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]

[a] Graduate School of Environmental Engineering, The University of Kitakyushu, 1-1 Hibikino, Wakamatsu, Kitakyushu, Fukuoka 808-0135, Japan
[b] Institute of Environmental Technology, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet Street, Cau Giay District, Hanoi, Viet Nam

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
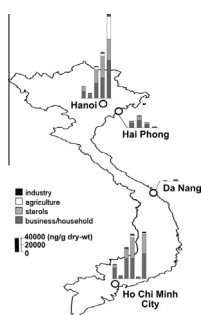
ARTICLE INFO

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.

© 2014 Elsevier Ltd. All rights reserved.

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 m^3/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 at 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