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Spatial–temporal distribution and potential ecological risk assessment of nonylphenol and octylphenol in riverine outlets of Pearl River Delta, China

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ABSTRACT

The aquatic environments of the Pearl River Delta in Southern China are subjected to contamination with various industrial chemicals from local industries. In this paper, the occurrence, seasonal variation and spatial distribution of alkylphenol octylphenol (OP) and nonylphenol (NP) in river surface water and sediments in the runoff outlets of the Pearl River Delta were investigated. NP and OP were detected in all water and sediment samples and their mean concentrations in surface water during the dry season ranged from 810 to 3366 ng/L and 85.5 to 581 ng/L, respectively, and those in sediments ranged from 14.2 to 95.2 ng/g dw and 0.4 to 3.0 ng/g dw, respectively. In surface water, much higher concentrations were detected in the dry season than those in the wet season. In sediments, the concentrations in the dry season were also mostly higher. High concentrations of NP and OP were found in Humen outlet, likely due to high levels of domestic and industrial wastewater discharges. An ecological risk assessment with the use of hazard quotient (HQ) was also carried out and the HQ values ranged from 3.6×10^{-5} to 35 and 64% of samples gave a HQ > 1, indicating that the current levels of NP and OP pose a significant risk to the relevant aquatic organisms in the region.

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Introduction

Alkylphenols (APs) are important intermediates in the production and degradation of alkylphenol ethoxylates (APEs), which are widely used as nonionic surfactants in industrial, agricultural and household applications (Ying et al., 2002). They are persistent lipophilic compounds and can be easily absorbed and bioaccumulate in organisms (Hsieh et al., 2013). Nonylphenol ethoxylates (NPEs) and octylphenol ethoxylates (OPEs) represent about 80% and 20% of the total APEs in use, respectively. APEs are

biodegraded in sewage treatment plants and the natural environment, resulting in alkylphenols (APs), such as 4-nonylphenol (NP) and 4-octylphenol (OP). Compared to their parent compounds, NP and OP are even more persistent and toxic in the environments (Giger et al., 1984; Soto et al., 1991; Isobe et al., 2001). In addition, NP and OP are known to disrupt endocrine functions in wildlife and humans. They can induce vitellogenin (VTG) synthesis and feminization in male fish at a concentration level of 1 µg/L. More importantly, they can enter into humans through cutaneous absorption, ingestion, or inhalation, and

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affect endocrine functions, particularly in newborns and fetuses (Hsieh et al., 2013). Due to their estrogenic activities, both NP and OP have been listed as priority hazardous substances in the Water Framework Directive (European Parliament, 2000), for which a substantial reduction policy is being implemented (Directive 2003/53/EC, 2003).

Marine environments such as oceans and coastal zones serve as reservoirs for contaminants from a variety of sources. Riverine runoff has been the most important contributor in the transportation of contaminants from terrestrial sources to coastal areas (Lu et al., 2009; Shimizu et al., 2013). Thus, accurate data on levels of contaminants in riverine are needed to understand their effects on marine environments. The Pearl River Delta is located in the southern coast of China and connects the Pearl River Estuary (PRE) to the South China Sea (SCS) through eight major runoff outlets. In recent decades, the Pearl River Delta has become one of the most rapidly developing regions in China (Wang et al., 2013). Rapid agricultural, industrial, and urban developments and associated heavy uses of chemicals have resulted in increasingly serious levels of environmental pollution. The annual discharge of wastewater from the Pearl River Delta region into the PRE and the SCS was estimated to be about $1.73 \times 10^9 \text{ m}^3$ (Xu et al., 2013). It has been reported that high concentrations of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) were detected in fish from the PRE and Daya Bay (Guo et al., 2008). It has also reported that stream effluent had estrogenic and androgenic effects on mosquitofish in Guangzhou (Wen et al., 2013).

Annual production of NP reached approximately 45,000 tons in the EU (Feenstra, 2008), 16,500 tons in Japan (JME, 2001) and 16,000 tons in China (Jin et al., 2004). In China, APs have been found in surface water and sediments in a number of rivers and estuaries such as Hai River, Yellow River, Pearl River and Pearl River Estuary (Jin et al., 2004; Wang et al., 2012; Zhao et al., 2009; Zhang et al., 2009; Gong et al., 2011; Chen et al., 2006). Recently, there have been several studies in Pearl River Delta that reported the occurrence and distribution of APs in surface water and sediments (Wang et al., 2012; Zhao et al., 2009; Zhang et al., 2009; Gong et al., 2011; Chen et al., 2006).

The purposes of the present study were to investigate the presence, seasonal variations and spatial distributions of NP and OP in surface water and sediments from six major runoff outlets of the Pearl River Delta and to assess the potential adverse risks to aquatic organisms in the riverine environment using the method of hazard quotient (HQ).

1. Materials and methods

1.1. Chemicals and materials

Standards of 4-nonylphenol (mixture of compounds with different isomers) and 4-t-octylphenol (97%) were purchased from Sigma-Aldrich. Dichloromethane and hexane were of analytical grade and redistilled by a glass distillation apparatus. Methanol was HPLC grade. Glass fiber filters (GF/F, pore size $0.45 \mu\text{m}$) were supplied by Whatman. Neutral silica gel (100–200 mesh) was baked at 500°C for 8 hr and then deactivated by adding 5% distilled water. All the glassware used for analysis of organic compounds were baked at 450°C for 6 hr prior to use in order to avoid any organic contamination. Stock solutions of chemicals were prepared at 10 g/L with methanol and stored at -18°C in the dark.

1.2. Site description and sample collection

Pearl River is the second largest river in China, with an annual discharge of $3.49 \times 10^{11} \text{ m}^3$ (Gong et al., 2011). It has three main

tributaries, namely, East River, North River and West River. They are the main drinking water sources for Guangzhou City and surrounding towns. They merge into SCS via eight major outlets including four eastern outlets, Humen, Jiaomen, Hongqimen, Hengmen, and four western outlets, Modaomen, Jitimen, Hutiaomen and Yamen. Pearl River flows through the city of Guangzhou, a metropolis of southern China, which is highly urbanized with a population of 14 million and a variety of industries (Fig. 1). East River supplies freshwater for Guangzhou, Dongguan, Shenzhen and Hong Kong. It runs through Dongguan City, which is a center for electronics manufacturing. East River and Pearl River join at the Shizhiyang Waterway and run into the Pearl River Estuary through the Humen outlets. West River and North River, located in the southwest of the Pearl River Delta, flow across rural and less industrialized and populated areas. North River flows into the Pearl River Estuary through Jiaomen, Hongqimen, and Hengmen outlets, and West River runs into the same estuary through Modaomen, Jitimen, Yamen and Hutiaomen outlets.

Seven sampling sites in six runoff outlets (marked S1–S7 in Fig. 1) were selected for sampling. Surface water and sediment were collected in January 2013 (dry season) and April 2013 (wet season). Three duplicated surface water samples from a depth of about 0.5 m were collected in pre-rinsed 4 L amber glass bottles at each sampling outlet. Sediment cores were also sampled with a core sampler from these sites. The total length of the sediment cores collected for each site was below 25 cm. At each sampling outlet, three duplicated sediment samples were collected. The cores were sectioned in intervals of 5 cm by using stainless steel plates. The same depth samples were combined and wrapped in aluminum foil. The collected water and sediment samples were immediately transported to the laboratory in a cooler.

Upon arrival at the laboratory, surface water samples were filtered through glass fiber filters (GF/F, Whatman, $0.45 \mu\text{m}$ pore size) for the separation of suspended soils before solvent extraction. All the filtered water samples were acidified by HCl to $\text{pH} < 2$ to prevent bacterial activities and stored at 4°C and analyzed within a week. The sediment samples were kept at -20°C until analysis.

1.3. Analytical procedure

The method of extraction for APs in surface water was modified from the literature (Oh et al., 2009). Each filtrate was extracted by liquid–liquid extraction with dichloromethane under acidic conditions ($\text{pH} 2\text{--}3$). A volume of 30 mL of dichloromethane was added into 1 L of aqueous sample and the solution was vigorously shaken for 10 min. The water sample was extracted for two additional times with 20 mL of dichloromethane. The dichloromethane fraction was collected and evaporated until dryness using a rotary evaporator, then re-dissolved in 1 mL of methanol. Three replicate samples were performed.

The extraction method for the APs in sediment was adapted from a previous study with some modifications (Cai et al., 2012). The sediments were extracted by using ultrasound-assisted solvent extraction. Ten grams of air-dried sediment were mixed with 20 mL of a mixture of dichloromethane and methanol (9:1, V/V) in a screw-top centrifuge tube. The tube was ultrasonicated for 10 min and centrifuged at 4000 r/min for 10 min,

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