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Spatial distribution and ecological risk assessment of phthalic acid esters and phenols in surface sediment from urban rivers in Northeast China

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ABSTRACT

Concentration and spatial distribution of six phthalic acid esters (PAEs) and eight phenols in sediments of urban rivers, namely the Xi River (XR) and Pu River (PR) in Shenyang city, Northeast China were investigated and the ecological risk of these target pollutants was assessed based on the risk quotient (RQ) approach. Target PAEs and phenols were detected in most of sediment samples collected from the XR and PR. The concentrations of total PAEs in sediments varied from 22.4 to 369 $\mu\text{g/g dw}$ in the XR and 3.71–46.9 $\mu\text{g/g dw}$ in the PR. The levels of phenols ranged from 2.72 to 106 $\mu\text{g/g dw}$ in the XR and 0.811–25.0 $\mu\text{g/g dw}$ in the PR, respectively. The dominant pollutants in both XR and PR were DEHP, phenol and 4-methylphenol. The sampling locations XR1–3 in the XR suffered severe contamination from PAEs and phenols. The sites PR1 and PR6 were heavily polluted by phenols and PAEs, respectively. Almost all target PAEs and phenolic compounds in sediment of the XR exhibited medium or high ecological risk to organisms and the ecological risk in the PR mainly originated from PEAs, phenol and 4-methylphenol. These results would provide guidance for individual pollutant control and indicate that it is imperative to take some effective measures to reduce the pollution of those contaminants.

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1. Introduction

Phthalic acid esters (PAEs) and phenols are two classes of important industrial chemicals and widely used for diverse purposes. The main application of PAEs is as plasticizers to improve the softness and flexibility of polyvinyl chloride (PVCs) materials, polyvinyl acetate, and cellulosic and polyurethane resins (Feng et al., 2002; Kawakami et al., 2011). The content of PAEs in plastic products accounts for up to 80 wt% (Rahman and Brazel, 2004). It has been reported that PAEs consumption in 2011 reached up to approximately 2.2 million tons in China (Wang et al., 2013). Nevertheless, because of the widespread application, PAEs have been considered as ubiquitous environmental pollutants and widely detected in air, water, sediments, soil and food (Blair et al., 2009; Chen et al., 2013; Fierens et al., 2012; Liu et al., 2013; Ma et al., 2013; Wang et al., 2014; Xu et al., 2014). Some PAEs and their metabolites have been also observed in wildlife and human,

implicating endocrine disrupting effects, such as reproductive physiology in mammals (Hogberg et al., 2008; Martine et al., 2013; Montuori et al., 2008; Oehlmann et al., 2009). Several most commonly detected PAEs have been listed as priority pollutants by USA Environmental Protection Agency (USEPA, 2014) and also by China (Zhou et al., 1991).

Phenols are important raw materials and additives for industrial purposes. Phenols can be used as precursors of synthetic chemical products such as phenolic resin, synthetic fiber and rubber, caprolactam, bisphenol A, salicylic acid and so on, as well as versatile precursor to a large collection of pharmaceuticals. China's market demand for phenol has been rising year by year. In 2013, the supply capacity reached up to 1.5 million tons, doubled that of four years ago (Nikkei, 2014). Due to their high solubility in water and strong reactivity, phenols are extensively present in aquatic environment (Bielicka-Daszkiwicz et al., 2004). The toxicity of phenols not only hinders survival and reproduction of aquatic organisms, but also endangers human health (Davi and Gnudi, 1999; Kottuparambil et al., 2014; Wolff et al., 2015).

The Xi River (XR) and Pu River (PR) are typical urban rivers in Shenyang city that is the center of economy, culture, transportation

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and trade in northeast of China. There are more than 1500 manufacturing enterprises around the city, where the proportions of industrial wastewater discharged into the XR and PR are up to 52.2 and 10.9%, respectively. The XR, as a main effluent canal of the city, is about 78 km long and an area of 99 km². It is receiving a large amount of industrial wastewaters from machining, plastic, chemical with pharmaceutical plants (Guo et al., 2011; Lin et al., 2013). Some PAEs and phenols have been detected with high concentration in surface water of the XR (Li et al., 2015).

The PR, inland river, is about 205 km long. With the development of industry, water quality of the PR has been severely ruined due to aggravation of water resource shortage as well as increasing of discharged effluent (Gao et al., 2015). Overall, the release of domestic and industrial wastewaters has led to the pollution from toxic and hazardous pollutants characterized by carcinogenic, teratogenic and mutagenic effects in the XR and PR, which have potential hazards to wildlife and human despite their presence in low concentration.

Most of researchers have paid attentions and efforts to investigate typical toxic and hazardous compounds focusing on polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) in water basin (Liu et al., 2015). However, it is still lack of information on the pollution level of commonly used PAEs and phenols in urban rivers, particularly in the riverine sediment. As of yet, limited work has reported on the risk of PAEs and phenols exposure in the XR and PR. The aims of this study were to investigate the distribution of PAEs and phenols in sediment of the XR and PR, and then to assess their potential ecological risks. The results from this study can not only facilitate better understanding for the pollution status of PAEs and phenols, but also provide data for making countermeasure and management scheme in contaminated rivers.

2. Materials and methods

2.1. Standards and reagents

Target phthalate standards were dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), diisobutyl phthalate (DiBP), di-n-octyl phthalate (DnOP) and bis(2-ethylhexyl) phthalate (DEHP). The target phenols included phenol, 4-methylphenol, 2,3-dimethylphenol, 2,4-dimethylphenol, 3,5-dimethylphenol, 2,4,6-trimethylphenol, 2,4-di-tert-butylphenol and 2,6-di-tert-butyl-4-ethylphenol. The internal standard compounds were 1,4-dichlorobenzene-d₄, naphthalene-d₈, acenaphthene-d₁₀. All standard compounds were supplied by Dr. Ehrenstorfer GmbH (Germany). The chromatographic-grade dichloromethane, methanol and hexane were obtained from J. T. Baker Chemical Company (USA).

2.2. Sample collection

Seven and nine surface sediment samples were collected from the XR and PR in May 2014, respectively, labelled as XR1–XR7 and PR1–PR9 from upstream to downstream. Their specific geographic information was shown in Fig. 1. Each sample was collected using a precleaned stainless steel grab sampler, packed into an aluminum container, and kept in a freezer at –20 °C.

2.3. Sample extraction

The sediment samples were freeze-dried, ground and sieved through a 0.9 mm mesh, and stored in precleaned dark glass bottles for the subsequent extraction. Approximately 5 g of dry sample was accurately weighed, transferred into a clean 50 mL glass-centrifuge

tube with 20 mL of extraction solvent (a mixed solvent of acetone-dichloromethane (1:2, v:v) and spiked with a known quantity of internal standard. The mixture was ultrasonicated for 30 min and centrifuged for 30 min at a speed of 3000 rpm. The supernatants were collected in a clean glass flask. The extraction procedure was repeated three times, yielding a total of 60 mL supernatant. The combined supernatant was concentrated to 3 mL by a rotary evaporator, blow-dried to 0.5 mL using high purity grade nitrogen gas and then re-dissolved in 500 mL ultrapure water for clean up by solid phase extraction (SPE).

Oasis HLB (500 mg/6 mL, Waters) and Envi-18 (500 mg/6 mL, Supelco) SPE cartridges were used for clean up. The extraction method was described in our previous study in detail (Li et al., 2015). Briefly, both Oasis HLB and Envi-18 columns in series were used for achieving a good recovery for all target chemicals. The cartridges firstly cleaned by dichloromethane, methanol and ultrapure water, respectively, to remove residual impurities, subsequently preconditioned by 5 mL each of methanol and ultrapure water for Oasis HLB columns and with 5 mL of dichloromethane before methanol and ultrapure water for Envi-18 column at flow-rate of 1–2 mL/min. After extraction, the columns were then rinsed with ultrapure water and evaporated to dry for 30 min. The enriched Oasis HLB and Envi-18 columns were eluted, respectively, with 15 mL of mixed dichloromethane-methanol (v:v, 7:3, 3 × 5 mL) and 15 mL of hexane-dichloromethane (v:v, 7:3, 3 × 5 mL). The elution rate was 1–2 mL/min. The eluent from Oasis HLB and Envi-18 columns was combined and evaporated to 1 mL using a rotary evaporator and nitrogen flowing, and then subjected to instrumental analysis.

2.4. Instrumental analysis

The concentrations of PAEs and phenols were analyzed using an Agilent 7890B gas chromatograph (GC) coupled with an Agilent 5977A mass selective detector (MSD). A DB-5MS capillary column (Agilent, 30 m, 0.25 mm i.d., 0.25 μm film thickness) was used to separate the target substances. Helium was used as the carrier gas with a column flow rate of 1.0 mL/min in a constant-flow mode. The injector, ion source and transfer line temperatures were set at 250, 230 and 305 °C, respectively. The GC oven temperature was programmed from 40 °C (2 min) to 100 °C at 15 °C/min, increased to 300 °C at 10 °C/min, and held constant for 5 min. The electron impact energy was set at 70 eV, and 1 μL of each sample was injected in splitless mode. PAEs and phenols were analyzed in the selected ion monitoring mode.

2.5. Quality assurance (QA) and quality control (QC)

To ensure the accuracy of extraction and analytical procedures, all data were subject to strict quality control procedures. To avoid contamination, plastic ware was excluded. The pretreatment of all samples were carried out in a super-clean workbench.

Blanks covering the entire analytical procedure, including extraction, clean up procedure and GC-MS analysis, were analyzed. The results showed that very low levels of PAEs (less than 83.1 ng/g) and phenols (less for 17.0 ng/g) were found in the blank, which made a little contribution to the samples. The concentration of these pollutants in the samples was blank corrected.

The limit of detection (LOD) for analytes was determined with a signal-to-noise ratio of 3:1, while the limit of quantification (LOQ) was determined with a signal-to-noise ratio of 10:1. The LOD and LOQ for target phthalates were 0.66–20 and 2.2–67 ng/g, and those of the phenols were 0.53–2.2 and 1.7–7.3 ng/g, respectively. Three matrix samples spiked with mixed standards at two levels of 500 and 1000 ng/g were run to monitor the

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