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Pharmaceutically active compounds in the Xiangjiang River, China: Distribution pattern, source apportionment, and risk assessment

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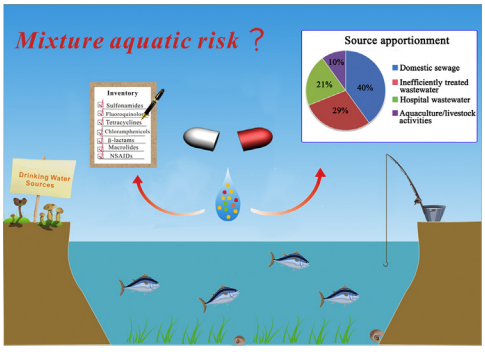
HIGHLIGHTS

- First investigation of categories of PhACs on the Xiangjiang River
- Urban areas were heavier impacted by pharmaceuticals than rural areas.
- Distribution of PhACs was closely related to the temperature and NH_3-N.
- Domestic sewage was the major contribution of PhACs on the surface water.
- Both single and mixture risk approaches were used to evaluate the aquatic risks.

GRAPHICAL ABSTRACT



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ABSTRACT

The occurrence of 36 pharmaceutically active compounds in surface water of the Xiangjiang River was investigated in two seasons ($n = 38$). Twenty-five of these compounds were detected, with cefotaxime (maximum concentration 830 ng L^{-1}) the most abundant compound followed by amoxicillin (maximum concentration 710 ng L^{-1}). The spatiotemporal distribution was observed; indicating that pollution hotspots were mostly located in economically developed and densely populated regions such as Changsha City. Lower concentrations were found in summer than winter, which may be attributed to the dilution effect of a flood event and higher water temperatures. The distribution of pharmaceuticals was significantly correlated with temperature and ammonia nitrogen content. A principal component analysis-multiple linear regression model estimated that domestic sewage was the main source of pharmaceuticals, although the source composition varied among different sampling sites. Risk assessment was conducted using both individual and mixture models for preliminary identification of potential hazards. Sulfamethoxazole, clarithromycin, and azithromycin posed a high risk to algae, while sulfamethoxazole, trimethoprim, and erythromycin-H_2O showed a medium risk to invertebrates. Moreover, the mixture risk quotients calculated using a concentration addition model ranged from 0.31 to 9.60 in winter, and from 0.06 to 0.61 in summer, indicating a potential risk to the aquatic environment. This study provides scientific support to policy-makers to establish contaminant management priorities and enriches the global data on emerging contaminants.

Abbreviations: ANOVA, analysis of variance; BOD_5, five-day biochemical oxygen demand; COD_{Mn}, chemical oxygen demand; DCA, detrended correspondence analysis; GDP, gross domestic product; LC-MS/MS, liquid chromatography-tandem mass spectrometry; MDLs, method detection limits; MLR, multiple linear regression; MQLs, method quantitation limits; MRM, multiple reaction monitoring; MRQ, mixture risk quotient; PCA, principal component analysis; RDA, redundancy analysis; STU, sum of the toxic unit; TOC, total organic carbon; TP, total phosphorus; WWTPs, wastewater treatment plants; NH_3-N, ammonium nitrogen; NSAIDs, non-steroidal anti-inflammatory drugs.

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1. Introduction

River systems often serve as important drinking water sources; simultaneously, they are among the most vulnerable water bodies due to natural and anthropogenic activities (Zhang et al., 2010). As reported in a worldwide study, over 65% of the rivers in the world are polluted (Vorosmarty et al., 2010). Emerging contaminants, especially pharmaceutically active compounds (PhACs), which were widely used in agricultural practices, as veterinary additives, and in human health care (Barceló and Petrovic, 2007), heavily impact water quality.

Even at trace levels, PhACs exhibit undesired biologically active effects on non-target organisms (Zhou et al., 2016). For example, ciprofloxacin may interfere with the photosynthesis pathway of higher plants, leading to morphological abnormalities or growth inhibition (Aristilde et al., 2010). Diclofenac also has high antiovulatory effects on aquatic vertebrates (Yokota et al., 2015). In addition, previous studies have provided evidence that the prevalence of antibiotics in water bodies was strongly correlated with the population of antibiotic-resistant bacteria and they can also promote the generation of antibiotic resistance genes (Jiang et al., 2013; Varela et al., 2014; Zhang et al., 2014). These genes could be shared between microorganisms, animals, and even to humans, through horizontal gene transfer (Liu and Wong, 2013).

There is a knowledge gap regarding the environmental implications of chemical mixtures since most risk assessments have been based on individual compound (Ding et al., 2017). It should be noted that PhACs are unlikely to exist as independent constituents, a broad range are applied in combination at any real sites (Lopez-Serna et al., 2012; Paiga et al., 2016), engendering a serious mixture effect referred to as the "cocktail effect" (Du et al., 2017). Backhaus and Faust (2012) introduced a tiered assessment approach, which introduces first tier screening for chemical mixtures to determine whether more elaborate mixture risk assessment is needed. Since then, certain studies have paid close attention to the environmental implications of chemical mixtures (Backhaus and Karlsson, 2014; Liu et al., 2015; Yao et al., 2017).

To date, several studies have focused on the occurrence of PhACs in the estuary (Yan et al., 2015; Zhao et al., 2017), central and lower areas of the Yangtze River (Wu et al., 2014). These studies give rise to concerns over the potential effects of pharmaceuticals in drinking water sources. However, data that characterize the sources, exposure, and effects of pharmaceuticals in this area are still very limited. In addition, tributaries can be important contributions to pollution in the main stream. To our knowledge, no study has ever systematically addressed the pharmaceutical contaminants in the Xiangjiang River, which is a main tributary of the Yangtze River. The Xiangjiang River is 856 km in length with a catchment area of 94,660 km^2, of which 90.2% is located in the Hunan Province. >40 million people live along the river bank. It is an important water resource for drinking, irrigation, industry, fisheries, and transportation. It is also the most important economic belt in the Hunan Province, and is responsible for 70% of the gross domestic product (GDP) of the province. However, water pollution in the Xiangjiang River is markedly exacerbated by increasing population, booming economy, and accelerated urbanization during recent years (Xie, 2016).

In this context, this study focused on the spatiotemporal distribution of multi-residue PhACs, which are frequently used for human and animal purposes in proximity to the Xiangjiang River. The linkages between PhAC concentrations and water quality parameters were explored. Potential pollution sources were also interpreted based on the concentration profile. In addition, both the single compound ecological risks and the mixture risks were evaluated for the aquatic environment. This work will serve to enrich the inventories of pharmaceutical pollution on a global scale, elucidate whether aquatic organisms are at risk, and help identify potential PhAC sources in the study region.

2. Materials and methods

2.1. Chemicals and reagents

Thirty-six PhACs with high purity grade (>98%) and obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany), were selected as the targets in this study. Detailed information on the physico-chemical properties is provided in Table S1. Surrogate standards (purity > 99%), including sulfamethoxazole-D_4, sulfamethazine-D_4, ciprofloxacin-D_8, ibuprofen-D_3, roxithromycin-D_7, and thiabendazole-D_4, were purchased from Toronto Research Chemicals (Oakville, Canada), and meclocycline was obtained from Sigma-Aldrich (Steinheim, Germany).

Methanol (>99.9%) and acetonitrile (LC-MS Grade) were supplied by Sigma-Aldrich. Formic acid (LC-MS Grade) was acquired from Fisher Scientific (Loughborough, UK). Analytical grade Na_2EDTA was purchased from Sinopharm Group Co. Ltd. (Beijing, China). Ultrapure water was produced using an Ultrapure Water Purification System from Ulupure Corporation (Sichuan, China).

2.2. Study area and sample collection

The Xiangjiang River basin covers urban and rural areas, husbandry areas, industrial districts, cage culture areas, hospitals, and pharmaceutical factories. It flows through five administrative regions in the Hunan Province, which from south to north are: Yongzhou, Hengyang, Xiangtan, Zhuzhou, and Changsha City, finally enters into the Dongting Lake in Yueyang City. The Chang-Zhu-Tan region is the most urbanized area and is one of the pioneers of urban agglomeration in China (Long et al., 2013). The basic information of the six study areas is presented in Table S2. There are >80 wastewater treatment plants (WWTPs) around the Xiangjiang River basin, and their effluents will flow through the tributaries or the sewer systems into the main stream. Therefore, pharmaceutical pollution in this area could potentially be widespread. The region is heavily influenced by the subtropical monsoon climate and is hot and wet in summer, cold and dry in winter. The average annual rainfall is about 1500 mm, of which 68% occurs from April to September (Xu et al., 2013). The average temperature is 6–9 °C in winter (December to February) and 24–29 °C in summer (June to August).

Sampling campaigns were conducted from upstream to downstream on January 6th, 2017 (winter) and August 8th, 2017 (summer, about three weeks after a flood). The sampling sites ($n = 38$) selected in this study were based on the state or province-controlled transects in the Xiangjiang River basin, Hunan Province. Samples were collected from three parallel sites perpendicular to riverbank (at least 5 m away from the right and left of riverbank and in the middle of the river) to objectively represent water quality within each transects. Sampling was conducted either from a boat or on a bridge. At each site, 2.5 L of water was collected at a depth of 0.5 m below the water surface using stainless steel samplers. The sampling locations are shown in Fig. 1. All samples were transported to the laboratory in coolers. On arrival, the samples were immediately filtered through 0.7 μm GF/F glass fiber filters (Whatman, England), then the pH was adjusted to 3 using 3 M H_2SO_4. The water samples were stored in a refrigerator at 4 °C before analysis.

2.3. Sample preparation and instrumental analysis

The water sample treatment procedure was based on the reported method of Zhou et al. (2012) with some adjustments (Text S1). Briefly, a mixture of isotope-labeled internal standards was added to 1 L water samples, followed by filtration and adjustment of the pH to 3, and the addition of 0.2 g Na_2EDTA. Subsequently, samples were extracted and enriched using Oasis HLB 3 cc SPE cartridges (60 mg, Waters, USA). The elutes were concentrated under gentle nitrogen blow-down and reconstituted in 1 mL of a mixture of methanol/0.1% formic acid in ultrapure water (20:80 v/v). Finally, to avoid losses ascribed to the filter