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Occurrence and ecological risk assessment of emerging organic chemicals in urban rivers: Guangzhou as a case study in China

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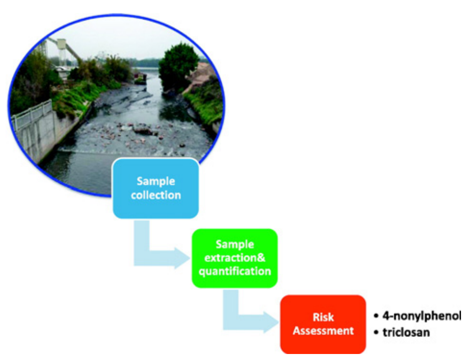
HIGHLIGHTS

- Investigation of EDCs and PPCPs in urban rivers in megacity Guangzhou;
- Higher contamination of EDCs and PPCPs was observed in rivers in urban area;
- Concentration levels of EDCs and PPCPs were consistent with physicochemical parameters;
- 4-nonylphenol and triclosan showed RQs >1 in more than 70% of the reported area;

GRAPHICAL ABSTRACT



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ABSTRACT

Urban rivers may receive contamination from various sources including point sources like domestic sewage and nonpoint sources (e.g., runoff), resulting in contamination with various chemicals. This study investigated the occurrence of emerging organic contaminants (3 endocrine disrupting compounds (EDCs), and 17 pharmaceuticals and personal care products (PPCPs)) in six urban rivers of a representative subtropical city, Guangzhou (southern China). Our results showed that EDCs and personal care products were frequently detected in the water phase and sediment phase. 4-nonylphenol (4-NP) was the most predominant compound with the highest concentration of 5050 ng/L in the water phase and 14,400 ng/g dry weight (dw) in the sediment. Generally, higher total concentrations of EDCs and PPCPs were detected in the four urban streams compared to the main stream Zhujiang River and the Liuxi River at the suburb area. A screening-level risk assessment showed that 4-nonylphenol and triclosan (TCS) pose potential risks to aquatic organisms in most sampling sites. For individual taxa, 4-NP may pose risks to various groups of aquatic organisms, while TCS only might pose high risks to algae. *Capsule:* Higher contamination of EDCs and PPCPs was observed in rivers in urban area; 4-nonylphenol and triclosan showed RQs > 1 in >70% of the reported area.

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1. Introduction

Guangzhou is a highly urbanized megacity in southern China with a population of 13.1 million (http://www.guangzhou.gov.cn/). Due to rapid economic development and urbanization, urban drainage pipe network is well developed in Chinese megacities, such as Guangzhou (http://www.gzepb.gov.cn/). Currently, 10,204 km of municipal drainage pipe network has been installed, and 48 WWTPs have been installed and is in use in Guangzhou. The treated domestic sewage amounts to 4.99 million tons/day. 93% and 48% of the produced domestic sewage in urban areas and rural area enter into the WWTPs, respectively (http://www.gzepb.gov.cn/). Therefore, a proportion of the produced domestic sewage in urban areas is still directly released into urban rivers (i.e., does not undergo wastewater treatment), which has become a serious environmental problem and has attracted growing concern of the Chinese government (Zhang et al., 2016). The Zhujiang River, which has the second highest flow rate in China, receives input from hundreds of tributaries in Guangzhou (Zhang et al., 2008). Particularly in megacities like Guangzhou, the majority of these tributaries receive discharges of treated and untreated wastewaters from surrounding residential areas resulting in increased levels of both nutrients and contaminants in the receiving waters. Lastly, the Chinese government has implemented a system to characterize water quality based on nutrient levels (i.e, five-day biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), total organic carbon (TOC), total phosphorous (TP), total nitrogen (TN), and ammonia-nitrogen (NH_3-N)), referred to as the Environmental Quality Standards for Surface Water (EQS, GB 3838-2002).

Regarding contaminants, endocrine disrupting chemicals (EDCs), and pharmaceuticals and personal care products (PPCPs) have raised significant concerns due to their wide applications in consumer products, bioaccumulation ability and potential adverse effects to the environment. In recent years, EDC and PPCP contamination have been widely detected in different environmental compartments, such as wastewater effluents (e.g., Zhao et al., 2009; Lange et al., 2015), surface water (e.g., Zhao et al., 2010a, 2010b; Klosterhaus et al., 2013; Salgueiro-González et al., 2015a), sediment (Zeng et al., 2008; Klosterhaus et al., 2013; Chen et al., 2014a) and aquatic organisms (Lee et al., 2014; Yang et al., 2014; Salgueiro-González et al., 2015b), with concentrations ranging from ng/L to μg/L in aqueous matrices and ng/g to μg/g in solid matrices and organisms.

Among EDCs, 4-*t*-octylphenol (4-*t*-OP), 4-nonylphenol (4-NP) and Bisphenol A (BPA) represents three of the most reported phenolic xenoestrogen compounds in China (Ying et al., 2002; Zhao et al., 2009). 4-*t*-OP and 4-NP are degradation products of alkylphenolethoxylate surfactants while BPA is an intermediate used in certain plastics and epoxy resins (Ying et al., 2002; Asimakopoulos and Thomaidis, 2015). These three chemicals have been found in biota samples (e.g., in China) including algae, fish and mollusc (Yang et al., 2014; Gu et al., 2016), and a maximum measured concentration of 19,891 ng/g wet weight (ww) for 4-NP was found in fish samples from the estuary of the Yangtze River (Gu et al., 2016). Recently, 4-NP and BPA were reported to pose potential ecological risks to organisms in several rivers in different regions of China (Gao et al., 2014; Guo et al., 2015). However, knowledge about the ecological risks posed by most of these EDCs to aquatic organisms is still limited, especially in sediment (Diepens et al., 2014, 2016).

PPCPs constitute another important group of emerging contaminants. The production and usage volumes of PPCPs in China have been growing rapidly, resulting in China being among the top three countries with the largest consumption of PPCPs (Liu and Wong, 2013). After use, PPCPs are discharged into municipal wastewater treatment plants (WWTP) or directly released into aquatic environments (Ying and Kookana, 2007; Chalew and Halden, 2009). So far, most freshwater acute test performed with pharmaceuticals has shown low or negligible toxicity to aquatic organisms (Fent et al., 2006; Kim et al., 2009). However, some researchers note that a continuous release of PPCPs to riverine environments may pose potential ecological impact due to chronic exposure (Han et al., 2010; Zhang et al., 2015a). Studies on long-term effects, however, are limited and chronic effects are still not well understood for some substances.

The few studies that have investigated EDCs and PPCPs contamination in urban rivers in China have mainly focused on contamination in the water phase (Peng et al., 2008; Zhao et al., 2009, 2010a; Yang et al., 2013; Dai et al., 2015). However, no thorough risk assessment was performed in those studies which were based on the assessment factor (AF) method. Though the AF approach is easy to use and practical if toxicity data is limited, the PNEC estimates provided by this method exhibit great uncertainty as they are solely dependent on the minimum toxicity value and a certain AF. Instead, statistical extrapolation based on species sensitivity distributions (SSD) method gives more reliable and reasonable statistics considering that the PNEC estimates are based on an established distribution of a full of toxicity data set (Lei et al., 2012). Moreover, an increasing concentration of sediment-associated EDC and PPCPs is expected in China due to the continuous release and the physical-chemical properties of a fraction of compounds (e.g., log Kow), which leads to adsorption to particles in the water column and subsequent precipitation and accumulation in the sediment compartment. Thus benthic organisms may be at risk from these compounds (Diepens et al., 2016). Therefore, further studies to elucidate potential ecological consequences of EDC and PPCPs contamination in aquatic sediments are needed.

Guangzhou and the surrounding rivers were selected as study area as this area provides a gradient in contamination and population density. The specific EDCs and PPCPs comprising three phenolic xenoestrogens, two polycyclic musks and two nitromusks, two antimicrobials and eleven acid pharmaceuticals (non-steroidal anti-inflammatory drugs and blood lipid regulators) were selected in this study as they have been studied to varying degrees both in the present study area (i.e., in surface waters and sediments collected from twelve sampling sites in six urban rivers in and surrounding Guangzhou) as well as in other economic/geographic regions.

The objective of the current study was to 1) assess the levels of general water quality in urban rivers in Guangzhou based on measurements of nutrients, and to measure concentration levels of the selected compounds: *i*) in a gradient from un-contaminated and low-density populated rural area to highly contaminated and high-density populated urban area, *ii*) between seasons (wet and dry season); 2) comparing measured values with published values in China and globally to identify spatial and temporal trends, and finally to 3) perform a screening-level ecological risk assessment of surface water and sediment by relating the measured environmental concentrations (MECs) in surface water or estimated concentrations in pore water with published toxicity data for water exposure.

2. Materials and methods

2.1. Chemicals and reagents

Twenty commonly used EDCs and PPCPs were selected as target compounds in the current study: 4-nonylphenol (4-NP), 4-*tert*-octylphenol (4-*t*-OP), bisphenol A (BPA), triclocarban (TCC), triclosan (TCS), galaxolide (HHCB) and tonalide (AHTN), musk xylene (MX), musk ketone (MK), clofibric acid, ketoprofen, naproxen, diclofenac, indometacin, ibuprofen, meclofenamic acid, mefenamic acid, fenoprofen, gemfibrozil and tolfenamic acid. Specific supplier sources of all the chemicals and reagents used in this study are provided in Supporting Information (Text S1), and the physicochemical properties of each compound is presented in Table S1 (Supplementary information). Individual stock solutions (100 mg/L) of EDCs, antimicrobials and acidic pharmaceuticals were prepared in methanol, while the