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Occurrence and indicators of pharmaceuticals in Chinese streams: A nationwide study☆

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ABSTRACT

Pharmaceutically active compounds (PhACs) are excreted by humans and animals and released into the aquatic environment through wastewater, which can have potential negative impacts on ecological systems. To conduct a nationwide investigation of the occurrence of PhACs in water resources in China, an analytical procedure based on solid-phase extraction (SPE) and LC-MS/MS was used to measure 45 PhACs in surface water samples from a network of 29 rivers across 31 provinces in China in 2014 and 2015. PhACs were prevalent in all sampled streams. The concentrations of commonly detected PhACs were comparable to those detected in other countries. High total concentrations (mean > 1 μg L^{-1}) of all tested PhACs were primarily detected in areas under extreme water stress, specifically northern and eastern coastal areas. Source apportionment based on the profiles of the target compounds found that 54% of the PhACs in China originated from freshly discharged untreated sewage. Metformin (MET) and its biodegradation product, guanylurea (GUL), were used as a pair of indicators to predict PhAC contamination levels and differentiate between biotreated and unbiotreated wastewater. High MET/GUL can be used to indicate untreated wastewater, whereas low MET/GUL values are a strong indicator of treated wastewater. Furthermore, wastewater biotreatment ratios were calculated. We estimated that the biotreatment ratios of most of the provinces in China were less than 50%. We conclude that more attention should be paid to untreated sewage water, especially water in rural areas rather than the existing concentration on urban sewage treatment-oriented management.

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1. Introduction

Great attention has been given to the presence of PhACs in surface waters because of their widespread and potential negative impacts on ecosystems (Schwarzenbach et al., 2006; Boxall et al., 2012; Abdelmelek et al., 2011). Pharmaceuticals for human use are discharged to the environment after passing through municipal wastewater treatment facilities, which are not planned to eliminate these chemicals from their effluents. Veterinary pharmaceuticals used in animal feeding operations can be released to surface waters in animal waste through leakage or the overflow from land applications or storage structures (Boxall, 2004; Boxall et al., 2011). Pharmaceuticals applied in aquaculture industries are spread into surface water directly (Boxall, 2004; Boxall et al., 2011). Thus, various transport processes exist for pharmaceuticals to enter and persevere in aquatic environments. The occurrence, transformation, and ultimate fate of pharmaceuticals have been the subject of much research by environmental scientists (Love et al., 2011; Managaki et al., 2007; Kasteel et al., 2010; Yan and Song, 2014; Guo et al., 2016; Ikehata et al., 2006; Yu et al., 2013; Yang et al., 2013a; Luo et al., 2012).

Pharmaceutical contaminants in surface waters have been widely observed worldwide, with concentrations up to the μg L^{-1} level. As early as 2002, Kolpin et al. (2002) employed 5 detection methods to determine the concentrations of 95 PhACs, endocrine disrupter compounds, and other organic pollutants in surface water samples from 139 rivers across the United States in 1999 and 2000. During his investigation, pharmaceuticals were detected in 80% of the samples, and 26 of the 41 PhACs were identified. Since then, a

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number of analogous studies have aimed to investigate pharmaceuticals on a nationwide scale (Focazio et al., 2008; Murata et al., 2011; Bouissou-Schurtz et al., 2014; Lopez et al., 2015). A study on the European Union (EU)-wide occurrence of 156 organic chemicals in 90 wastewater treatment plants (WWTPs) was reported by Loos et al. (2013) and the target contaminants included PhACs, PFCs, pesticides and their degradation products. A total of 125 chemicals (80% of the target chemicals) were identified in European sewage effluents at levels ranging from low ng L^{-1} to mg L^{-1}. The compounds that were present at the highest levels were artificial sweeteners, benzotriazoles, flame retardants, and X-ray contrast media (ICM). The maximum levels of acesulfame reached 2.5 mg L^{-1}, and the average levels of acesulfame, sucralose, and iopromide were all >1 μg L^{-1}.

Comprehensive studies in this area of research have been performed in the United States (Kolpin et al., 2002; Focazio et al., 2008), Europe (Bouissou-Schurtz et al., 2014; Lopez et al., 2015; Loos et al., 2013), Japan (Murata et al., 2011), etc. Regarding the occurrence of PhACs in Chinese streams, a number of studies have focused on local watersheds, such as the Haihe Basin (Luo et al., 2011), Liao Basin (Bai et al., 2014), Yangtze River Basin (Jiang et al., 2011; Wu et al., 2014), and Pearl River Basin (Yang et al., 2013b). However, no single study has reported the occurrence of PhACs in Chinese streams at a nationwide level. Recently, Zhang et al. (2015) studied the national consumption, emissions, and multimedia fate of 36 commonly used antibiotics in China based on medicines sales data. The total usage of the selected 36 target antibiotics were estimated at 92,700 tons, and the total emissions of these 36 antibiotics was assessed to be 53,800 tons, with 46% and 54% received by the water and soil compartments, respectively. Based on emissions data, the concentrations of these 36 antibiotics were predicted in 58 basins, and the pharmaceuticals with the maximum expected levels in water were amoxicillin, doxycycline, erythromycin, florfenicol, pefloxacin, and sulfadiazine. No information on the distribution of PhACs contamination is available on a nationwide scale. Therefore, the primary goal of this research was to conduct the first nationwide investigation of the occurrence of PhACs in surface waters across China. China is one of the fastest developing countries in the world, with a large territorial area, a population of 1.3 billion, and diverse climate types. The production and usage of PhACs are increasing annually. The production of antibiotics alone was estimated to be 248,000 tons in 2013 (Zhang et al., 2015). Therefore, China provides the perfect location to explore the occurrence and temporal and spatial distribution of PhACs in rapidly developing regions on a large scale. In this study, the occurrence of 45 PhACs in river samples obtained from a network of 29 rivers across 31 provinces was investigated in 2014 and 2015. The primary PhACs in Chinese surface waters and the spatial variations in their occurrence were revealed.

It is known that the majority of anthropogenic PhACs sources are the municipal wastewater treatment facilities, which are not designed to eliminate these chemicals from their effluents. In addition to these sources, freshly discharged untreated domestic sewage and unknown sources, including pharmaceutical manufacturing facilities and non-point source PhACs from domestic wastewater, could contribute to PhAC concentrations. The contributions of such potential sources to PhAC concentrations vary significantly by area and season; therefore, the identification of those sources is necessary to reduce and control PhACs in the environment, and reduce the risk of exposure. Furthermore, quantifying PhACs in aquatic environments is challenging for two potential reasons. First, adequate analytical methods are lacking. It has been conservatively predicted that less than 4% of the PhACs thought to be in the aquatic environment are actually evaluated (Hughes et al., 2013). Second, approximately 5000 pharmaceuticals are currently in use (Hughes et al., 2013). New drugs are continuously entering the market, and the numbers of prescriptions of traditional drugs are decreasing. Therefore, the pharmaceuticals of interest will change with time. Consequently, the development of indicators is an approach to resolve these challenges. In the current study, we attempted to correlate the concentrations of indicator compounds to the total concentrations of identified PhACs. Metformin (MET) and its biodegraded product from wastewater treatment, guanylurea (GUL), are proposed as a suitable indicator pair to indicate wastewater contamination in surface waters. Furthermore, the ratio of MET/GUL could be applied to distinguish between biotreated and unbiotreated wastewater sources, and could also be used to quantify the contribution of different sources. We estimate that the ratio of biotreated wastewater in the receiving wastewater of most sampling locations was less than 50%.

2. Experimental section

2.1. Chemicals and reagents

All PhAC standards were bought from Toronto Research Chemicals (Toronto, Canada), Tokyo Chemical Industry (Tokyo, Japan) or Sigma (St. Louis, MO). All isotope internal standards were acquired from Toronto Research Chemicals or Cambridge Isotope Laboratories (Wellesley, MA). Strata-X (500 mg, 6 c.c.) and Strata-X-CW (200 mg, 6 c.c.) cartridges were bought from Phenomenex (Torrance, CA).

2.2. Site description and sample collection

Surface waters were targeted for this study. Sites in Chinese streams were randomly selected in 2014 and 2015, and no endeavor was made to examine the temporal distribution patterns in the PhAC levels. Therefore, the occurrence and levels of PhACs are indicative of the limited situations at the time of sampling. Although the site assortment did not strictly adhere to a statistically representative design, 217 surface-water samples were selected from 31 provinces, and this sampling network included an extensive range of potential sources of pollution and environmental situations, along with variations in the population served. Wastewater influents and effluents from three municipal wastewater treatment plants (Shanghai01, Shanghai02 and Taicang) were sampled in June 2014. Wastewater treatment in all examined WWTPs comprised at least a preliminary sediment process followed by a biological treatment process, which mainly comprised a traditional activated sludge treatment procedure. Samples were collected using precleaned amber glass bottles. Once the samples arrived at the lab, they were filtered immediately through a 0.8 μm glass microfiber membrane bought from Millipore (Billerica, MA) and then extracted by SPE.

2.3. Analytical methods

The surface water samples were enriched by SPE using 500 mg Strata-X cartridges in an automated SPE system (AutoTrace 280, Dionex). Before treatment, the samples (1.0 L) were adjusted to pH 3.0 using sulfuric acid, and then spiked with 1 mL of 5% Na_2EDTA; then, 17 isotopically labeled internal standards were added at 50 ng L^{-1}. The SPE columns were first pretreated with 10 mL of methanol (MeOH), then by 5 mL of acidified MeOH (0.1% formic acid) and 10 mL of deionized water. The samples were flowed through the polymeric cartridges at 10 mL per minute, and the columns were subsequently cleaned with 10 mL of 5% MeOH and dried under nitrogen flow for 5 min. The extracts were finally eluted with 5.0 mL of MeOH, then by 5.0 mL of basified MeOH (0.1%

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