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Occurrence and distribution of phthalate esters in riverine sediments from the Pearl River Delta region, South China

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ABSTRACT

Sixty-eight sediment samples collected from Dongjiang River, Xijiang River, Beijiang River and Zhujiang River in the Pearl River Delta (PRD) region, Southern China, were analyzed for 16 phthalate esters (PAEs). PAEs were detected in all riverine sediments analyzed, which indicate that PAEs are ubiquitous environmental contaminants. The Σ_{16}PAEs concentrations in riverine sediments in the PRD region ranged from 0.567 to 47.3 μg g^{-1} dry weight (dw), with the mean and median concentrations of 5.34 μg g^{-1} dw and 2.15 μg g^{-1} dw, respectively. Elevated PAEs concentrations in riverine sediments in the PRD region were found in the highly urbanized and industrialized areas. Of the 16 PAEs, diisobutyl phthalate (DiBP), di-*n*-butyl phthalate (DnBP) and di(2-ethylhexyl) phthalate (DEHP) dominated the PAEs, with the mean and median concentrations of 1.12 μg g^{-1} dw, 0.420 μg g^{-1} dw and 3.72 μg g^{-1} dw, and 0.429 μg g^{-1} dw, 0.152 μg g^{-1} dw and 1.55 μg g^{-1} dw, respectively, and accounted for 94.2–99.7% of the Σ_{16}PAEs concentrations. Influenced by local sources and the properties of PAEs, a gradient trend of concentrations and a fractionation of composition from more to less industrialized and urbanized areas were discovered. As compared to the results from other studies, the riverine sediments in the PRD region were severely contaminated with PAEs. Information about PAEs contamination status and its effect on the aquatic organisms in the PRD region may deserve further attention.

Phthalate esters (PAEs) are a class of synthetic compounds mainly used as non-reactive plasticizers in polyvinylchloride (PVC), polyvinyl acetates, cellulosics and polyurethanes, and as non-plasticizers in the manufacturing of cosmetics, paints, glues, photographic films, and insect repellents (Staples et al., 1997; Gómez-Hens and Aguilar-Caballos, 2003). The global demand for PAEs is reported to be 6.0 million tons $year^{-1}$ (Xie et al., 2007). Widespread use of PAE-containing products has led that elevated levels of PAEs are ubiquitous in various environmental matrices, such as in air (Xie et al., 2005; Kong et al., 2013; Pei et al., 2013; Zhang et al., 2013; Cousins et al., 2014), water (Chang et al., 2002; Fromme et al., 2002; Wang et al., 2008; He et al., 2013; Sun et al., 2013; Gao et al., 2014; Liu et al., 2014), soil (Zeng et al., 2009a, b; Wang et al., 2013), biota as well as in tissues and fluids of wildlife and human (Hines et al., 2009; Guo et al., 2011; Kim et al., 2011; Liu et al., 2012). Some PAEs (e.g. di-*n*-butyl phthalate (DnBP), di(2-ethylhexyl) phthalate (DEHP) and butylbenzyl phthalate (BBP)) and their metabolites are estrogenic and exhibit adverse reproductive effects (Harris et al., 1997; Kavlock et al., 2002; Scholz, 2004; Ema et al., 2008; Chen et al., 2011a, b). Currently, the occurrence, fate, and potential ecological risks of PAEs in aquatic environment are causing increasing concern (Gao et al., 2014).

PAEs, like other anthropogenic compounds, can enter into the aquatic environments from a variety of sources including direct/indirect discharge, surface run-off and atmospheric deposition, etc (Chang et al., 2002; Fromme et al., 2002; Wang et al., 2008; Zeng et al., 2008a; Adeniyi et al., 2011; He et al., 2013; Sun et al., 2013; Liu et al., 2014). Due to their high hydrophobicity, PAEs in the aquatic environments tend to be associated with particulate matters that can be settled to bottom sediments and accumulated continuously. Therefore the sediments act both as a long-term pollutant sink and reservoir, and as a source of contaminants through re-suspension. They may also pose a potential environmental threat to aquatic organisms (Adeniyi et al., 2011; Sun et al., 2013; Liu et al., 2014). However, very little information is currently available in developing countries, like China, which one

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of the world's largest producer and consumer of PAEs (Zeng et al., 2008a).

The Pearl River is the third largest river in China. It has a great number of tributaries and streams, forming a complicated watershed called the Pearl River Delta (PRD). The PRD region, with an area of 53,580 km^2 and a population of more than 40 millions, is located in South China adjacent to the South China Sea, covering Hong Kong, Macau and nine prefectures of Guangdong Province, including the major urban centers Guangzhou, Dongguan, and Foshan (Fig. 1). As a result of rapid economic development in recent decades, the PRD region is experiencing accelerated environmental deterioration. Elevated levels of the toxic chemicals, including organochlorine pesticides(OPs) (Luo et al., 2004; Guan et al., 2009; Li et al., 2011), polybrominated diphenyl ethers (PBDEs) (Mai et al., 2005; Zhang et al., 2009; Chen et al., 2013) and polycyclic aromatic hydrocarbons (PAHs) (Luo et al., 2004; Zhang et al., 2011), polychlorinated biphenyls (PCBs) (Guan et al., 2009), Perfluorinated compounds (PFCs) (Zhao et al., 2011), endocrine-disrupting chemicals (ECDs) (Zhao et al., 2009; Gong et al., 2011; Feng et al., 2012), and chlorinated paraffins (CPs) (Chen et al., 2011a, b) have been detected in both abiotic and biotic compartments in the aquatic environment in the PRD region. This study is part of our efforts to characterize the sources, distribution and fate of PAEs in the aquatic and atmospheric environments around the PRD region (Zeng et al., 2008a, b, 2009a, b, 2010; Lan et al., 2012), given the encouraged growth of electronics, plastics and textile manufacturing activities. The main objective of this study was to investigate the concentrations, compositions and distributions of 16 PAEs in the riverine sediments from the PRD region, and discuss their contamination profiles and possible sources of PAEs.

Sixteen PAEs standard mixture, containing dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (D*i*BP), di-*n*-butyl phthalate (D*n*BP), dimethylglycol phthalate (DMGP), di(4-methyl-2-pentyl) phthalate (DMPP), di(2-ethoxyethyl) phthalate (DEEP), di-*n*-amyl phthalate (D*n*AP), di-n-hexyl phthalate (D*n*HP), butylbenzyl phthalate (BBP), di(hexyl-2-ethylhexyl) phthalate (HEHP), di(2-*n*-butoxyethyl) phthalate (DBEP), dicyclohexyl phthalate (DCHP), di(2-ethylhexyl) phthalate (DEHP), di-*n*-nonyl phthalate (D*n*NP), di-n-octyl phthalate (D*n*OP) at 1000 μg mL^{-1} each, and surrogate standards, consisting of diisophenyl phthalate, di-*n*-phenyl phthalate, di-*n*-benyl phthalate, in a mixture solution of 500 μg mL^{-1} each, were supplied by Dr. Ehrenstorfer (Augsburg, Germany). Internal standard, benzyl benzoate, was acquired initially as a solid of 99% purity (Aldrich Chemicals, Gillingham, Dorset, USA).

Neutral silica gel (80–100 mesh), and alumina (100–200 mesh) were cleaned with methanol (MeOH), dichloromethane (DCM), and n-hexane using Soxhlet extractor for 72 h, activated at 180 ± 1 °C, 250 ± 1 °C for 12 h, and then deactivated with 3% (w/w) of deionized water (extracted with DCM/n-hexane), respectively. Anhydrous sodium sulfate was baked at 420 °C for 12 h and stored in sealed glass jars. Filter paper was extracted with methanol, DCM, and n-hexane with Soxhlet extractor for 72 h prior to use. Water was filtered by Milli-Q and double distilled. All organic solvents used were of analytical grade, and redistilled using glass system. Laboratory glassware was soaked overnight in K_2CrO_7/H_2SO_4 solution, washed with tap water and redistilled water, baked at 300 °C for 12 h, and then rinsed with acetone, DCM and n-hexane.

The Pearl River is the largest and most complex water system in Southern China. It mainly comprises four tributaries, namely, the Zhujiang River, Dongjiang River, Beijiang River and Xijiang River,

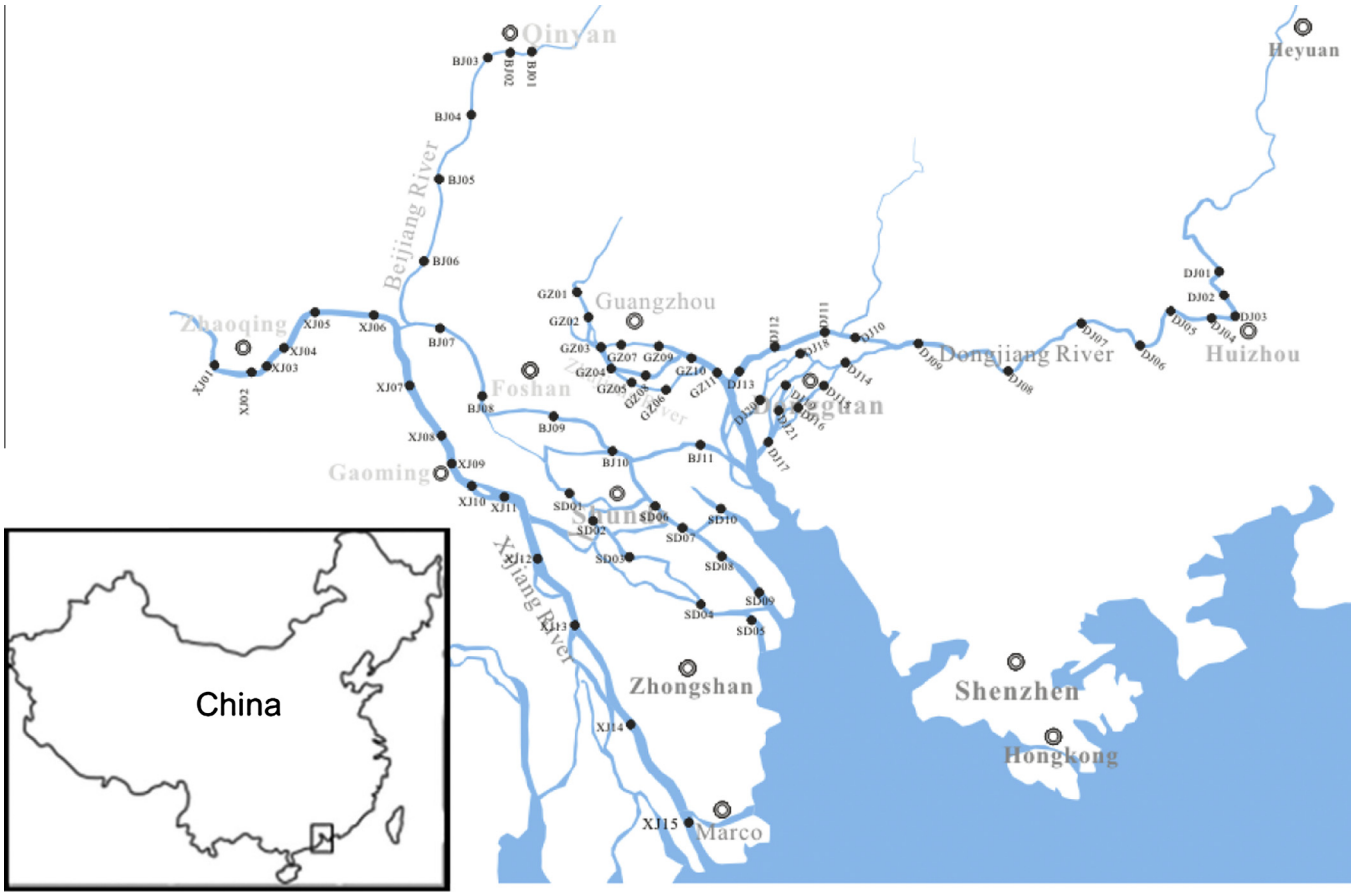

Fig. 1. Map of the Pearl River Delta (PRD) in southern China and location of sampling sites.

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