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Pharmaceuticals and personal care products (PPCPs) and artificial sweeteners (ASs) in surface and ground waters and their application as indication of wastewater contamination

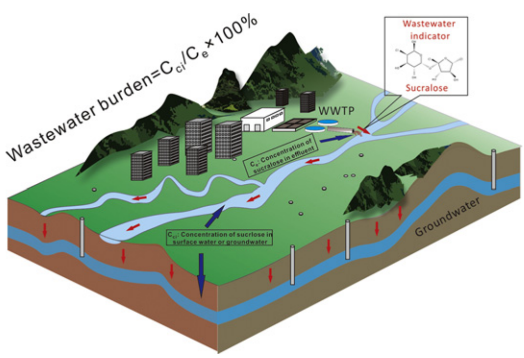
Yuan-Yuan Yang [a,d], Jian-Liang Zhao [a], You-Sheng Liu [a], Wang-Rong Liu [a,c], Qian-Qian Zhang [a], Li Yao [a], Li-Xin Hu [a], Jin-Na Zhang [a], Yu-Xia Jiang [a], Guang-Guo Ying [a,b,]*

[a] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[b] The Environmental Research Institute, MOE Key Laboratory of Environmental Theoretical Chemistry, South China Normal University, Guangzhou 510006, China
[c] South China Institute of Environmental Sciences, Ministry of Environmental Protection of PRC, Guangzhou 510655, China
[d] The University of Chinese Academy of Sciences, Beijing 100049, China

HIGHLIGHTS

- We investigated PPCPs and ASs in surface water and groundwater.
- ASs were widely detected at high levels in surface water and ground water.
- Sucralose was a suitable conservative indicator to evaluate wastewater burden.
- Those indicators can quantitatively reflect the contamination with wastewater.

GRAPHICAL ABSTRACT



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ABSTRACT

We systematically investigated the occurrence and distribution of 93 pharmaceuticals and personal care products (PPCPs) and 5 artificial sweeteners (ASs) in surface water and groundwater of Dongjiang River basin in south China. In surface water, 52 compounds were detected with median concentrations ranging from 0.06 ng/L to 504 ng/L, while in groundwater, 33 compounds were detected with concentrations up to 4580 ng/L for acesulfame. PPCPs and ASs were widely detected in the surface water and groundwater samples, which indicated contamination by domestic wastewater in the surface water and groundwater of Dongjiang River basin. Temporal and spatial variations of the detected chemicals were observed in surface water. Acesulfame, sucralose and cyclamate can be used as wastewater indicators to imply contamination in groundwater caused by domestic wastewater due to their hydrophilicity, anthropogenic sources and ubiquity in groundwater. Moreover, the detection of the readily degradable ASs, cyclamate, was a strong indication of untreated wastewater in groundwater. Sucralose was found to be a suitable wastewater indicator to reflect domestic wastewater contamination in surface water and groundwater qualitatively and quantitatively, and it can be used to evaluate wastewater burden in surface water and groundwater of Dongjiang River basin. The wastewater burden data from this survey implied serious contamination in surface water and groundwater by domestic wastewater at Shima River, a tributary of the Dongjiang River. The findings from this study suggest that the selected labile and conservative

* Corresponding author at: State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China.
E-mail address: guang-guo.ying@gig.ac.cn (G.-G. Ying).

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chemicals can be used as indication of wastewater contamination for aquatic environments qualitatively and quantitatively.

1. Introduction

Pharmaceuticals and personal care products (PPCPs) are a broad range of chemicals which are active and inert ingredients in non-prescription and prescription pharmaceuticals for human and veterinary use and personal care products (Lishman et al., 2006). Artifical sweeteners (ASs) are widely used as sugar substitutes in a broad range of food, beverages and drugs in substantial quantities (Buerge et al., 2011; Lange et al., 2012). Over the past decade, PPCPs and ASs have been frequently detected as emerging organic contaminants at pg/L to mg/L levels in various aquatic environments such as surface warter and groundwater (Gan et al., 2013; Liu et al., 2015; Postigo and Barcelo, 2015; Yang et al., 2011). This is attributed to incomplete removal of PPCPs and ASs in wastewater treatment plants (WWTPs) (Buerge et al., 2009; Luo et al., 2014) and direct discharge of untreated wastewater (Lapworth et al., 2012; Richardson, 2009). Hence, PPCPs and ASs have been suggested to indicate domestic wastewater contamination (Glassmeyer et al., 2005; Nakada et al., 2008; Tran et al., 2014a).

Wastewater indicators are useful tools to evaluate the impact of wastewater on surface water or groundwater qualitatively and quantitatively (Buerge et al., 2009; Kahle et al., 2009). For example, Glassmeyer et al. (2005) investigated the occurrence of 110 PPCPs in 10 rivers of the USA and suggested that carbamazepine, diethyltoluamide (DEET) and caffeine were suitable wastewater indicators of river water, the presence of these compounds in river water is a strong indication of wastewater contamination. Buerge et al. (2009) demonstrated that acesulfame could reflect contamination by domestic wastewater in surface water and groundwater quantitatively. Moreover, the ratio of labile indicators to conservative indicators could be used to identify the contribution of raw or treated wastewater discharged to surface water (Kasprzyk-Hordern et al., 2009; Lv et al., 2014; Sun et al., 2016). The usage and pattern of these chemicals may vary among different regions. In our previous study, we screened a range of wastewater related organic chemicals (93 PPCPs and 5 ASs) in WWTPs and selected suitable wastewater indicators in the Pearl River Region, south China (Yang et al., 2017). Sucralose and fluconazole were selected as conservative indicators in the region, while cyclamate, saccharin, methyl paraben, ethyl paraben, propyl paraben, paracetamol, salicylic acid and caffeine were selected as labile indicators.

As one of the three major rivers in the Pearl River Basin, Dongjiang River was selected as the study area in this study. This river has a drainage area of 32,275 km^2 and is an important drinking water source for the people in the region. In Dongjiang River Basin, the urban land, arable land, garden plot, forest land and other land accounted for 9.39%, 8.42%, 5.67%, 71.4% and 5.12%, respectively in 2009 (Ren et al., 2011). Dongjiang River flows through several fast developing cities including Huizhou, Shenzhen and Dongguan in South China. From the year of 1990 to 2009, the permanent residents in Dongjiang River Basin increased from 10.2 million to 28.7 million, and the gross domestic product (GDP) increased from 37.5 billion yuan to 1.60 trillion yuan (Ren et al., 2011). Moreover, the urban land in the Dongjiang River Basin increased from 2258.4 km^2 to 3283.3 km^2 from 2000 to 2009 (Ren et al., 2011). Rapid urbanization has resulted in increasing wastewater discharge in the region. Taking Dongguan as an example, the discharge of wastewater has increased from 690.49 million ton to 1.14 billion ton from 2005 to 2015 (Statistics Information Network of Dongguan City, 2016).

The objectives of this study were firstly to investigate the contamination levels of PPCPs and ASs in surface water and groundwater of Dongjiang River Basin, and then to evaluate the wastewater burden in surface water and groundwater by applying the selected wastewater indicators. The results from this study can facilitate better understanding of surface water and ground water contamination in Dongjiang River Basin.

2. Materials and methods

2.1. Target chemicals

93 PPCPs including 48 antibiotics, 19 biocides, 15 acidic and neutral pharmaceuticals (11 anti-inflammatory/analgesics drugs, 2 antiepileptic drugs, and 2 lipid regulators), 6 X-ray contrast agents (ICMs), 4 corrosion inhibitors and caffeine, as well as 5 ASs (acesulfame, aspartame, cyclamate, saccharin, sucralose) were selected as target chemicals in this investigation. Detailed information of the target chemicals is summarized in Table S1 (supplementary information).

2.2. Study area and sample collection

Dongjiang River Basin was chosen as the study area. The sampling sites of surface water and groundwater in Dongjiang River basin are shown in Fig. 1. For surface water, grab samples (1 L each) were collected from 13 sampling sites (SF1–13) in the middle and lower reaches of Dongjiang River in March (dry season) and July (wet season) in 2015. Four sampling sites (SF1, SF4, SF8, and SF13) were located in the main stream of Dongjiang River, while the other 9 sampling sites were located in the tributaries of Dongjiang River. Grab groundwater samples (1 L each) were obtained from private wells from 11 sampling sites (GW1–11) during October to Novermber in 2015. The sampling sites GW1–5 were located on both sides of Shima River, while the sampling sites GW6–11 were located on both sides of Xizhijiang River. Detailed information of the sampling sites are summarized in Table S2 and Table S3.

Since all target chemicals were extracted and analyzed by five different analytical methods, five groups of water samples were collected for surface water and groundwater. Three replicates for each site were sampled for each group. In other word, 15 bottles (1 L each) of water samples were collected at each sampling site. Each group of samples were acidified with 4 M H_2SO_4 to pH 3.0 and 5% methanol (*v*/v) were added to all the samples except for the group used for analyzing ASs, X-ray contrast agents and caffeine as it could make these highly hydrophilic compounds hard to retain on solid-phase extraction (SPE) columns. All water samples were kept on ice during transport to the laboratory, and then stored in a 4 °C cold room in darkness. All the water samples were then extracted within two days.

Basic water quality parameters, including pH, electrical conductivity (EC) and dissolved oxygen (DO) of surface water and groundwater samples were measured by a multi-parameter water quality monitor on site (YSI-Pro2030, YSI Incorporated, USA), while their other quality parameters, such as chemical oxygen demand (COD), ammonia nitrogen (NH_3-N), total nitrogen (TN) and total phosphorus (TP) were determined in the laboratory according to the standard methods (Clesceri et al., 2001). The basic quality parameters of surface water and groundwater samples are listed in Table S4 and Table S5.

2.3. Sample preparation and analysis

Multiple methods were applied to extract and analyze the target chemicals. Before extraction, all the water samples were vacuum filtered through 0.7 μm glass fiber filters (GF/F, Whatman) and then spiked with