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Occurrence of 1153 organic micropollutants in the aquatic environment of Vietnam

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Abstract The rapid increase in the number and volume of chemical substances being used in modern society has been accompanied by a large number of potentially hazardous chemicals being found in environmental samples. In Vietnam, the monitoring of chemical substances is mainly limited to a small number of known pollutants in spite of rapid economic growth and urbanization, and there is an urgent need to examine a large number of chemicals to prevent impacts from expanding environmental pollution. However, it is difficult to analyze a large number of chemicals using existing methods, because they are time consuming and expensive. In the present study, we determined 1153 substances to grasp a pollution picture of microcontaminants in the aquatic environment. To achieve this objective, we have used two comprehensive analytical methods: (1) solid-phase extraction (SPE) and LC-TOF-MS analysis, and (2) SPE and GC-MS analysis. We collected 42 samples from northern (the Red River and Hanoi), central (Hue and Danang), and southern (Ho Chi Minh City and Saigon-Dongnai River) Vietnam. One hundred and sixty-five compounds were detected at least once. The compounds detected most frequently (>40 % samples) at μg/L concentrations were sterols (cholesterol, beta-sitosterol, stigmasterol, coprostanol), phthalates (bis(2-ethylhexyl) phthalate and di-*n*-butyl phthalate), and pharmaceutical and personal care products (caffeine, metformin). These contaminants were detected at almost the same detection frequency as in developed countries. The results reveal that surface waters in Vietnam, particularly in the center of large cities, are polluted by a large number of organic micropollutants, with households and business activities as the major sources. In addition, risk quotients (MEC/PNEC values) for nonylphenol, sulfamethoxazole, ampicillin, acetaminophen, erythromycin and clarithromycin were higher than 1, which indicates a possibility of adverse effects on aquatic ecosystems.

Keywords Screening analysis · Micropollutants · GC/MS · LC/TOF-MS · Pesticides · PPCPs

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Introduction

Urbanization, industrialization, and intensive farming are having a negative impact on Vietnam's environment. As a result, surface water of rivers running through residential and industrial areas has been increasingly polluted by organic contaminants (Ministry of Natural Resources and Environment (MONRE) 2010). Untreated medical, industrial, and municipal wastewater are combined in municipal sewage systems and then discharged to canals and rivers. In particular, water pollution problems originating in domestic wastewater were clearly evidenced in large cities (MONRE 2010). For example, Ho Chi Minh City [HCMC, the most densely populated city in Vietnam (GSO 2013)], discharges 413,000 m^3 of wastewater per day, Hanoi discharges 155,000 m^3/day, and Hue-Danang discharge 58,800 m^3/day.

Water pollution was also found in rural or suburban areas of these cities. The main cause of water pollution in rural areas is pesticide and fertilizer residuals (Dang and Thiemann 2002;

Anyusheva et al. 2012). Statistical data show that pesticide consumption rapidly increased from 66,000 t in 2005 to 124 000 t in 2012 (GSO 2013). Because of poor cropping practices, pesticides and fertilizers are often overused and enter waterways. High-density industrial development and agricultural activities in certain major river basins may also pollute rivers. For example, surface water of the Red River and Saigon-Dongnai River (SDR) is extensively used for irrigation, drinking, and cooking. Therefore, water pollution may affect large numbers of the population. The Red River is one of the main sources of water in northern Vietnam and has the second largest basin, covering 26 % of the area of Vietnam (MONRE 2006). Another important basin is that of the SDR; this basin encompasses the southeast principal economic zone including HCMC, Binhduong, Dongnai, and Baria-Vungtau provinces. These provinces comprise the most important industrial area in the country, with a high rate of economic growth.

In Vietnam, there have been few studies focusing on a small number of organochlorine pesticides, PCBs, PAHs, and others in surface or in sediments (e.g., Nhan et al. 2001; Dang and Thiemann 2002; Nguyen et al. 2007; Duong et al. 2008; Pham et al. 2010; Lamers et al. 2011). Owing to rapid economic growth and urbanization, monitoring of a large number of chemicals is needed to prevent expansion of environmental pollution. However, it is difficult to analyze such large numbers using existing methods because of the substantial time and expense involved with operating multiple definitive tests. We have developed novel screening methods that can measure hundreds of chemicals simultaneously (Jinya et al. 2013). In the present study, we applied the methods to river water in Vietnam and analyzed 1153 substances composed of 843 semi-volatile organic compounds (SVOCs) and 310 polar organic compounds (POCs), to elucidate the pollution status of the aquatic environment in Vietnam. From the results, a complete pollution picture of the aquatic environment in the country is portrayed.

Materials and methods

Materials

All solvents, *n*-hexane, acetone, and dichloromethane (DCM) for pesticide residue analysis, methanol of LC-MS grade, Na_2HPO_4, and NaH_2PO_4 were supplied by the Kanto Chemical Company (Tokyo, Japan). Reagents of target compounds and internal standards were purchased from Wako Pure Chemical Industries (Osaka, Japan), Kanto Chemical Company, and Sigma-Aldrich (Tokyo, Japan). Purified water was obtained using a Millipore Milli-Q Advantage system (Nihon Millipore K.K., Tokyo, Japan).

Water sample collection

All 42 samples were collected in March 2013. Fourteen samples were collected from the Red River (Fig. 1a, upstream to downstream). In Hanoi, three samples were taken in urban zones including the Kimnguu River (HN1), Lu River (HN2), and Tolich River (HN3). Other two samples (HN4, HN5) were collected from the Nhue River in a suburban zone of Hanoi (Fig. 1b). Figure 1c is for Hue (five samples, in an urban area HU4, and in a rural area HU1, HU2, HU3, HU5). Figure 1d is for Danang (seven samples, in an urban area DN3, DN7, and in a suburban area DN1, DN2, DN4, DN5, DN6). Four out of six HCMC samples were taken in the Thamluong (HCM7), Nhieuloc-Thinghe (HCM8), Logom (HCM9), and Tauhu (HCM10) canals (Fig. 1e), which appeared to be wastewater canals within urban areas. Since water from these canals has been collected and treated at wastewater treatment plants, water quality has improved (HCMC PC 2014). However, their surface water quality still does not meet national standards. Other two samples were taken from Anha (HCM6) and Kenhdoi (HCM11) canals in a suburban zone. For the SDR, three of five samples were collected from the Saigon River (HCM2, HCM3, HCM4) and one from the Dongnai River (HCM1); there was one other sample from the downstream of these two rivers (HCM5) (Fig. 1e). Detailed information and figures of sampling sites are given in Duong et al. (2015).

Surface water at the center of a stream was sampled from a bridge with a stainless steel bucket, which was pre-cleaned with solvents, purified water, and sample water. Each water sample was stored in a 1-L glass bottle previously washed with solvents and purified water. Bottles containing water samples were kept in an icebox and transported to our laboratory.

Sample extraction and analysis

The GC-MS and GC-MS-MS analytical method for 950 SVOCs was undertaken according to the method of Jinya et al. (2013). A water sample (1 L), spiked with 1 mL of phosphate buffer (1 M, pH 7.0) to adjust the pH of each sample to 7, was fitted inside a vacuum manifold (3M Company, St. Paul, MN, USA) with flow rate less than 100 mL/min in a sequence with a glass microfiber disk (GMF 150, 47 mm, Whatman, Maidstone, UK), a styrene-divinylbenzene disk (Empore™ SDB-XD, 47 mm, 3M Co.), and an active carbon disk (Empore™ AC, 47 mm, 3M Co.). These disks were preconditioned by passing 10 mL of DCM, 10 mL of acetone, 10 mL of methanol, and 20 mL of purified water through them before use. After passing water sample through the disks, water remaining in the disks was completely removed using a vacuum for 30 min. The GMF and XD disks were eluted together with 5 mL of acetone (twice), followed by 5 mL of DCM. The AC disk was eluted with 5 mL of acetone (twice).

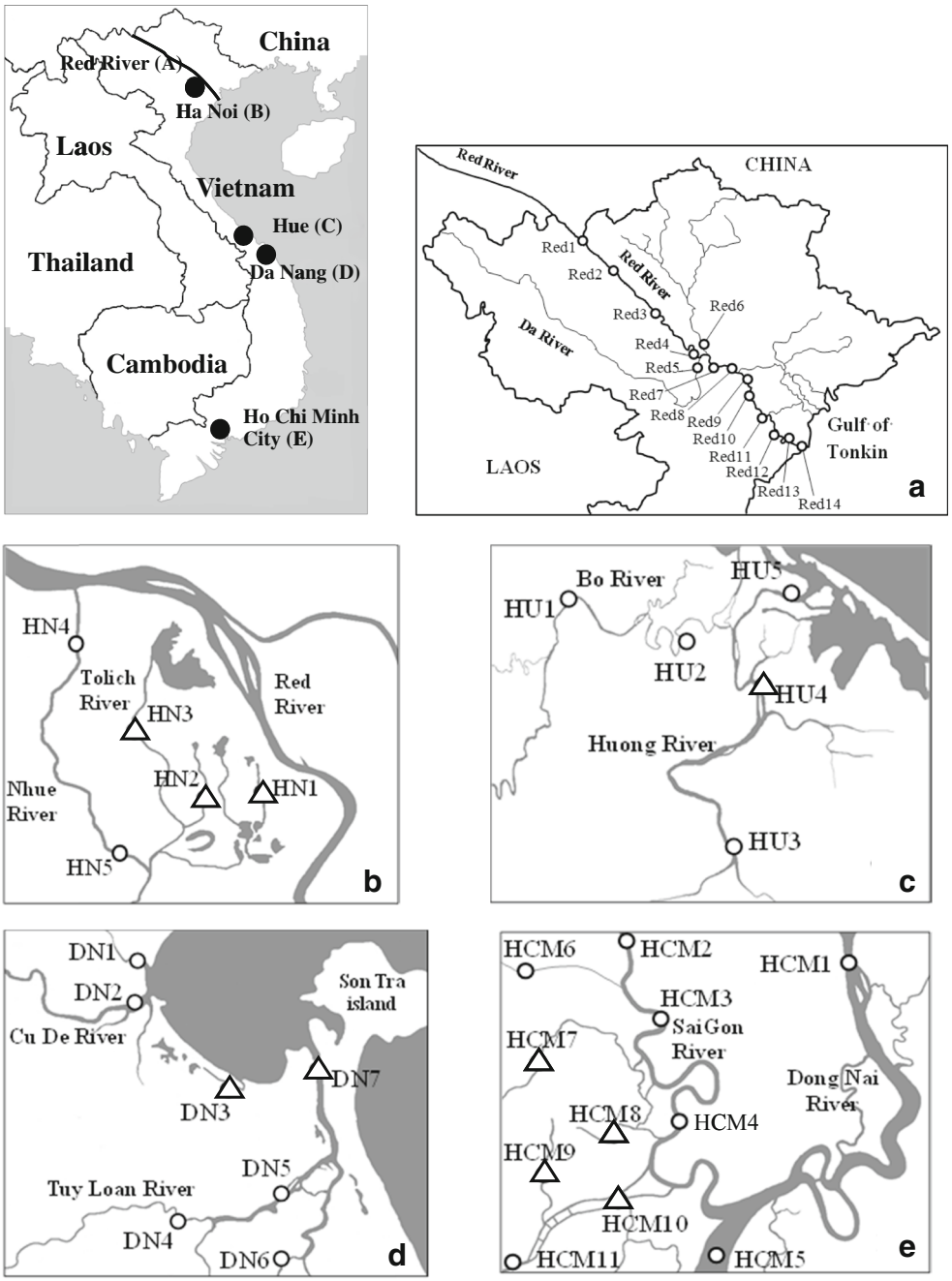

Fig. 1 Location of 42 sampling sites. **a** Red River, **b** Hanoi, **c** Hue, **d** Danang, **e** Ho Chi Minh City and Saigon-Dongnai River. *Empty triangles* represent urban area; *empty circles* represent suburban area

The eluates were combined and concentrated into 1 mL with a nitrogen stream. The concentrate was diluted with 10 mL of hexane and dehydrated by adding Na_2SO_4 (preheated at 700 °C for 6 h). The dehydrated solution was concentrated to 1 mL, and then mixed internal standards (IS; 4-chlorotoluene-d_4, 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, fluoranthene-d_{10}, chrysene-d_{12}, perylene-d_{12}) were added prior to instrumental analysis [GC-MS-SIM/Scan (QP-2100 Plus, Shimadzu, Tokyo, Japan) and GC-MS-MS-SRM (TSQ Quantum XLS, Thermo Fisher Scientific, Yokohama, Japan)].

For the analysis of 300 POCs, 1 mL of phosphate buffer (1 M, pH 7.0) was added to a water sample (500 mL) and filtered with a 1.2-μm glass fiber filter (Whatman, GF/C). Suspended solids (SS) were subjected to ultrasonic extraction with methanol twice. The filtrate was passed through a PS-2 Sep-Pak short cartridge (Waters Corporation) and an AC 2 Sep-Pak (Waters) using a Chratec Sep-Pak Concentrator (SPC 10-C; Chratec, Kyoto, Japan) with a flow rate of 10 mL/min, and then rinsed with 10 mL of purified water. The cartridges were then dried with nitrogen to remove water for 40 min. The cartridges were eluted with methanol (5 mL)

Table 1 Concentrations (μg/L) of the chemicals found and the numbers of chemicals found (in parentheses)

Group	Type of compound	Compound	*N*	Mean-max value of measured concentration (number of detected compound)					
				Red River (14 samples)	Hanoi (5 samples)	Hue (5 samples)	Danang (7 samples)	Saigon–Dongnai River (5 samples)	HCMC (6 samples)
Household chemicals	Leaching from tire	2(3H)-benzothiazolone, 2-(methylthio)-benzothiazol, acetophenone, benzyl alcohol, phenylethyl alcohol	5	nd	3.9–6.9 (4)	0.043–0.087 (2)	nd	0.0044–0.022 (1)	3.3–12 (5)
	Petroleum		25	2.4–8.8 (22)	23–37 (24)	1.1–4.3 (22)	4.1–8.0 (19)	2.9–4.7 (21)	33–100 (25)
	Plasticizers	Bis(2-ethylhexyl)phthalate, bisphenol A, butyl benzyl phtalate, di(2-ethylhexyl) adipate, diethyl phthalate, di-*n*-butyl phthalate, triphenylphosphate	7	4.3–17 (7)	14–22 (6)	0.11–0.47 (3)	1.3–5.1 (4)	2.3–4.0 (7)	13–38 (6)
	Disinfectants	2-methylphenol, 3- and 4-methylphenol, phenol	3	0.011–0.040 (1)	15–28 (2)	nd	nd	nd	17–63 (3)
	Others	4-methyl-2,6-di-t-butylphenol; 4-*tert*-octylphenol; nonylphenol	3	0.051–0.11 (1)	3.7–7.0 (3)	0.017–0.086 (1)	0.020–0.044 (1)	0.056–0.11 (2)	7.2–28 (3)
Industrial chemicals	Intermediates	2,4-dichloroaniline; 2-ethyl-1-hexanol; 2-phenylphenol; 3,4-dichloroaniline; 3,5-dimethylphenol; biphenyl; dicyclohexylamine; quinoline	8	0.026–0.076 (1)	3.9–5.4 (7)	0.048–0.067 (1)	0.40–1.8 (2)	0.10–0.16 (1)	4.2–21 (6)
	PAHs	1,3-dimethylnaphthalene; 2,6-dimethylnaphthalene; 2-methylnaphthalene; fluoranthene; phenanthrene; pyrene	6	3.2–44[a] (3)	0.090–0.17 (3)	nd	11–74[a] (3)	nd	0.35–1.3 (4)
	PCBs		32	0.057–0.15[a] (2)	1.8–5.3[a] (14)	0.086–0.14[a] (1)	0.18–0.35[a] (3)	0.19–0.27[a] (2)	1.7–7.6[a] (28)
	Paint/solvent	Isophorone	1	0.010–0.14 (1)	0.23–5.2 (1)	0.069–0.26 (1)	nd	nd	0.35–1.4 (1)
Pesticides	Fungicides	Azoxystrobin, carbendazim, cyprodinil, epoxiconazole, ethoxyquin, hexachlorobenzene, isoprothiolane, tricyclazole	8	0.12–0.29 (2)	0.14–0.21 (3)	0.029–0.11 (3)	0.17–0.35 (2)	0.15–0.28 (4)	0.15–0.22 (5)
	Herbicides	Acetochlor, alachlor, ametryn, atrazine, bensulfuron-methyl, butachlor, diuron, flufenacet, naproanilide, prometryn, siduron, tebuthiuron	12	0.11–0.29 (4)	0.16–0.34 (5)	0.025–0.12 (3)	0.13–0.90 (2)	0.075–0.21 (4)	0.54–1.2 (4)
	Insecticides	Acetamiprid; a-HCH; aldrin; carbofuran; *cis*-chlordane; trans-chlordane; dimethoate; fenobucarb; fenoxycarb; imidacloprid; o,p'-DDD; p,p'-DDD+o,p'-DDT; p, p'-DDE; permethrin 1; permethrin 2; piperonyl butoxide; promecarb;	17	0.039–0.14[a] (3)	1.8–2.9 (12)	0.036–0.10 (3)	0.034–0.22 (7)	0.054–0.10 (5)	1.0–3.0 (9)
	Sterols	Cholestanol, cholesterol, coprostanol, beta-sitosterol, stigmasterol	5	5.3–17 (4)	121–194 (5)	3.8–6.5 (4)	9.6–39 (4)	8.6–11 (4)	58–159 (4)
PPCPs	Antibiotics	Ampicillin, clarithromycin, erythromycin, griseofulvin, lincomycin, oleandomycin, roxithromycin, spiramycin, sulfadiazine,	13	0.017–0.24 (3)	3.7–5.5 (10)	nd	0.12–0.86 (2)	0.26–0.63 (2)	2.1–4.4 (10)

Table 1 (continued)

Group	Type of compound	Compound	*N*	Mean-max value of measured concentration (number of detected compound)					
				Red River (14 samples)	Hanoi (5 samples)	Hue (5 samples)	Danang (7 samples)	Saigon–Dongnai River (5 samples)	HCMC (6 samples)
		sulfanilamide, sulfamethoxazole, sulfapyridine, trimethoprim							
	Other pharmaceuticals	Acetaminophen, atenolol, acetohexamide, antipyrine, caffeine, carbamazepin, cimetidine, cotinine, diethyltoluamide, lidocaine, hexamethylenetetramine, L-menthol, losartan, metformin, nicotine, phenacetin, propranolol, sulpiride, testosterone, theophylline	20	0.058–0.25 (4)	22–38 (14)	0.14–0.55 (2)	0.27–1.5 (7)	1.1–3.1 (8)	17–60 (16)
Total number of detected compounds			165	58	113	46	56	61	129

N number of detected compounds detected in all 42 samples at least once, *nd* not detected

[a] Concentrations were calculated in the unit of ng/L

and DCM (3 mL). After combining the eluates and the extract from SS, the mixture was concentrated to 50 μL and then spiked with 40 μL of three IS (5 μg/L, mixture of methomyl-d_3, pirimicarb-d_6, imazalil-d_5). The concentrate was diluted to 1 mL with purified water, filtered through a 0.2-μm syringe filter (Millex-LG) into an analysis vial, and subsequently measured by LC-TOF-MS.

Analytical quality control

Method accuracy and precision were studied by recovery studies using surface water and effluent of sewage treatment plants spiked at different concentrations. The procedure blanks were analyzed every 6 samples to check for cross-contamination and interference.

For SVOC analysis, quality control measures were as described by Jinya et al. (2011, 2013). Two hundred-two SVOCs were selected as model compounds (MCs) having a wide range of physicochemical properties (structure, functional group, boiling points (145–536 °C)). The MCs included polycyclic aromatic hydrocarbons (PAHs), amines, alkyl phenols, halogenated phenols, phthalates, benzenes, alcohols, and some classes of pesticides. Recoveries were determined by analyzing purified and environmental sample spiked standards at two concentrations (0.1 and 0.5 μg/L). Most of the model compounds, which are representative of the target SVOCs, had recoveries of over 50 % (Jinya et al. 2013). Method detection limits (MDL) of chemicals measured by SIM and/or SRM were 0.0004–0.3 μg/L. The MDL of compounds measured by TIM were 0.005 to 0.5 μg/L.

For the polar substance analysis, the recoveries of 264 MCs from spike experiments at 0.05 and 0.2 μg/L were determined using purified water (replication $n=7$ for each level of concentration) and effluent wastewater ($n=5$) to be in the range 50–120 %. The relative standard deviation (RSD) values for recovery tests using purified water were in the range 3–25 % and the RSD of effluent samples between 5 and 30 %. Quantitation was performed by IS method using a peak area obtained at 100 V of fragmentor voltage. MDLs of POCs ranged from 0.008 to 0.4 μg/L. The correlation coefficients of calibration curves are higher than 0.99 for all the compounds analyzed.

Results and discussion

Detection of micropollutants in surface water samples

One hundred and sixty-five out of 1153 target compounds were detected at least once in surface water samples (Table S1). The total number of compounds found in Hanoi and HCMC samples were similar (113 and 129 compounds, respectively; Table 1), and two to three times higher than at

other sampling sites (Red River 58, Hue 46, Danang 56, SDR 61). Overall, the concentrations of substances detected in Hanoi and HCMC were much higher than in Hue, Danang, the Red River, and SDR (except for fungicides and herbicides; Fig. 2), because of differences in population density and economic activity. When comparing data from large cities and other sites, household chemicals, PAHs, and sterols had nearly identical numbers of detected compounds but vastly different total concentrations. The numbers and concentrations of fungicides and herbicides did not vary greatly between sites. PCBs, insecticides, and pharmaceutical and personal care products (PPCPs) were found in much higher numbers and concentrations in the large cities than at other sites (Table 1). When comparing the number and concentrations of detected organic compounds between urban and suburban area of cities, sampling sites in Hanoi urban area (HN1, HN2, and HN3) had high concentrations of household chemicals and PPCPs compared to those in suburban areas (HN4 and HN5; Fig. 2). This pattern was also observed among samples collected in urban area and suburban area of HCMC, Danang, and Hue (Fig. 2).

We screened 13 plasticizers; seven of these [bis(2-ethylhexyl)phthalate (DEHP), bisphenol A, butyl benzyl phthalate, di(2-ethylhexyl)adipate (DEHA), diethyl phthalate (DEP), di-*n*-butyl phthalate (DBP), triphenylphosphate (TPP)] were detected in very high concentrations (μg/L level) at each sampling site. Maximum and average values of total detected concentrations were 38 and 13 μg/L in HCMC, 22 and 14 μg/L in Hanoi, and 17 and 4.3 μg/L in the Red River. DEHP was predominant, with high concentrations accounting for 71 % of the mean concentration of plasticizers detected in the Red River, 75 % in Hanoi, 76 % in SDR, and 65 % in HCMC.

The highest concentration of PAHs was 1334 ng/L (mean 64 ng/L), about three times lower than the value in a previous report from Vietnam (Duong et al. 2014) and about four times lower than in Tianjin, China (Kong et al. 2014). The number of detected PCBs (32) was similar to that reported by Duong et al. (2014), but their total concentrations were <7.6 ng/L (mean 0.54 ng/L), two times lower than previously reported values.

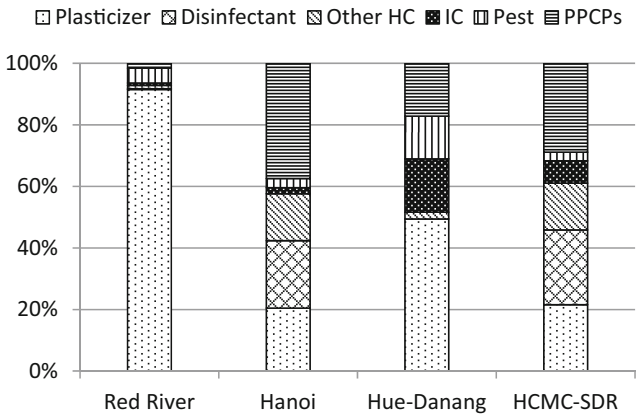

Fig. 3 Percentages of concentrations of compounds detected at each location (*other HC*: other household chemicals; *ICs*: industrial chemicals)

Only five out of the 12 sterols examined were observed and occurred at the highest concentration compared with the other compounds detected in this survey (Hanoi (194 μg/L), HCMC (159 μg/L)). A ratio of coprostanol/cholesterol ≥0.2 indicates sewage contamination (Grimalt et al. 1990). Generally, values near or greater than 0.2 were found in populous locations such as Hanoi (site HN1 0.96, HN2 0.86, HN3 0.88, HN4 0.37, HN5 0.82), Red10 (0.32, downstream of Hanoi), urban areas of Hue (HU4 0.19) and Danang (DN3 0.46), and HCMC (HCM6 0.30, HCM7 0.67, HCM9 0.79, HCM10 0.3, HCM11 0.20) (Table S1). Glassmeyer et al. (2005) suggested that a ratio exceeding 0.3 indicates fecal contamination. This means that wastewater containing feces from households was directly discharged into rivers or canals in urban areas, and domestic wastewater treatment plants were not operating effectively.

Thirty-three PPCPs were found in the survey, among which 13 compounds were antibiotics (ampicillin, clarithromycin, erythromycin, griseofulvin, lincomycin, oleandomycin, roxithromycin, spiramycin, sulfadiazine, sulfamethoxazole, sulfanilamide, sulfapyridine, and trimethoprim). The total

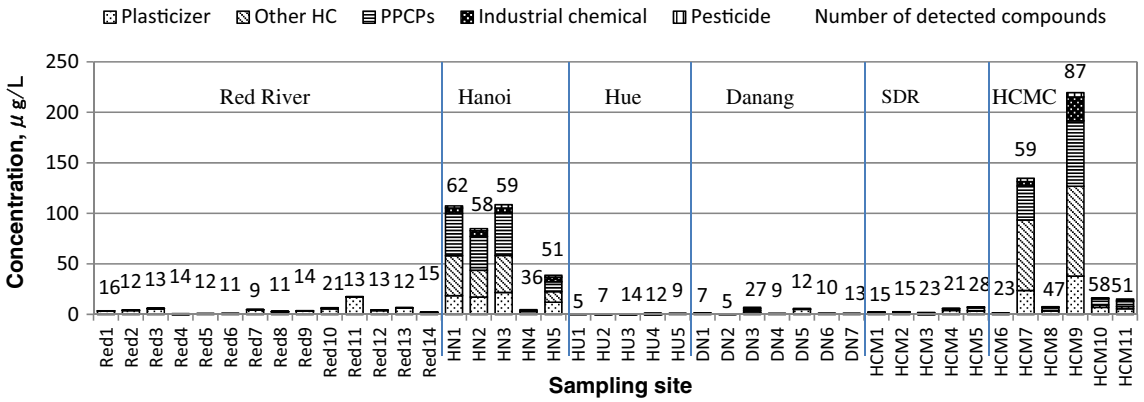

Fig. 2 Concentrations and number of compounds detected at each sampling site

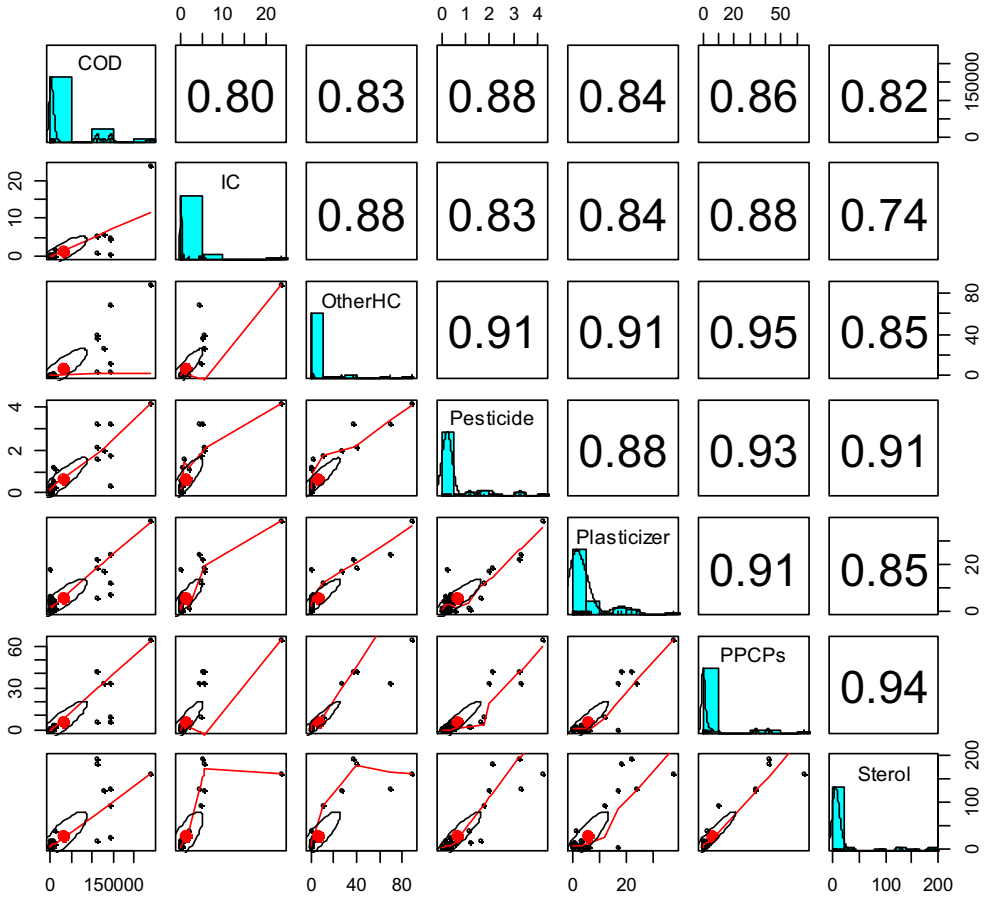

Fig. 4 Correlation between groups of detected organic compounds (*COD* definition of chemical oxygen demand, *IC* industrial chemical, *Other HC* other household chemical)

concentration of all detected antibiotics was highest in Hanoi (5.5 μg/L; mean 3.7 μg/L), followed by 4.4 μg/L in HCMC (mean 2.1 μg/L). In Vietnam, antibiotics are dispensed without a doctor's prescription (Nguyen et al. 2011) and may enter the environment through feces or urine. However, it is possible that important point sources of antibiotics are hospitals because hospital wastewater contains high levels of antibiotics, and removal values through wastewater treatment plants are smaller than those in developed countries (Duong et al. 2008).

Distribution of micropollutants in surface waters

More than 50 % of total micropollutant concentrations detected in both urban and suburban areas were household chemicals (Red River 92 %, Hanoi 58 %, Hue-Danang 52 %, HCMC-SDR 71 %; Fig. 3). The distributions of contaminants in the environment of Hanoi and HCMC-SDR were nearly identical but were very different to those of Hue-Danang and the Red River (Fig. 3).

Plasticizers are commonly used, and with millions of tons produced worldwide annually (Koch et al. 2003), these chemicals have become widespread in the environment (Fromme et al. 2002; Fauser et al. 2003). In the present study, plasticizers were a large proportion of detected contaminants, accounting for 21–22 % in Hanoi and HCMC-SDR, 50 % in Hue-Danang, and up to 91 % in the Red River. A likely source of plasticizers in the environment of large cities is storm water (Clara et al. 2010; Björklund et al. 2009). However, in the case of Hue-Danang and the Red River, untreated wastewater from craft villages is considered the main plasticizer source. Craft villages are classified into many different groups according to their products, such as textiles, construction materials, recycled metal, paper, or plastics. Most of these villages are in northern and central Vietnam, and the Red River basin has the largest number of craft villages, accounting for 60 % of all such villages in the country (MONRE 2008). All these villages have been facing environmental pollution problems. Pollution in these villages has not decreased and, in fact, has tended to increase. This may explain why industrial chemicals constituted large proportions of the contaminant composition in Hue-Danang (17 %).

Many pharmaceuticals and their metabolites have been detected in aquatic environments (Hereber 2002; Caliman and Gavrilescu 2009). In the present study, PPCPs contributed greatly to the total distribution; 37 % in Hanoi, 29 % in HCMC-SDR, and 17 % in Hue-Danang (Fig. 3). Because PPCPs are one of the major contaminants in surface samples

Table 2 List of most frequently detected compounds in 42 samples

Compound	Type of compound	LOD (ng/L)	Number > LOD	Number > 0.1 μg/L	Number > 1 μg/L	Number > 10 μg/L	Maximum (μg/L)	Median (μg/L)
Beta-sitosterol	Sterol	100	42	42	31	7	25.2	1.98
Cholesterol	Sterol	100	42	42	34	8	70.6	1.66
Stigmasterol	Sterol	100	42	42	30	2	16.4	1.84
PCB #1	PCB	0.03	35	0	0	0	0.32[a]	0.11[a]
Dicyclohexylamine	Intermediate	8	34	14	3	0	3.32	0.07
Coprostanol	Sterol	10	29	22	12	6	57.8	0.12
4-Methyl-2,6-di-t-butylphenol	Antioxidant	25	28	7	0	0	0.41	0.04
Bis(2-ethylhexyl)phthalate	Plasticizer	10	27	26	24	6	19.0	2.25
Cotinine	Nicotine metabolite	8	27	10	5	0	2.84	0.01
Di-*n*-butyl phthalate	Plasticizer	10	26	19	7	0	4.92	0.08
Triphenylphosphate	Plasticizer	20	26	1	0	0	0.14	0.01
p,p'-DDE	Insecticide	0.03	25	0	0	0	4.14[a]	0.04[a]
Di(2-ethylhexyl)adipate	Plasticizer	10	24	14	0	0	0.44	0.03
Atrazine	Herbicide	10	24	0	0	0	0.03	0.01
Lidocaine	Anesthetic/antiarrhythmic	8	23	4	0	0	0.23	0.02
Diethyl phthalate	Plasticizer	10	22	15	6	0	7.49	0.03
Bisphenol A	Plasticizer	10	21	9	2	0	7.82	0.01
Carbendazim	Fungicide	8	19	9	0	0	0.21	nd
Metformin	Antidiabetic	8	19	13	7	0	8.25	nd
Ethoxyquin	Fungicide	8	18	6	0	0	0.29	nd
Tricyclazole	Fungicide	8	18	0	0	0	0.10	nd
4-*tert*-Octylphenol	Nonionic detergent metabolite	10	17	3	0	0	0.85	nd
Fenobucarb	Insecticide	8	17	1	0	0	0.22	nd
Caffeine	Food product	10	17	16	8	1	13.0	nd

LOD limit of detection

[a] Calculated concentrations have units ng/L

of crowded cities, more research is needed on their fates and effects in the environment. Pesticides and industrial chemicals comprised only 3 and 2 % in Hanoi, and 3 and 7 % in HCM-SDR, respectively, or 2–7 times lower than the rates found in Hue-Danang.

Correlations between organic compounds detected in surface waters

The water quality parameters pH, total suspended solids (SS), and chemical oxygen demand (COD) were measured in this survey (Table S1). COD was observed in the range from 0.32 to 240 mg/L. Seven sampling sites had COD values more than 5 times higher than Vietnam's 20 mg/L national surface water quality regulation (QCVN 08: 2008/BTNMT; HN1, HN2, HN3, HCM7, HCM9, HCM10, and HCM11). These sites are located in urban areas of Hanoi and HCMC. There were strong, positive correlations between COD and all groups of detected organic compounds (industrial chemicals, household chemicals, pesticides, plasticizers, and sterol; Fig. 4). Therefore, it can be said that there was no specific sources of contaminants, and surface water has become polluted by wastewater discharges from domestic, hospitals, factories, and agricultural activities.

Most frequently detected compounds in surface waters

Twenty-four substances were found frequently (≥40 % samples, with detected concentrations >LOD; Table 2), including 4 sterols [beta-sitosterol, cholesterol, stigmasterol (100 %), and coprostanol (69 %)], 6 plasticizers [DEHP (64 %), DBP and TPP (62 %), DEHA (57 %), DEP (52 %), bisphenol A (50 %)], 6 pesticides [pp'-DDE (60 %), atrazine (57 %), carbendazim (45 %), ethoxyquin, tricyclazole (43 %), fenobucarb (40 %)], 4 PPCPs [cotinine (64 %), lidocaine (55 %), metformin (45 %), caffeine (40 %)], 2 industrial chemicals [PCB#1 (83 %), dicyclohexylamine (81 %)], and 2 household chemicals [4-methyl-2-6-di-t-butylphenol (67 %), 4-*tert*-octylphenol (40 %)]. The substances showing high concentrations (>1 μg/L) were sterols such as cholesterol (81 %), beta-sitosterol (74 %), stigmasterol (71 %), coprostanol (29 %), phthalate plasticizer of DEHP

Table 3 The MEC/PNEC ratios of detected compounds

Compound	MEC (μg/L)	PNEC (μg/L)	MEC/PNEC
Nonylphenol	26.9	0.21[a]	128
Sulfamethoxazole	2.16	0.027[b]	80
Ampicillin	0.64	0.075[c]	8.6
Acetaminophen	5.64	1[b]	5.6
Erythromycin	0.09	0.02[b]	4.3
Clarithromycin	0.17	0.07[b]	2.4
Sulfadiazine	0.11	0.135[b]	0.8
Bisphenol A	7.82	11[a]	0.7
Propranolol	0.13	0.244[b]	0.5
Trimethoprim	0.18	2.6[b]	0.1
Lincomycin	2.66	82[b]	0.03
Roxithromycin	0.05	4[b]	0.01
Atenolol	0.27	30[b]	0.01
Cimetidine	0.19	35[b]	0.01
Carbamazepin	0.03	13.8[b]	0.002
Sulfapyridine	0.03	21.61[b]	0.002

[a] MOE 2001

[b] Verlicchi et al. 2012

[c] Kümmerer and Henninger 2003

(57 %), DBP (17 %), followed by caffeine and metformin (19 %).

Of the plasticizers, DEHP was detected at the highest concentrations (>1 μg/L at each sampling location) of 19 μg/L (HCMC), 13.5 μg/L (Hanoi), and 13.0 μg/L (Red River), followed by bisphenol A (HCMC 7.82), DEP (HCMC 7.49, Hanoi 6.41), DBP (Danang 4.92, Red River 4.22, HCMC 3.24, Hanoi 1.45). Other studies have also suggested high detection frequencies (>50 %) of these substances in surface waters but at higher concentrations. For example, Clara et al. (2010) reported DEHP with a detection frequency of 100 %, and maximum concentration of 34 μg/L; DEP 100 %, 9.2 μg/L; DBP 53 %, 8.7 μg/L. Higher concentrations have also been reported in France, Germany, and Canada [DEHP: maximum 44 μg/L, DEP 25 μg/L (Dargnat et al. 2009); DEHP 97.8 μg/L, DBP 8.8 μg/L (Fromme et al. 2002); DEHP 70 μg/L (Barnabé et al. 2008), respectively].

In our study, we detected caffeine in surface waters at a maximum concentration of 13.0 μg/L, much lower than the 91.6 μg/L reported by Duong et al. (2014) but higher than in other studies [1.43 μg/L (Kong et al. 2014); 6.9 μg/L (Edwards et al. 2015)]. Another PPCP, metformin (an antidiabetic), was detected at the highest concentration compared with other PPCPs found in this survey (Hanoi 8.23 μg/L at maximum, HCMC 2.25 μg/L), albeit these concentrations were more than two times lower than the maximum concentration found in a study in China (20 μg/L; Kong et al. 2014). Lower concentrations of metformin in surface waters have been observed in many developed countries, such as the maximum 735 ng/L in France (Vulliet and Cren-Olivé 2011) and 1700 ng/L in Germany (Scheurer et al. 2009).

Environmental risk assessment of organic compounds

The ratios of the measured environmental concentration (MEC, maximum concentration in surface water) and the predicted no effect concentration (PNEC) were used to assess the environmental risk of detected compounds. The MEC/PNEC values were <1 indicating no toxic potential (Quinn et al. 2008). Of the 16 substances that were evaluated, six substances, nonylphenol (nonionic detergent metabolite), sulfamethoxazole, ampicillin, erythromycin, clarithromycin (antibiotic), and acetaminophen (analgesic), had MEC/PNEC >1 (Table 3). It indicates that these compounds are of concern and may warrant tier three toxicity assessment.

Conclusions

In the present study, 165 out of 1153 micropollutants examined were detected in surface waters, and of which more than 100 contaminants occurred at μg/L level of concentrations in Hanoi and HCMC. Rivers in large cities were heavily polluted by a large number of organic microcontaminants, mainly from domestic sources such as PPCPs, plasticizers, and other household chemicals. Compared with large cities, Hue-Danang, the Red River, and Saigon-Dongnai River were less contaminated, and their pollutant sources were not just domestic but also agricultural and small-scale industries. The most frequently detected contaminants were plasticizers (DEHP, DEP, DBP, bisphenol A), dicyclohexylamine, and PPCPs (caffeine, metformin, cotinine). Their concentrations were high (>1 μg/L) higher than those found in international studies. One of the causes of serious pollution is that construction speed of sewage treatment plants does not catch up economic growth and urbanization. Therefore, accelerated construction of sewage treatment plants and enlightenment about chemicals are necessary to prevent expansion of pollution. Nonylphenol, sulfamethoxazole, ampicillin, acetaminophen, erythromycin, and clarithromycin had risk quotients (MEC/PNEC) >1, suggesting these chemicals may be causing ecological harm, although further detailed field study is required to confirm this hypothesis.

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