

Screening analysis of a thousand micro-pollutants in Vietnamese rivers

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ABSTRACT

This study provides the first detailed information on 950 organic micro-pollutants in Vietnamese rivers. Water samples were taken from 21 rivers and canals flowing through four big cities (Hanoi, Haiphong, Danang and Ho Chi Minh) between March 2011 and February 2012, and analyzed by a comprehensive gas chromatography-mass spectrometry database analytical method. The number of detected chemicals ranged from 29 to 103 (median 61 out of 950), with 235 analytes detected at least once. The highest concentrations of polycyclic aromatic hydrocarbons, polychlorinated biphenyls, sterols, pharmaceuticals and personal care products (PPCPs) and pesticides were observed in rivers in Hanoi and Ho Chi Minh, indicating that the development of these cities with high population and dense industrial zones results in heavy pollution of rivers with untreated wastewater. Sterols (coprostanol, cholesterol) and PPCPs (caffeine, L-menthol) were found in almost 100% and 70% of samples, respectively. Fenobucarb, an insecticide used in paddy fields, was the most frequently detected pesticide (84%). Some banned pesticides, such as hexachlorocyclohexanes and chlordanes were also detected. By determining such a large number of chemical concentrations, the pollution status of these Vietnamese rivers was clarified, indicating that rivers and canals were heavily polluted by domestic chemicals. The adverse effects of these chemicals on aquatic organisms should be examined in both urban and rural rivers.

Keywords: GC-MS, AIQS-DB, micro-pollutants, comprehensive analysis, river water

INTRODUCTION

Vietnam has experienced rapid development accompanied with extensive changes in its social and economic structure. Urbanization and industrial expansion lead to increase in industrial and municipal wastes, and especially, contaminations of water systems with compounds released from domestic, industrial and agriculture sources into the environment (Nhan *et al.* 2001, Duong *et al.* 2008). This has turned some rivers, particularly rivers in city areas, into open sewers receiving mainly domestic wastewater discharged in the cities (Pham *et al.* 2010). Domestic chemicals, such as pharmaceutical and personal care products (PPCPs) and sterols have become a matter of concern in Vietnam because its population is growing rapidly without establishing proper wastewater management systems (Takada *et al.* 2002). Investigations on organic micro-pollution in Vietnam have been carried out in different environmental compartments (water, soil, sediment, food and biota), although the number of chemicals studied is limited, mainly focusing on specific chemical classes such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs) or dioxins (Iwata *et al.* 1994; Schecter *et al.* 1989, 2001; Kishida *et al.* 2001; Nhan *et al.* 2001; Hung & Thiemann, 2002; Toan *et al.* 2007; To *et al.* 2007). However, a large number of chemicals are expected to contaminate the environment, and no research has been conducted to grasp a whole pollution picture of organic pollutants in Vietnamese aquatic environment. In response to this situation, a comprehensive survey on nearly 1000 organic micro-pollutants in rivers throughout Vietnam was carried out. To achieve this, the combination of an automated identification and quantification system with a gas chromatography-mass spectrometry (GC-MS) database (AIQS-DB) and a developed comprehensive analytical method to fully utilize the AIQS-DB was used.

MATERIALS AND METHODS

Sample collection

In the dry (March, 2011 and February, 2012) and the rainy (October, 2011) seasons, 58 water samples were collected at 21 rivers and canals in towns, suburban districts and the center of four big cities: Hanoi, Haiphong, Danang and Ho Chi Minh (Fig. 1). Sampling sites were selected that were representative of points that receive water discharged from human activities in the survey areas. Surface water at the center of a stream were sampled from a bridge by scooping the water with a stainless steel bucket and then transferring the sample into a glass bottle (1 L) previously washed successively with detergent, purified water, acetone and hexane. The bottles containing water samples were kept in an ice-box and were transported to a laboratory. Water samples were stored in the dark at a temperature of 4°C and extracted within 2 weeks after sampling.

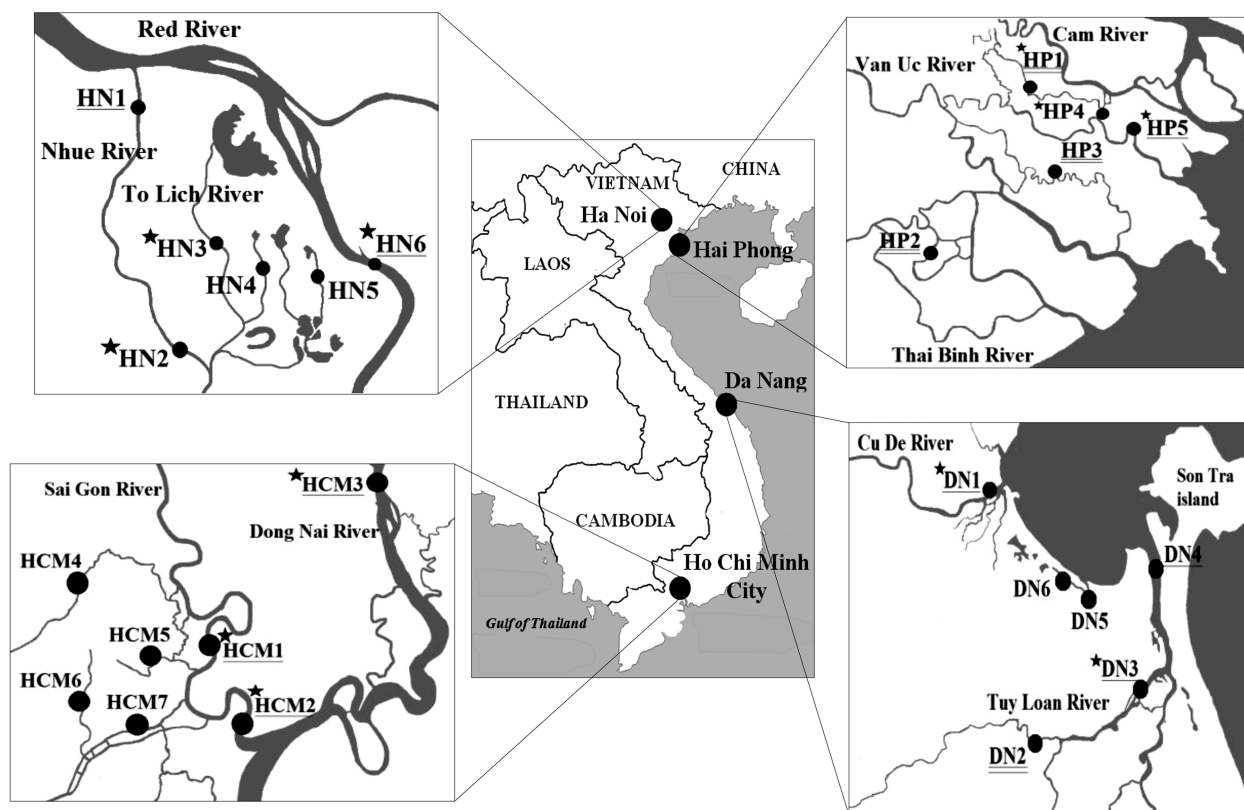


Figure 1 Location of 24 sampling sites in Hanoi, Haiphong, Danang and Ho Chi Minh City. [HN1, HN2: Nhue River; HN3: ToLich River; HN4: Lu River; HN5: KimNguu River; HN6: Red River; HP1: Re River; HP2: ChanhDuong River; HP3: DaDo River; HP4: TamBac River; HP5: LachTray River; DN1: Trang River; DN2: TuyLoan River; DN3: CamLe River; DN4: Han River; DN5, DN6: PhuLoc Canal; HCM1, HCM2: SaiGon River; HCM3: DongNai River; HCM4: 19-5 Canal; HCM5: NhieuLoc Canal; HCM6: LoGom Canal; HCM7: TauHu Canal. Sites located in suburb and rural areas are indicated with a single and double underline whereas sites located in urban areas are indicated without an underline. Star symbols point out the sites that were sampled 3 times (March, October 2011 and February 2012).].

Chemical analysis

After the addition of 30 g of sodium chloride (pre-heated at 700°C for 6 hours) to a 1-L of sample, the pH of the sample was adjusted at 7.0 with a phosphate buffer. The sample was extracted three times with 100 ml, 50 ml and 50 ml of dichloromethane for 10 min each. Extracts were combined and dehydrated by passing through an anhydrous sodium sulfate column, then concentrated to approximately 5 ml. Hexane (20 ml) was added to the concentrate and the mixture was re-concentrated to 5 ml; this procedure was repeated twice. The extract was finally concentrated into 1 ml under a gentle nitrogen stream, and internal standards (Restek, Bellefonte, PA, USA) were added to the final concentrate. Instrumental analysis was done with two GC-MS systems: GC-MS and GC-MS-MS.

The 950 substances in the AIQS-DB system were measured using a GC-MS by selected and total ion monitoring (SIM/TIM) (QP 2010 Plus, Shimadzu, Kyoto, Japan). The GC-MS conditions were as described previously (Kadokami *et al.* 2009). The method detection limits (MDL) of PAHs, OCPs, sterols and PCBs measured by SIM were 1 ng/l, 2 ng/l, 8–320 ng/l and 0.4–1.6 ng/l, respectively. The MDL of the remaining compounds measured by TIM were 5 to 500 ng/l.

Quantitative analysis of PCBs and OCPs was carried out by a GC-MS-MS (TSQ Quantum GC; Thermo Scientific, Waltham, USA) with selected reaction monitoring (SRM) because some chemicals cannot be measured correctly by SIM due to effects of interference substances. The GC conditions were the same as those of GC-MS-SIM/TIM. The MDL of PCBs and OCPs were 0.4–1.6 ng/l and 0.1–16 ng/l, respectively.

Quality control

The accuracy of individual sample analysis was checked by examining the recoveries of 38 surrogates (deuterium-labeled internal standards), which were chosen as being representative of the 950 compounds based on their physico-chemical properties. In this study, good recoveries (70% to 127%) were obtained for most surrogates except for highly polar compounds such as phenols and amines, which are difficult to extract with dichloromethane. The relative standard deviations (RSDs) of the recoveries were below 21%. These results were confirmed that all the sample analyses were done correctly. Blank samples were processed regularly for every set of 10 samples using 1-L of purified water previously washed successively 3 times with dichloromethane (50 ml each). When reporting data, blank concentrations were subtracted from sample concentrations.

RESULTS AND DISCUSSION

Overview

Two hundred and thirty-five substances of a variety of chemical groups were detected at least once (Table 1), with the number of compounds detected higher in the rainy season (198) than in the dry season (177). This number of observations was higher than that observed in streams in Japan using the same method (188; Kadokami *et al.* 2009). The rivers in Hanoi (HN2 to 5) and Ho Chi Minh City (HCM4 to 7) produced the largest number of detected compounds as well as the highest concentrations (Fig. 2). Sterols were the most abundant compounds, contributing more than 40% of total concentrations at most sites. Chemicals from domestic sources were dominant in comparison with those from agricultural and industrial sources. This finding implies that untreated wastewater from domestic sources in highly populated urban areas was the main cause of river pollution.

Sterols and caffeine

Of the 10 sterols analyzed, β -sitosterol, campesterol, cholesterol, coprostanol, and coprostanone were the most abundant, being observed in nearly 100% of samples. The sum of sterol concentrations ranged from 0.39 $\mu\text{g/l}$ (DN4) to 669 $\mu\text{g/l}$ (HN3) with a mean value (42.6 $\mu\text{g/l}$). The maximum concentrations of total sterols were around 2 times higher than those in Mekong Delta and about 10 times higher than in Tokyo (Takada *et al.* 2004). The canals flowing through dense population centers (e.g., Hanoi: HN2–5 and Ho Chi Minh: HCM4–7) were extremely polluted, suggesting that they are derived from sewage.

Coprostanol was first suggested as an indicator of fecal pollution in the late 1960s (Murtaugh & Bunch, 1967) and has been used as a powerful molecular marker for fecal pollution monitoring in several environmental matrices (Eganhouse *et al.* 1988; Leeming *et al.* 1996). The highest concentrations of coprostanol (189 and 53.2 $\mu\text{g/l}$) were observed at sites located inside Hanoi and Ho Chi Minh (HN3 and HCM6). The contamination levels were higher than those in Japan in the 1970s (24.0 $\mu\text{g/l}$; Itoh & Tatsukawa, 1978), and much higher than in other urban centers worldwide (Takada *et al.* 2002). The ratio of coprostanol to cholesterol can be used to indicate sewage (>0.2) (Grimalt *et al.* 1990) or human feces (>0.3) contamination (Glassmeyer *et al.* 2005). In this study, coprostanol to cholesterol ratios over 0.8 were found in canals in Hanoi and Ho Chi Minh, with the high ratio confirming that human feces were discharged to the canals without treatment.

Caffeine has been detected in wastewater, surface water and groundwater worldwide (Buerge *et al.* 2003, 2006). This ubiquitous compound has been identified as an anthropogenic marker for wastewater contamination of surface waters or as an indicator of untreated wastewater (Nakada *et al.* 2008). Caffeine was found in 57 out of 58 samples at concentrations up to 91.6 $\mu\text{g/l}$ (HN3, dry season). These concentrations were higher than maximum concentrations in Germany (0.13 $\mu\text{g/l}$; Prösch & Puchert, 1998) and Greece (0.16 $\mu\text{g/l}$; Patsias and Papadopoulou-Mourkidou, 2000). The distribution of caffeine in the aquatic environment in Vietnam is likely to correlate with population density; therefore, urban areas (Hanoi and Ho Chi Minh) were expected to be hotspots of such contamination due to the lack of wastewater treatment facilities. The high detection frequency of caffeine (98%) and coprostanol (100%) with high concentrations at most sites again verified that wastewater from domestic sources is a major cause of pollution in the rivers.

Pesticides

Thirty-eight out of the 457 pesticides in the database were found: 25 insecticides, 5 herbicides and 8 fungicides (Table 1). The most frequently detected pesticide was fenobucarb, a carbamate insecticide widely used in paddy fields in Vietnam, followed by metabolites from dichlorodiphenyltrichloroethane (DDT) (above 31%). Several organochlorine insecticides

Table 1 Concentrations ($\mu\text{g/l}$) of chemicals categorized by use or origin.

Origin	Category	No. ^a	Rainy season		Dry season		
			No. ^b	Concentration, Mean (range)	No. ^c	Concentration, Mean (range)	
Agriculture	Insecticides	25/186	18	0.01–9.84 (2.70)	14	0.01–12.1 (1.58)	
	Herbicides	5/120	3	0.01–0.31 (0.07)	3	0.008–1.68 (0.25)	
	Fungicides	8/117	6	0.01–2.79 (0.37)	4	0.02–4.71 (0.44)	
	Other pesticides	0/34	0	0	0	0	
Business Household	Antioxidants	2/7	2	0.03–0.52 (0.11)	1	0.01–0.87 (0.24)	
	Fire retardants	2/13	2	0.01–1.17 (0.26)	2	0.01–0.93 (0.10)	
	Disinfectants and insecticidal fumigants	3/4	0	0	3	0.01–267 (41.8)	
	Fatty acid methyl esters	2/36	0	0	2	0.01–0.10 (0.03)	
	Metabolites of detergents	0/3	0	0	0	0	
	Fragrances and cosmetics	4/9	4	0.01–7.25 (1.64)	4	0.01–45.9 (3.57)	
	Leaching compounds from tires	11/23	10	0.01–16.9 (2.47)	0	0.01–38.5 (3.05)	
	Petroleum	26/26	26	0.27–86.2 (12.2)	24	0.13–113 (11.1)	
	Plants and animal steroids	10/10	10	0.39–131 (31.7)	10	1.05–669 (50.4)	
	Plasticizers	8/13	8	0.69–25.8 (10.2)	7	0.35–111 (12.2)	
	PCPPs	10/14	7	0.03–32.5 (7.84)	9	0.06–159 (11.0)	
	Other substances of domestic origin	7/34	4	0.01–19.8 (2.34)	3	0.01–19.8 (7.10)	
Industry	Intermediates for dye manufactures	6/26	5	0.01–7.95 (1.14)	2	0.02–0.53 (0.27)	
	Intermediates for resins	4/11	3	0.01–5.39 (1.28)	3	0.01–3.71 (0.74)	
	Intermediates for pesticides manufactures	2/6	1	0.55	1	0.01–0.02 (0.01)	
	Intermediates in organic synthesis	19/59	15	0.03–45.9 (4.40)	13	0.001–34.3 (2.03)	
	PAHs	33/47	31	0.01–4.14 (0.88)	24	0.001–4.56 (0.44)	
	PCBs	36/62	33	0.0004–0.013	28	0.0005–0.017	
	PCNs	0/28	0	(0.004)	0	(0.004)	
	Solvents	7/17	6	0	7	0	
	Explosives	0/6	0	0.05–16.7 (4.74)	0	0.01–48.2 (4.32)	
	Other substances of industrial origin	5/39	4	0	4	0	
	Total		235/950	198	0.001–0.13 (0.03)	177	0.002–0.20 (0.02)

^aThe number of compounds detected at least once per the number of target compounds.

^bThe number of compounds detected in the rainy season (October 2011).

^cThe number of compounds detected in the dry season (March 2011 & February 2012).

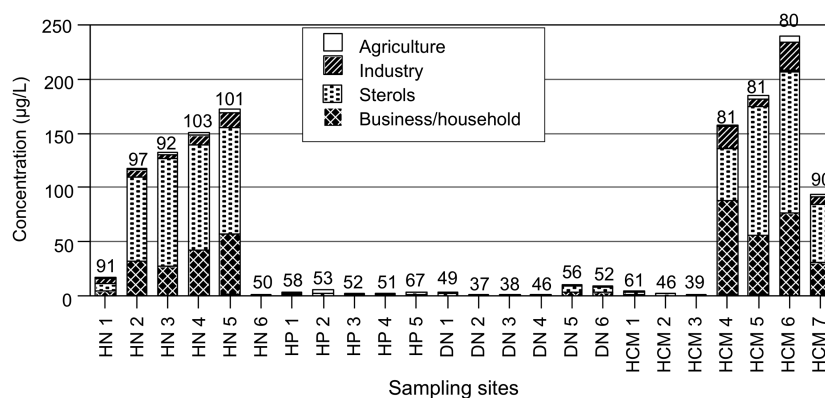


Figure 2 Concentrations and compounds categorized by origin at each site (rainy season). [n-Alkanes and phthalates were excluded because these compounds were detected in reagent blanks. Figures above each column show the number of compounds detected. Contents of origins are referred to category in Table 1].

that have been banned from use in Vietnam since 1990s (Hung & Thiemann, 2002), including the hexachlorocyclohexane (HCHs), drins, DDTs, chlordanes and heptachlor, were detected in some survey samples, but their concentrations were one-twentieth of those reported by Hung and Thiemann (2002) and were much lower than the allowable limit of Vietnamese standard for surface water (QCVN 08:2008/BTNMT/category B1) (Table 2).

Table 2 Temporal trend of banned pesticides (ng/l).

Location	Year	n	HCHs	Drins	DDTs	Reference
Red river						
	1990	1	3.2	–	0.68	Iwata <i>et al.</i> (1994)
Dry season	1998/1999	11	28.3	27.4	65.7	Hung and Thiemann (2002)
Rainy season		11	29.8	23.8	48.6	
Dry season	2011/2012	1	ND	(0.33)	(0.10)	This study
Rainy season		1	ND	ND	ND	
Irrigation canals						
Dry season	1998/1999	6	7.19	11.4	58.6	Hung and Thiemann (2002)
Rainy season		6	17.3	11.0	49.7	
Dry season	2011/2012	5	(1.01)	(0.24)	1.34	This study
Rainy season		5	(0.66)	ND	1.94	
QCVN 08:2008/BTNMT (B1)			130 ^a	8 ^b	4 ^c	

n: the number of sample; ND: not detected; '()': trace concentration (below detection limit); HCHs: sum of α -, β -, γ -, δ -HCH; Drins: sum of aldrin, dieldrin, endrin; DDTs: sum of p,p'-DDE, o,p'-DDE, p,p'-DDD, o,p'-DDD, p,p'-DDT, o,p'-DDT. QCVN 08: 2008/BTNMT: National technical regulation on surface water quality. a: regulation of HCHs; b: regulation of (aldrin+ dieldrin); c: regulation of DDTs. These values are for Category B1 applied to surface water used for irrigation.

Although its metabolites were detected at relatively high concentrations, DDT was not found in any of the sampling sites. The causes of the absence of DDT could be attributed not only to natural decrease such as dilution, degradation, washout and evaporation, but also to the reduction of emission of DDT in the study areas.

In terms of currently used pesticides, permethrin and its synergist (piperonyl butoxide) were the most dominant compounds, contributing more than 55% to total pesticide concentrations in urban areas such as Hanoi (HN1 to HN5) and Ho Chi Minh (HCM4 to HCM7). The highest concentration of permethrin-1 was found at HCM6 (4.39 $\mu\text{g/l}$) followed by HN3 (3.30 $\mu\text{g/l}$), HN5 (2.17 $\mu\text{g/l}$) and HCM5 (1.89 $\mu\text{g/l}$), indicating that they were used for hygiene purposes rather than crop protection. Sites HP1, HP2 and HP3 located in paddy fields and near to water supply sources for Haiphong City were contaminated by some pesticides (14, 15 and 8 pesticides, respectively). Therefore, it is imperative to conduct a detailed survey of pesticides in tap water.

A larger number of pesticides (27) were detected in the rainy season than in the dry season (21), particularly in rural rivers (HP1–3), which may reflect that these pesticides were applied to areas near the sampling sites before sampling. Since storm-water run-off contains many kinds of chemicals (Zgheib *et al.* 2011) and a large number of pesticides has indeed been reported in storm-water drain in developed countries (Phillips & Bode, 2004), intense rainfalls in Vietnam may bring various pollutants (including pesticides) to the receiving canals.

Pharmaceuticals and personal care products

A wide variety of PPCPs are used for humans, veterinary medicine, agriculture and aquaculture (Laville *et al.* 2004). Recent studies have reported the occurrence of various PPCPs in surface, drinking and ground water as well as in soil and sediments (Kim *et al.* 2009; Nakada *et al.* 2008). This implies a widespread occurrence of PPCPs in the environment and is raising concerns among chemists and toxicologists regarding their potential environmental fates and effects (Richardson *et al.* 2005). However, there is a lack of studies on PPCPs in the environment in Southeast Asia, including Vietnam (Richardson *et al.* 2005).

Six PPCPs well known as molecular markers of sewage contamination (carbamazepine, crotamiton, diethyltoluamide, ibuprofen L-menthol and triclosan; Nakada *et al.* 2008), and three other PPCPs (nicotine, squalane, thymol) were observed. The most frequently detected compound was diethyltoluamide (86%), L-menthol (71%) and squalane (47%) at the concentrations of 0.01–1.07, 0.01–61.2, and 0.01–2.57 $\mu\text{g/l}$, respectively. Concentrations of carbamazepine, diethyltoluamide, ibuprofen and crotaminton at sites in Hanoi and Ho Chi Minh were higher than in Korea and Tokyo (Kim *et al.* 2009; Nakada *et al.* 2008). The amount of PPCPs consumed in Vietnam is unknown, although it is expected that there is direct discharge into river waters via untreated wastewater. The number of PPCPs identified in this study may be an underestimate since there are a limited number of PPCPs in the AIQS-DB (14 substances). Consequently, a

more detailed survey on PPCPs in surface and ground water in Vietnam is required after new PPCPs are registered in the system's database.

Polychlorinated biphenyls

At sites located in Hanoi and Ho Chi Minh, PCBs were frequently found with Σ PCB concentrations from 0.4 to 16.8 ng/l (median: 0.19 ng/l). The highest total concentration was found at HCM6 (16.8 ng/l), followed by HN3 (12.5 ng/l) and HCM7 (9.64 ng/l). These high concentrations seem to be related to industry, atmospheric deposition and domestic wastewater. The number of PCB congeners detected in the rainy season (33) was larger than in the dry season (28). The leakage of PCBs from the PCBs-containing oils in old transformers and capacitors may be the cause of this PCBs pollution, and it has been reported that there are more than 11800 PCB-containing pieces of electrical equipment in Vietnam containing 7000 tons of PCB-containing oils (MONRE, 2006), and PCBs could be used currently as a components of lubricating oils for motor vehicles (Toan *et al.* 2007). In order to confirm the sources of PCBs in these study areas, sediment samples at the water sampling sites need to be examined.

Polycyclic aromatic hydrocarbons

The concentrations of PAHs were in the range 1 to 4560 ng/l (mean 570 ng/l), which indicated low to moderate contamination in relation to global levels. The distribution of PAHs was dominated by naphthalene, phenanthrene, pyrene and fluoranthene. The abundance (>80%) of low molecular-weight PAHs (2 and 3 rings) observed in rivers in Hanoi and Ho Chi Minh reflected the intensive inputs of petrogenic PAHs to the studied areas, primarily from leakage of refined products from urban vehicle traffic. Some sites (e.g., HN1, 2, 4, and HCM4) had a mixed contamination pattern (pyrogenic and petrogenic inputs), probably due to urban runoff, wastewater discharges and vehicle exhaust gases, especially from motorcycles. In rural areas, pyrogenic contamination was the dominant source of PAHs, probably from the burning of rice straw after harvest.

Bisphenol A and nonylphenol

Bisphenol A (BPA) is an endocrine disrupting chemical (USFDA, 2010) and was found in 26 out of 47 samples at concentrations from 0.005 to 5.3 μ g/l (mean 0.93 μ g/l). These levels were higher than those in rivers in Japan (<0.50–0.90 μ g/l; Kang & Kondo, 2006) and Europe (mean 0.025 μ g/l; n = 122; Loos *et al.* 2009). BPA concentrations in Hanoi and Ho Chi Minh were 3 times higher than in other regions of Vietnam. The maximum concentration observed in this study (5.3 μ g/l) was lower than the predicted no-effect concentration (PNEC) for aquatic organisms (11 μ g/l; MOE, 2001).

Nonylphenol is a degradation product of a nonylphenol polyethoxylates that are ubiquitous in industrial and household products (Derbalah *et al.* 2003). It was only found in canals in Hanoi (HN1 to HN5) and Ho Chi Minh (HCM4 to HCM7) at concentrations from 0.02–9.7 μ g/l (mean 3.0 μ g/l) and 2.0–20 μ g/l (mean 9.7 μ g/l), respectively. The mean values are much higher than those in European rivers (0.13 μ g/l, n = 122; Loos *et al.* 2009) and surface waters (including river, lake and sea water) in Japan (0.17 μ g/l, n = 1574; MOE, Japan). Extremely high concentrations (20, 16 and 9.7 μ g/l) were observed at HCM4, HCM6 and HN5, respectively, probably due to the wide range of contamination sources and heavy use of household products near these sites. In this study, nonylphenol concentrations in 15 out of 17 samples were higher than the PNEC for aquatic organisms (0.21 μ g/l; MOE, Japan), which implies that nonylphenol concentrations in rivers in Hanoi and Ho Chi Minh may be occasionally hazardous to aquatic organisms.

CONCLUSIONS

The results of this study provide the first baseline data on a wide spectrum of organic micro-pollutants in river water in Vietnam. The main findings are that (1) 235 analytes from a range of chemical groups were detected, indicating that Vietnamese rivers are as polluted by numerous chemicals as developed countries; (2) sterols and PPCPs were detected at high concentrations, indicating that rivers are heavily polluted by domestic wastewater; (3) organochlorine pesticides still remain in the environment although they have been banned for 20 years; (4) some urban rivers were heavily contaminated by insecticides used for hygienic purposes. In addition, several sources of drinking water were found to be contaminated by numerous pesticides, which implies a need for a detailed survey on pesticides in raw water and tap water. Bisphenol A and nonylphenol, the endocrine disrupting chemicals, were found at elevated concentrations in metropolitan areas, implying needs for a further investigation of surface and ground water.

The large number of organic micro-pollutants observed in Vietnam were similar to those found in developed countries, but the concentrations were much higher due to lack of wastewater treatment facilities. In addition, some compounds are potentially threatening to human health and ecosystems. Therefore the results indicate needs of in depth studies not only on the detected and related substances but also on effects to human and the aquatic ecosystem.

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