) using an Eckman–Barge grab sampler (15 × 15 cm). The 17 sampling sites were divided into three categories: (1) urban areas (HN2, HN3, HN4, HN5, HCM3, HCM4, HCM5, HCM6), (2) suburban areas (HN1, HP4, DN1, HCM1, HCM2), and (3) rural districts (HP1, HP2, HP3, DN2). The sediment samples were stored in stainless steel bottles and were transported to a laboratory in boxes packed with ice and kept at −20 °C until analysis. Moisture contents of sediments were determined by measuring the weight loss in 10 g subsamples after oven-drying at 105 °C for 2 h. Volatile solid was analyzed by igniting the dry residue obtained after removing moisture in a muffle furnace at a temperature of 550 °C (Standard method, 2005).

2.2. Chemical analysis

Semi-volatile organic compounds (SVOCs) (Table S1 in Supporting Information) in the sediments were analyzed using the method of Kadokami et al. (2012). Briefly, 10 g of wet sample was extracted with dichloromethane/acetone (1:1) using an accelerated solvent extractor (ASE 350; Japan Dionex, Osaka, Japan). Liquid–liquid extraction with dichloromethane was further performed on the extract before SPE cleanup step. After concentration of the extract, the concentrate was applied to a silica-gel cartridge (Sep–Pak VAC 2 g/12 mL; Waters Associates, Milford, MA, USA) and was separated into three fractions by sequential elution of hexane (Fr-1), 5% acetone–hexane (Fr-2), and 30% acetone–hexane (Fr-3). Fr-1 was treated with activated copper (reduced copper, granular, super grade; Kishida Chemical, Tokyo, Japan) to remove sulfur. Fr-3 was treated with an activated carbon column (ENVI-carb; Supelco, Bellefonte, PA, USA) to remove colored substances. After adding internal standards (Restek, Bellefonte, PA, USA) to the final concentrate (about 1 ml) of each fraction, we measured them with two instruments: GC–MS-SIM/Scan (QP-2100 Plus, Shimadzu, Kyoto, Japan) and GC–MS–MS–SRM (TSQ Quantum XLS, Thermo Fisher Scientific, Yokohama, Japan). Measurement conditions for both instruments are shown in Tables S2 and S4. Total ion current
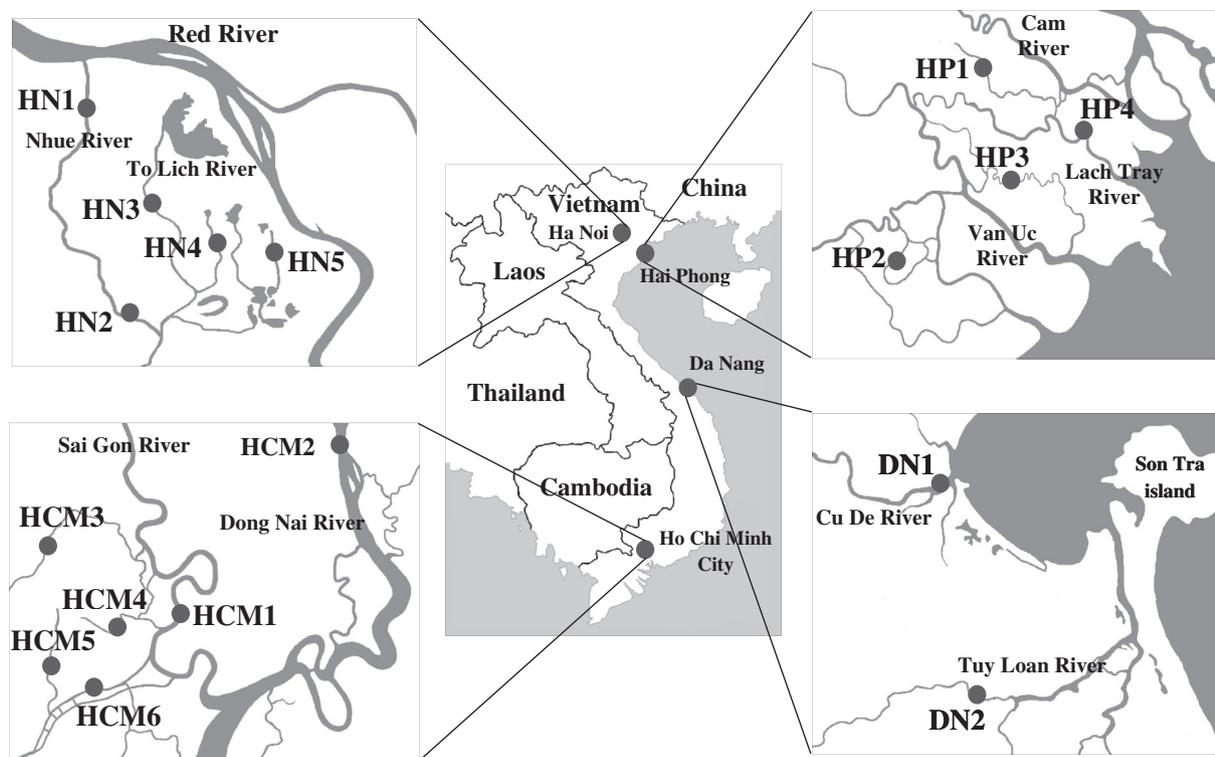
Fig. 1. Location of 17 sampling sites in Hanoi, Haiphong, Danang and Ho Chi Minh City. HN1, HN2: Nhue River; HN3: To Lich River; HN4: Lu River; HN5: Kim Nguu River; HP1: Re River; HP2: Chanh Duong River; HP3: Da Do River; HP4: Lach Tray River; DN1: Trang River; DN2: Tuy Loan River; HCM1: Sai Gon River; HCM2: Dong Nai River; HCM3: 19-5 Canal; HCM4: Nhieu Loc Canal; HCM5: Lo Gom Canal; HCM6: Tau Hu Canal.

chromatograms obtained by a GC–MS–Scan were treated with an identification and quantification system with a GC–MS database (AIQS-DB) (Kadokami et al., 2005), that can determine the concentrations of the 940 semi-volatile organic compounds (Table S1). Target substances by SIM and SRM quantified by internal standard method were listed in Tables S3 and S5, respectively. If samples were measured by multiple methods (Scan, SIM and/or SRM), we preferentially used results by SRM, next by SIM and lastly by Scan. The method detection limit (MDL) for the substances were estimated from concentration ratio (or, ratio of the dry weight of a sample to the volume of a final concentrate), and the instrument detection limit (IDL) of Scan (Table S1). The MDL of the chemicals in the database was ⩽2ng/g dry-wt. The MDL of the substances measured by SIM was ⩽0.2 ng/g dry-wt and SRM was ⩽0.02 ng/g dry-wt.

2.3. Quality control

Quality controls were performed by blank analysis, reproducibility and repeatability tests and the analysis of a certified reference material (NIST 1941b – Organics in Marine Sediment; National Institute of Standards and Technology, Gaithersburg, MD, USA). Laboratory blank samples were carried out for every batch of six samples for cross-verification. Prior to extraction, sediment and blank samples were spiked with 38 surrogate compounds (Table S6), which have the same range of broad physicochemical properties as found among the SVOCs measured, and were used to assess whether recoveries of surrogates are acceptable or not. Good recoveries (73–126%) were obtained for 23 out of 38 surrogate compounds except for six highly polar compounds, which are poorly extracted with dichloromethane (Kadokami et al., 2012). Two compounds, benzidine-d8, 3,3′-dichlorobenzidine-d6, were not recovered even in blank samples due to oxidative losses

during concentration steps (EPA-8270D, 2007). Six surrogate compounds showed high recovery rates (over 150%) probably due to the matrix effect (Kadokami et al., 2012). Relative standard deviations of 31 surrogates were below 20% (Table S6), confirming that sample analyses were acceptably precise. When reporting data, blank concentrations were subtracted from sample concentrations. The reported concentrations were not corrected for recovery values.

Analytical results of a certified reference material (NIST 1941b) were shown in the previous study (Kadokami et al., 2012). The results were in good agreement with the certified values. Duplicate analyses were performed on the sample from HCM4 (Table S7). The relative average deviations of 152 out of the 158 detected substances were below 20%, indicating that the method produced results with good reproducibility and repeatability and sufficient for environmental surveys.

2.4. Statistical analysis

Statistical analysis was performed using Microsoft Excel 2007 (Microsoft Japan, Tokyo, Japan) and IBM SPSS Statistics Ver. 20 (IBM Japan, Tokyo, Japan).

3. Results and discussion

3.1. Overview

One hundred and eighty-five of the 940 analytes, belonging to 26 different chemical groups were detected at least once (Tables S7 and 1). This number of observations was similar to those (184) observed in sediments in Japan using the same method (Kadokami et al., 2013). The sum of the concentrations of detected compounds varied from 1600 ng/g dry-wt (DN1) to 247000 ng/

Table 1
Sediment concentrations (ng/g dry-wt) and the number of chemicals belonging to different chemical categories and origins at each sampling site.

Origin	Category	HN1	HN2	HN3	HN4	HN5	HP1	HP2	HP3	HP4	DN1	DN2	HCM1	HCM2	HCM3	HCM4	HCM5	HCM6
Agriculture	Insecticides	6.6	0.55	7908	7721	66131	12	29	5.2	0.49	0.02	0.84	3.9	0.84	605	5557	0	2810
	(187)	(7)	(4)	(13)	(12)	(12)	(10)	(9)	(9)	(6)	(1)	(6)	(5)	(6)	(7)	(19)	(0)	(16)
	Herbicides	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	(117)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)
	Fungicides	0.05	0	2.9	3.8	0.79	0	0.02	0	0	0	0	0	0	0.19	1.6	0	1.4
	(112)	(1)	(0)	(1)	(1)	(1)	(0)	(1)	(0)	(0)	(0)	(0)	(0)	(0)	(1)	(1)	(0)	(1)
	Other pesticides	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	(36)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)
Business/household/ traffic	Antioxidants	406	391	447	490	703	254	172	32	177	24	95	284	191	152	629	75	1182
	(8)	(4)	(3)	(4)	(3)	(3)	(4)	(3)	(1)	(3)	(2)	(2)	(3)	(3)	(3)	(4)	(3)	(3)
	Fire retardants	3.8	0	0	115	0	0	0	0	0	0	0	41	0	0	0	0	119
	(13)	(1)	(0)	(0)	(1)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(1)	(0)	(0)	(0)	(0)	(1)
	Disinfectants and insecticidal fumigants	3.5	2.2	38	6.3	35	0.37	0	0.77	1.2	0	0.58	0.86	0.50	13	4.4	0.84	0.64
	(2)	(1)	(1)	(2)	(2)	(2)	(1)	(0)	(1)	(1)	(0)	(1)	(1)	(1)	(2)	(1)	(1)	(1)
	Fatty acid methyl esters	67	7.9	10	210	0	124	296	77	24	3.2	9.0	113	1.4	0	208	19	290
	(34)	(2)	(3)	(2)	(1)	(0)	(2)	(2)	(2)	(3)	(2)	(3)	(3)	(1)	(0)	(1)	(2)	(1)
	Metabolites of detergents	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	(3)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)
	Fragrances and cosmetics	1.3	6.7	72	110	71	0	22	12	0	0	8.0	43	0.99	42	44	0.91	44
	(13)	(1)	(2)	(2)	(3)	(2)	(0)	(1)	(1)	(0)	(0)	(1)	(3)	(1)	(2)	(1)	(1)	(2)
	Leaching compounds from tires	10	0	145	0	174	0	9.0	0	0	0	0	8.8	1.8	39	43	0	0
	(21)	(2)	(0)	(2)	(0)	(2)	(0)	(1)	(0)	(0)	(0)	(0)	(1)	(1)	(2)	(2)	(0)	(0)
	Petroleum	6859	5964	12019	24809	61839	9566	15345	9305	1139	1056	2254	22319	5408	27329	27612	2002	34794
	(26)	(22)	(19)	(23)	(23)	(25)	(18)	(22)	(19)	(15)	(14)	(18)	(22)	(18)	(25)	(24)	(16)	(23)
	Plant or animal steroids	23354	4409	59763	85426	92444	7576	16997	5113	1209	335	1741	12373	2403	46494	79103	3142	83307
	(10)	(9)	(8)	(9)	(9)	(9)	(9)	(9)	(9)	(8)	(9)	(8)	(9)	(9)	(9)	(9)	(9)	(9)
	Plasticizers	4107	764	11886	6880	9983	1659	1939	529	475	177	870	3987	622	8475	8562	1056	6395
	(14)	(6)	(6)	(7)	(7)	(5)	(6)	(5)	(6)	(5)	(4)	(6)	(7)	(5)	(8)	(6)	(8)	(7)
	PPCPs	176	93	210	1361	1094	0	0	0	67	0	70	310	0	0	211	3.5	889
	(19)	(1)	(1)	(1)	(1)	(1)	(0)	(0)	(0)	(1)	(0)	(1)	(1)	(0)	(0)	(1)	(1)	(1)
	Other substances of domestic origin	8.3	0	47	4558	7869	3.7	11	0	6.8	0	7.4	501	0	5263	4112	45	4246
	(29)	(1)	(0)	(1)	(3)	(3)	(1)	(2)	(0)	(1)	(0)	(1)	(2)	(0)	(3)	(3)	(1)	(1)
Industry	Intermediates for dye manufacture	0	0	0	0	0	0	12	0	0	0	0	18	3.1	0	0	0	0
	(24)	(0)	(0)	(0)	(0)	(0)	(0)	(1)	(0)	(0)	(0)	(0)	(1)	(1)	(0)	(0)	(0)	(0)
	Intermediates for resins	0.98	8.2	0	2.5	0	0	0.67	0.57	0	0	0	716	0	3.8	0	0	4.5
	(9)	(1)	(2)	(0)	(1)	(0)	(0)	(1)	(1)	(0)	(0)	(0)	(2)	(0)	(1)	(0)	(0)	(1)
	Intermediates for pesticide manufacture	0	0	0	0.63	0	0	0	0	0	0	0	0	0	0	0.55	0	0.46
	(5)	(0)	(0)	(0)	(1)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(1)	(0)	(1)
	Intermediates in organic synthesis	28	23	88	132	156	13	19	33	0	0	4.9	42	5.9	117	82	8.8	31
	(57)	(3)	(2)	(2)	(3)	(3)	(2)	(2)	(3)	(0)	(0)	(2)	(3)	(3)	(2)	(3)	(2)	(2)
	PAHs	475	2951	1417	3060	5811	661	640	645	35	10	180	1021	364	3025	3305	28	2221
	(50)	(27)	(25)	(26)	(26)	(28)	(25)	(28)	(27)	(22)	(17)	(24)	(24)	(23)	(27)	(27)	(16)	(26)
	PCBs	1.2	0.07	35	42	39	0.40	0.12	0.16	0.08	0	0	4.7	0.64	12	103	N.Q.	57
	(59)	(22)	(3)	(44)	(36)	(40)	(13)	(5)	(4)	(3)	(0)	(0)	(36)	(12)	(32)	(49)	N.Q.	(49)
	PCNs	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	(27)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)
	Solvent	60	33	197	389	542	25	206	10	51	0	62	71	47	189	301	7.7	140
	(11)	(4)	(3)	(4)	(5)	(2)	(2)	(3)	(3)	(1)	(0)	(3)	(5)	(2)	(3)	(3)	(1)	(5)
	Explosives	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	(6)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)
	Other substances of industrial origin	11	1.2	13	702	150	0	1.7	2.1	2.6	0	1.4	30	0	130	243	2.5	185
	(48)	(2)	(1)	(2)	(2)	(2)	(0)	(1)	(1)	(2)	(0)	(1)	(2)	(0)	(2)	(3)	(2)	(3)

Table 1 (continued)

Origin	Category	HN1	HN2	HN3	HN4	HN5	HP1	HP2	HP3	HP4	DN1	DN2	HCM1	HCM2	HCM3	HCM4	HCM5	HCM6
	Total (940)	35577 (117)	14656 (83)	94296 (145)	136019 (140)	247043 (140)	19895 (93)	35701 (96)	15764 (87)	3187 (71)	1604 (49)	5305 (77)	41888 (131)	9051 (86)	91890 (129)	130120 (158)	6392 (63)	136716 (153)

Parentheses show the number of chemicals.
N.Q.: not quantified.

g dry-wt (HN5). Contamination levels in sediments from highly populated urban areas (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). We observed a similar contamination pattern in river water at the same sampling sites (Hanh et al., 2012), clearly indicating the discharge of untreated sewage from municipal areas to the rivers. Cluster analysis of pollutants was carried out on 17 sites using the standardized concentrations of 185 identified compounds. The results highlight clear differences between the sampling sites (Fig. 3). For instance, HN5 is clearly different from other sites, probably due to the extremely high contamination levels. A very tight group composed of the sites located inside city areas (HN1, HN3-4, HCM3-4, and HCM6) implies similar pollution characteristics, while the other suburban sites representing the third group (HN2, HP1-3, DN2, and HCM1-2). Sites HP4, DN1 and HCM5 were identified as a separate group due to their low contaminants concentrations. In addition, the observation of contamination levels and categories of chemicals detected in urban sediments in HN and HCM revealed that, although there is a large latitudinal gap between two cities, a similar pollution profile was still observed in sediments of these cities, perhaps as a result of their similar social features. Low concentration level of urban sediment (HCM5) is the consequence of low volatile organic contents (Table S7).

3.2. Sterols

Nine out of the 10 sterols analyzed were detected in all the sediment samples. Coprostanol, cholestanol and cholesterol appeared at the highest mean concentration values (7100; 4700; 4300 ng/ g dry-wt, respectively) (Table S7). Total sterol concentrations (summed concentrations of 10 analyzed sterols) ranged from 335 (DN1) to 92 400 ng/g dry-wt (HN5) (median 12 400 ng/g dry-wt), and contributed the highest proportion of total detected chemicals in these sediment samples. Elevated concentrations of total sterols were observed in the metropolitan areas (HN3-5, HCM3-4, HCM6) (Fig. 2); these levels are about 2 times higher than those in other Asian developing countries (Isobe et al., 2002), clearly indicating their derivation from untreated municipal sewage.

Coprostanol is an indicator of fecal pollution (Murtaugh and Bunch, 1967) and that a ratio of copostanol to cholesterol (>0.2) indicates sewage (Grimalt et al., 1990) or human feces (>0.3) (Glassmeyer et al., 2005). 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 these studied rivers were seriously contaminated by raw sewage (Quéméneur and Marty, 1994). A higher percentage of coprostanol relative to total sterols (%Cop) indicates greater contributions of fecal matter of human origin to fecal pollution (Hatcher and McGillivary, 1979; Isobe et al., 2002). The %Cop (>20%) was higher in sediments from urban canals (HN1-5, HCM4-6) than those in rural and suburban areas, which suggests the direct input of human feces to urban canals.

3.3. Organochlorine pesticides and current use pesticides

Twenty-five out of the 457 pesticides in the database were detected: 4 current use insecticides (chlorpyrifos, deltamethrin, permethrin-1, permethrin-2), 19 banned insecticides, one fungicide (hexachlorobenzene) and the pesticide synergist, piperonylbutoxide (Table S7). The most frequently detected pesticides were DDT metabolites (more than 80% of samples), followed by lindane (γ-HCH) (60%) and dieldrin (60%).

In terms of currently used pesticides, pyrethroid insecticides (such as permethrin-1 and -2) and their synergist (piperonyl-
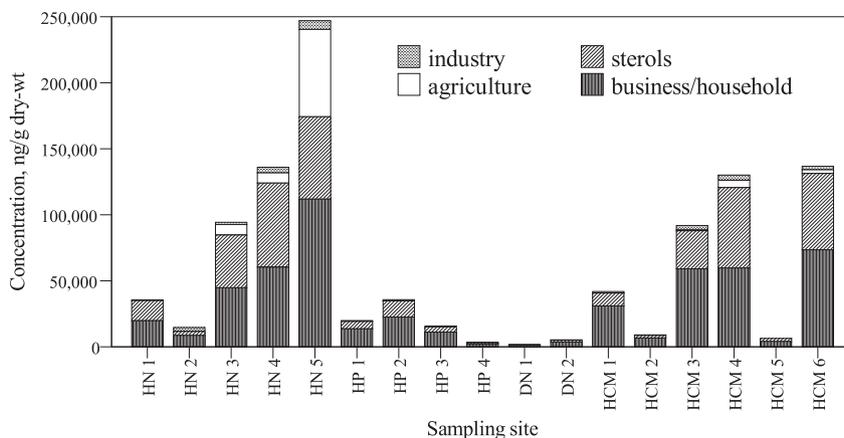
Fig. 2. Concentration (ng/g dry-wt) from different emission sources at each site.
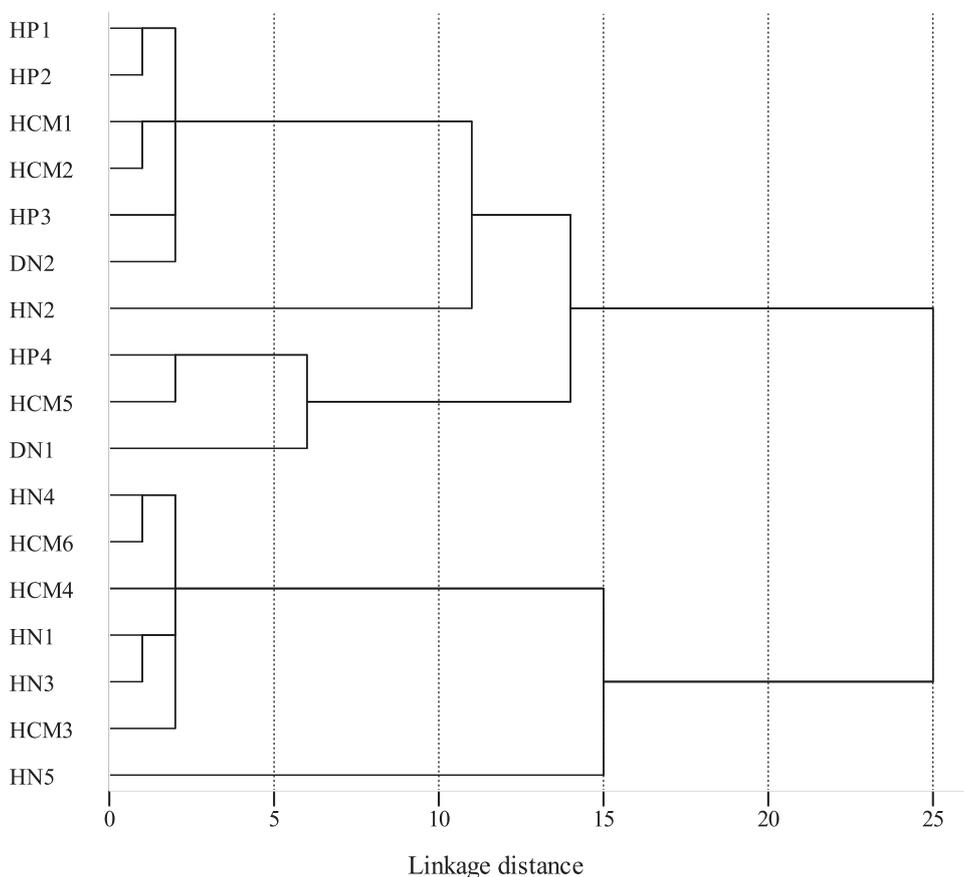

Fig. 3. Hierarchical dendrogram of sampling sites obtained by cluster analysis (Ward's method and squared Euclidean distance) using standardized concentrations of 185 substances at 17 sites.

butoxide) were the most dominant (more than 98% of total detected pesticides, although only found in sediments from urban areas of HN and HCM (Table S7). These results agree well with those observed in water samples in our previous study (Hanh et al., 2012). Pyrethroids are one of the most widely used classes of insecticides for various uses such as agriculture, in the home and/or garden and have been steadily increasing in use in urban areas (Sourlock and Lee, 2008). Since these pyrethroids were found in only the center of HN and HCM, these seem to be used for vector controls such as mosquitoes and flies. An elevated concentration of

deltamethrin was only found at HN5 (60 000 ng/g dry-wt), contributing over 90% of total pesticides in the sample (Table S7). The emission source of deltamethrin is currently unknown, however, it has been hypothesized that the inputs of this compound are due to an accidental release before our sampling, which demonstrates the need for additional monitoring. The high concentrations of pyrethroids observed in stream sediments in USA resulted in the highest pyrethroids toxic units and contributed to sediment toxicity (Kuivila et al., 2012). The pyrethroid contamination levels in sediments in this study were over 70 times higher than those

Table 2
Comparision of organochlorines in Vietnamese sediments with those 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 et al. (2007a)
	2012	4	15–121	1.4–127	1.2–3.1	0.19–1.6	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. (2007b)
	2004	9	0.33–22	0.21–23	<0.01–0.03	<0.001–0.6	0.016–1.0	Minh et al. (2007a)
	2012	2	0.85–5.5	0.34–3.8	0–0.18	N.D.	N.D.	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	0.38–45	0–2.8	0–3.8	0–0.51	Present study
Hanoi (outskirt)	1995–1996	2	2.2–11[g]	7.0–14	–	–	–	Nhan et al. (1998)
	2012	1	1.7	6.0	0.11	0.05	N.D.	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 suburban 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.
N.D.: not detected.
[a] Concentration in ng/g dry-wt.
[b] Sum of 24 PCB congeners (PCB 8, 18, 31, 28, 33, 52, 44, 70, 66, 95, 101, 110, 118, 105, 149, 138, 153, 187, 174, 180, 170, 199, 196, 194) by multiplication with the value of 1.64 [percentage contribution of 24 major congeners (in average = 60.9%) to total PCBs in KC-MIX formulation] (Takasuga et al., 2006).
[c] Sum of 6 DDT isomers (o,p′-DDE, p,p′-DDE, o,p′-DDD, p,p′ DDD, o,p′-DDT, p,p′-DDT).
[d] Sum of 3 HCH isomers (α-HCH, β-HCH, γ-HCH).
[e] Hexachlorobenzene.
[f] Sum of 4 HCLs (trans-chlordane, cis-chlordane, trans-nonachlor, cis-nonachlor).
[g] As alochlor 1254 mixture.
[h] Sum of 7 PCB congeners (28, 52, 101, 118, 138, 153, 180) by multiplication with the value of four (Froescheis et al., 2000).
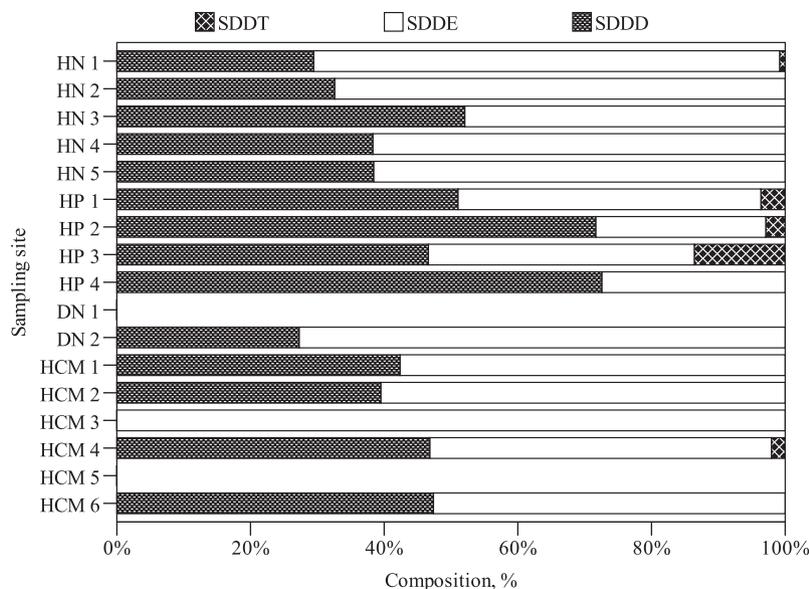

Fig. 4. DDTs composition in sediments at each site. SDDT = o,p′-DDT + p,p′-DDT; SDDE = o,p′-DDE + p,p′-DDE; SDDD = o,p′-DDD + p,p′-DDD.

reported in USA (Kuivila et al., 2012), and so probably pose significant potential toxicity to benthic animals.

An organophosphorus insecticide, chlorpyrifos, was found in agriculture areas close to water supply sources for HP (HP1-3) (Table S7), indicating their wide spread use in paddy fields in Vietnam.

DDT has been used in large quantities for agricultural and public health purposes in Vietnam over the last few decades (Viet et al., 2000), yet DDTs residue levels were highly variable among sampling sites, ranging from not detected (DN1) to 127 ng/g dry-wt (HCM4) (Table S7). This range was similar to those reported by Minh et al. (2007b) (<0.01–110 ng/g dry-wt). The DDTs levels in

the sediments in this study were several times lower in comparing with those in early 1990s (Table 2). The risk assessment of these compounds was carried out based on the guidelines issued by The Canadian Council of Ministers of the Environment (CCME, 2002). Accordingly, nine urban sediments in the present study exceed the Probable Effect Level (PEL) value and three had levels over the Interim Sediment Quality Guideline (ISQG) for DDD and DDE (Table S8). This implies there is a potential risk from DDTs to aquatic organism in the rivers. The ratios of the three major compounds, DDT, DDE, and DDD, can be used to understand the chronology of input of DDT in the environment. For instance, the ratio of DDT/DDE can be used to indicate recent input of DDT (>0.5) or past input (<0.3) (Strandberg et al., 1998). In addition, the ratio of (DDE + DDD) to total DDTs ((DDE + DDD)/ΣDDTs) can be used to indicate old DDTs residues (>0.5) or recent input (<0.5) (Hong et al., 1999; Zhang et al., 1999). In this study, the high proportion (>80%) of DDE and DDD to ΣDDTs (Fig. 4) in conjunction with the ratio of (DDE + DDD)/ΣDDTs and DDT/DDE were higher than 0.5, and less than 0.3, respectively, clearly demonstrating that there have been no recent inputs of DDT in the study areas.

The spatial distribution of HCHs was similar to that of DDTs. Total HCHs concentration (ΣHCHs) ranged from not detected (HN2, HP4, DN1-2, HCM1) to 3.1 ng/g dry-wt (HCM6), which is around 20 times lower than ΣDDTs (Table 2). Although the concentrations of ΣHCHs in HN and HCM appear to have decreased from 1990 to 2004, their concentration in some sediment samples was still higher than those reported in 2004 (Table 2), suggesting recent input of HCHs to the environment. On a global scale, the highest ΣHCHs concentrations in urban sediments in HN and HCM was comparable with those in Thailand, whilst less than half of those reported in Japan and India, and much higher than those in Indonesia and Taiwan (Table 2).

Lindane (γ-HCH), an insecticide available in Vietnam under the trade name of "666" (Nhan et al., 2001) was found at higher concentration compared to other HCH isomers in sediments (Table S7). In particular, four sediments had γ-HCH values beyond the ISQG and three of them had values exceeded PEL (CCME, 2002) (Table S8), again suggesting recent use of lindane and potential toxicological stress on aquatic biota of the rivers.

Similar to HCHs compounds, the concentration levels of drins (aldrin, endrin and dieldrin) were low compared with DDTs in this study (Table S7). Aldrin, endrin and dieldrin were sporadically found in some sampling sites. Total drins concentrations appear higher in HCM than those in HN, perhaps due to the highly use amount of drins in HCM than HN. However, further work is required to test the hypothesis that there are differencies in contamination levels between two cities. The concentration of dieldrin at two urban sediments (HN3 and HCM4) was slightly higher than the ISQG (Table S8), again suggesting the potential risk of dieldrin to aquatic organism in the rivers.

3.4. Polychlorinated biphenyls

The cluster analysis was carried out on 9 sites (except for DN1-2, HCM5 that PCBs was not detected and HN2, HP2-4, HCM2 that showed less PCB congeners detected) using composition ratios of 24 PCB congeners of 5 commercial formulations reported by Takasuga et al. (2006) (Fig. S1). As the result, all analyzed sites are classified into the same group of KC-MIX, which indicates the inputs of PCBs into the environment possible originated from technical KC-MIX mixture. An estimation of the total PCB burden (ΣPCBs) of sample was calculated by the multiplication of the sum concentrations of 24 congeners by a factor of 1.64 (percentage contribution of 24 congeners (in average = 60.9%) to total PCBs in KC-MIX formulation).

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) (Table S8). PCBs levels in urban areas of HN and HCM were almost 100 times higher than those from rural areas, which suggested that the metropolitan areas are the major sources of PCBs pollution to the river. Comparing the ΣPCBs values with the Canadian Environmental Quality Guideline for protection of aquatic life (CCME, 2002), it showed that concentrations of 5 out of 17 sediments are much higher than the ISQG values (Table S8), suggesting possible toxicological effect caused by PCBs contamination in the sediment of these rivers.

In urban areas of HN, PCBs levels were comparable to those in previous study in 1997 (Nhan et al., 2001), but lower than observed in 2006 (Hoai et al., 2010) (Table 2). A similar trend in PCB contamination was also observed in HCM where urban areas had extremely high PCBs levels compared to those in suburban areas (Table S8). PCB concentrations in urban areas and outskirts of HCM were around 2 times lower than those reported in 2004 (Minh et al., 2007a), whilst over 5 times lower compared to early 1990s (Iwata et al., 1994) (Table 2), which implies a decreasing trend of PCBs in the river system in HCM.

In global scale, PCBs levels in the city's canals of HN and HCM were similar to those reported in the Minjiang River (Zhang et al., 2003), but more than 20 times higher than those reported in the Pearl River estuary (China) (Table 2). However, the present range of PCBs in Vietnamese sediments was several times lower than those in sediments collected in other Asian countries in 1990s (Iwata et al., 1994) (Table 2). This trend implying the local source of PCBs in Vietnam is less than the other above countries. However, since greater residues were occasionally found in some places, point sources of PCBs in Vietnam are still remaining.

3.5. Polycyclic aromatic hydrocarbons

Twenty-eight PAHs were detected, with mean total PAHs concentrations (except for perylene which is naturally occurring (Hites et al., 1980; Boonyatumanond et al., 2006)) in HN, HP, DN and HCM being 2700, 500, 100 and 1700 ng/g dry-wt, respectively (Table S7). Total PAHs in urban areas (median 3000 ng/g dry-wt) were higher than those in outskirts (median 420 ng/g dry-wt). The concentrations of naphthalene, acenaphthene, fluorene, phenanthrene, benzo(a)anthracene, chrysene and triphenylene, fluoranthene, pyrene and benzo(a)pyrene in six sediments located in urban sites were extremely high, exceeding the ISQG values for protection of aquatic life (Table S8). These results demonstrate the toxicological stress of these compounds on aquatic biota in the rivers and require further monitoring for sediments observed at greater values than ISQG.

The composition profiles of 2- to 6-ring aromatic PAHs (except for perylene) in the 17 sediment samples were similar among the sites (Fig. S2), while obviously different from those detected in waters (Hanh et al., 2012). 2- and 3-ring PAHs were the most abundant in water samples whilst in sediments, the composition of 2- to 5-ring PAHs varied. This probably due to the concentration of smaller molecular PAHs gradually decreasing by degradation and evaporation in the high temperatures of a tropical region, such that only large molecular PAHs are sufficiently resistant to degradation that they can survive to reach the sediment bed (Guo et al., 2007).

Ratios of methylphenanthrene isomers to phenanthrene (ΣMPs/P) above 1.6 were observed in high densely populated areas, such as HN2-5, HCM3 and HCM6 (Table S9-1), indicating that PAHs pollution was mainly caused by uncombusted petroleum (i.e. of petrogenic origin) (Zakaria et al., 2002). This is probably a common phenomenon in Southeast Asia countries because petrogenic PAHs inputs to urban sediments were also observed

in Malaysia and Thailand (Zakaria et al., 2002; Boonyatumanond et al., 2006). Whereas, values of ΣMPs/P less than 1 were observed in suburban and rural areas, such as HN1, HP1-3, DN2 and HCM2 (Tables S9-1 and S9-2), suggesting the pyrogenic PAHs inputs (Zakaria et al., 2002). This result agrees well with previous research (Kishida et al., 2007), which indicates the combustion of fossil fuels and/or biomass such as rice straw after harvest is probably major sources of pyrogenic PAHs in rural and suburban areas. Similar findings were also observed with fluoranthene/pyrene (Flu/Pyr) and fluoranthene/(fluoranthene + pyrene) (Flu/(Flu + Pyr)) ratios (Tables S9-1 and S9-2). However, some inner city sites (HN3-5 and HCM3-6) showed the values of Flu/(Flu + Pyr) between 0.4 and 0.5, suggesting the existence of liquid fossil fuel (vehicle and crude oil) combustion (Yunker et al., 2002).

Since HN and HCM are well known to have the highest private vehicle density (especially motorcycle) in Vietnam, the leakage of refinery products (such as gasoline, diesel fuel and fuel oil) from urban vehicle traffics and/or small scale vehicle maintenance facilities were considered to be the main contributors to petrogenic PAH inputs in these canals via surface runoff. However, the pyrogenic PAH inputs in the city canals are considered due to vehicle exhaust gases from motorcycles.

3.6. Emerging chemicals

Of the 7 phthalate compounds (PHCs) detected (Table S7), the two most widely used compounds in industrial production (di(2-ethylhexyl)phthalate (DEHP) and di-n-butyl phthalate (DBP)) (Vitali, 1997) were found in almost all of the sediments at significant levels (Table S7). Total PHCs (ΣPHCs) concentration ranged from 180 to 11 000 ng/g dry-wt, with an average value of 3900 ng/g dry-wt. This latter value is over 4 times higher than alluvial sediment in JiangHan, China (927 ng/g dry-wt) (Liu et al., 2010). Considering ΣPHCs concentration calculated for each sediment sample, it appears evident that the high concentration of

PHCs in urban areas (HN3-5, HCM3-6) is related to the input of urban untreated wastewaters. In addition, DEHP, an endocrine disrupting chemical, (Akingbemi et al., 2004) has a mean concentration (3400 ng/g dry-wt) over 10 times and 20 times higher than those in JiangHan, China (329 ng/g dry-wt) (Liu et al., 2010) and in Italy (161 ng/g dry-wt) (Vitali, 1997). When compared with the soil cleanup guidelines used in New York, USA, the concentration of DEHP in 6 out of 17 sediments exceeded the recommended allowable values (4350 ng/g dry-wt).

Bisphenol A (BPA), 4-tert-octylphenol (OP) and nonylphenol (NP) have confirmed the estrogenic potential even at low concentrations (Jin et al., 2004). The high concentrations of these compounds in sediments are associated with metropolitan areas, while low concentration associated with rural areas (Table S7). This pattern suggests that BPA, OP and NP pollution is caused by urbanwaste discharge possibly due to the increasing population densities and lack of adequate wastewater treatment facilities, (Peng et al., 2007). The concentration of NP was enriched in sediments collected from urban areas (HN4-5, HCM3-4, HCM6), probably due to the wide range of contamination sources and heavy use of household products (detergent) near these sites. NP levels (not detected to 7800 ng/g dry-wt) appeared to be much higher than those reported in sediments from Jiao Zhou bay, China (3.6–299 ng/g dry-wt) (Fu et al., 2007) and Okinawa and Ishigaki Island, Japan (not detected to 44 ng/g dry-wt) (Kawahata et al., 2004), while comparable to those of Pearl River Delta, China (59–7808 ng/g dry-wt) (Chen et al., 2006).

Of the 14 PPCPs analyzed, triclosan, L-menthol and squalane were found in the sediment samples. Elevated concentrations of PPCPs were observed at HN4-5 and HCM6 (Table S7), implying the discharge of untreated domestic wastewater to the rivers. Squalene, which has application in numerous vaccine and drug delivery emulsions (Fox, 2009), was observed at 9 out of 17 sediment samples, while triclosan and L-menthol were only found at HCM4 and HCM5, respectively (Table S7). Caffeine, the most
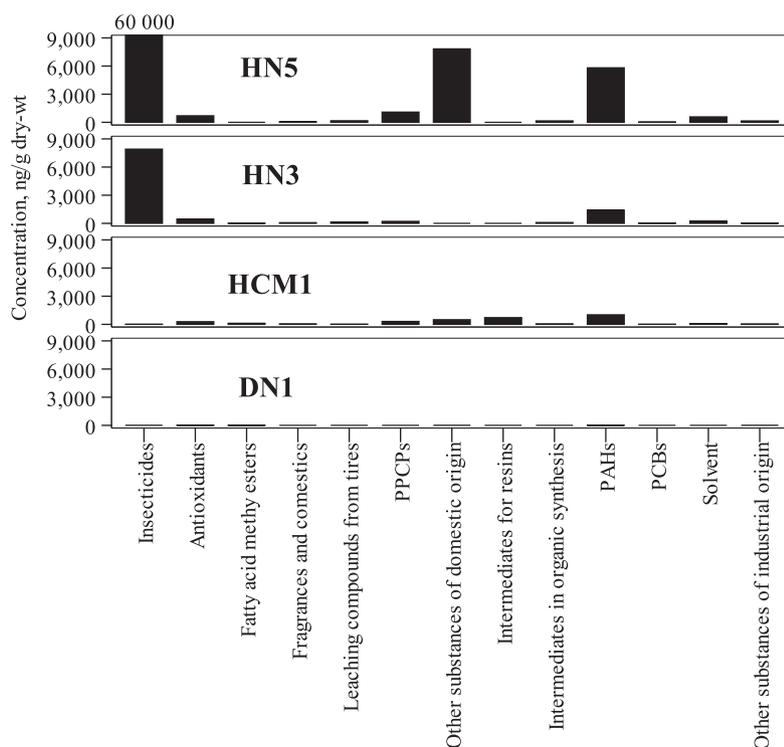

Fig. 5. Typical pollution profile of four rivers. Pollution profile is a graph composed from 13 groups summed up by concentrations of compounds categorized by usage or type. Figure above a column is concentration (ng/g dry-wt).

dominant compound, was found at nearly 100% of water samples (Hanh et al., 2012), but none of the sediment samples. The high solubility (13.5 g/L), low octanol–water partition coefficient (log-Kow = 0.01) (Ferreira, 2005) and microbial degradation (Nakada et al., 2008) of caffeine may act against the adsorption to sediment layer. However, since caffeine has been found in metropolitan's ground water (Nakada et al., 2008), the leakage of caffeine contributes to the ground water contamination. Therefore, it is required to conduct a detailed monitoring on caffeine and other highly soluble compounds in ground waters in Vietnam.

3.7. Pollution characteristics between sampling sites

The 17 sampling sites can be divided into four major groups (Fig. 3). The first group has one site (HN5) and is remarkably different from other 16 sites. The pollution profile of HN5 demonstrates that the river was seriously polluted by chemical originated from domestic sources, such as insecticides (pyrethroid compounds), PAHs (originated from traffic activities), and other substances of domestic origin. The source of the extremely high concentration of deltamethrin (60 000 ng/g dry-wt) is currently unknown, and requires further detailed research. The second group includes inner city sites (HN1, HN3-4, HCM3-4, and HCM6). The third group includes the sites mainly located in suburban areas (HN2, HP1-3, DN2, and HCM1-2), and the remaining sites were distinguished into the fourth group. A pollution profile was created for a representative river in each group by summing up the concentration of compounds categorized by usage into 13 typical groups (Fig. 5). Sterols compounds were excluded in the pollution profile due to their wide spread existence in sediment samples. HN3, a representative site of second group, was mainly contaminated by insecticides (pyrethroid compounds), antioxidants and PAHs. Chemicals in this group may be regarded as typical of pollution of urban areas, where insecticides are commonly used for vector controls, such as mosquitoes and flies. The high density of private vehicles, especially motorcycles, is a source of petrogenic PAH. A representative site of the third group (HCM1) is located in suburban area, and while it has less contamination, is considered to have mixture of industrial and domestic contamination. The pollutants at this site were composed of chemicals used as intermediates for resins, PAHs, PPCPs and other substances of domestic origin. The general characteristics of the fourth group, as represented by DN1 are low concentration of pollutants associated with fewer detected contaminants due to low volatile organic contents in sediment samples (Tables 1 and S7).

4. Conclusions

This paper presents the first comprehensive study on a wide spectrum of organic micro-pollutants in river sediments in Vietnam and in doing so provides important baseline data. Important findings derived from our results are as follows: (1) 185 analytes of the detected, or 20% of the substances analyzed, are the same as those found in developed countries; (2) extremely high concentrations of domestic chemicals, including fecal sterols, were found in the center of big cities, the dominant source being untreated domestic wastewater; (3) high concentrations of pyrethroid insecticides were found in the center of big cities, indicating that these insecticides are widely used in urban areas in Vietnam for hygienic purpose; (4) OCPs and PCBs that were banned several decades ago are still detected, mainly big cities, but their concentrations were low compared with those of previous studies; (5) the levels of PAHs were high in urban areas and low in suburban areas. Contamination source of PAHs in urban areas is mixed from pyrogenic and petrogenic inputs, whilst pyrogenic PAHs was the major source of PAHs in suburban and rural areas.

From these results, it was concluded that the pollutants that are detected in developed countries pollute throughout Vietnam, but their concentration levels are much higher than developed countries due to lack of wastewater treatment facilities. This in turn suggests an urgent need for the construction of sewerage systems and other wastewater treatment systems in Vietnam, particularly in the major cities. In addition, since the concentrations of some compounds exceed Canadian Environmental Quality Guideline values for protection of aquatic life, a detailed study on their effects on the aquatic ecosystems is needed.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2014.01.064.

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