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Antibiotics in surface water and sediments from Hanjiang River, Central China: Occurrence, behavior and risk assessment

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ABSTRACT

Thirteen antibiotics including sulfonamides (SAs), tetracyclines (TETs) and fluoroquinolones (FQs) were measured in Hanjiang River (HR) during two periods. The total concentrations of 13 antibiotics in surface water and sediments ranged from 3.1 to 109 ng/l and from 10 to 45 ng/g dry weight, respectively. SAs were dominant in water while the concentrations of TETs were the highest in sediments in two seasons. For their spatial distribution, total concentrations of 13 antibiotics in both matrices were significantly higher in the lower section of HR ($p < 0.02, F > 5.15$) due to wastewater release, agricultural activities and water transfer project. Obvious seasonal variations of sulfadiazine, sulfameter, trimethoprim and oxytetracycline in water were observed ($p < 0.05, F > 4.62$). Phase partition of antibiotics between water and sediments suggested a greater affinity of TETs and FQs to sediments. In addition, significantly positive relationships were found between SAs (sulfameter, sulfamethoxazole and trimethoprim) and sediment TOC ($p < 0.05$). Risk assessment indicated that the hazard quotients of antibiotics were higher in the sediment than those in the water. Moreover, antibiotic mixtures posed higher ecological risks to aquatic organisms.

1. Introduction

Antibiotics have been extensively applied in veterinary medicine and human therapy, and as growth promoters in aquaculture, livestock and agriculture (Gibs et al., 2013; Rodriguez-Mozaz et al., 2015; Wang et al., 2013). They have been drawing extensive attention because of their high water solubility, resistance to degradation and potential risks to ecosystem and human health (Białk-Bielińska et al., 2011; Tang et al., 2015). China is one of the world's largest producers and consumers of antibiotics (Jiang et al., 2011; Lei et al., 2015). Although some antibiotics (e.g. sulfamethazine, tetracycline) have been regulated in animal feeds since 1989, the amount used was up to 162,000 t in 2013 (Zhao et al., 2016), approximately 150 times higher than that in United Kingdom (Zhang et al., 2015). Among all antibiotics, sulfonamides (SAs), tetracyclines (TETs) and fluoroquinolones (FQs) are the most frequently used compounds for human treatment and veterinary medicine (Wang et al., 2017; Zhou et al., 2011), accounting for 12%, 14% and 15% of the total usage, respectively (Zhao et al., 2010). Due to the large usage and the lack of effective management of these antibiotics, they are widely distributed in surface water (Chen and Zhou, 2014; Dong et al., 2016; Gao et al., 2012; Jiang et al., 2011; Tang et al., 2015; Xu et al., 2013).

Antibiotics in the aquatic environment generally originated from the effluent of wastewater treatment plants, direct discharge of livestock and poultry waste in farmlands, and runoff from aquaculture fields (Dong et al., 2016; Kümmerer, 2009; Liang et al., 2013). Once entering into water, these antibiotics may have direct toxicity to aquatic organisms, even at low concentrations (ng/l or μg/l level) (Chen et al., 2015; Hernando et al., 2006; Wollenberger et al., 2000). For example, they could cause phytoplankton toxicity, inhibition of microbial activity and change the microbial community structure (Liao et al., 2017). Additionally, antibiotics could promote the development of bacterial resistant genes (McKinney et al., 2010; Zhang et al., 2013), which might be potentially harmful to the ecosystem and human health. Several studies have confirmed that sediments are not only major sinks for antibiotics (Yang et al., 2010; Zhao et al., 2016; Zhou et al., 2011), but also potential secondary sources of these pollutants (Chen and Zhou, 2014). They would be released into the water when environmental conditions change (e.g. pH, organic carbon) (Liang et al., 2013). Moreover, sediments also provide habitats and food sources for benthic organisms, thus antibiotics in sediments might pose great potential risk to aquatic ecosystems through food chains (Zhao et al., 2016). Therefore, it is essential to study the behavior of antibiotics and assess their risk to aquatic organisms in sediments. Recently, there are many studies

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about the occurrence and potential adverse effects of antibiotics in water in China (Deng et al., 2016; Dong et al., 2016; Li et al., 2012; Tang et al., 2015), but the risk data of antibiotics in sediments is limited (Liu et al., 2016; Xue et al., 2013).

Hanjiang River (HR), the largest tributary of the Yangtze River, goes through Hubei and Shaanxi, and joins the Yangtze River at Wuhan (Wang et al., 2015). It covers approximately 159,000 km^2 with the length of 1577 km. As the middle route of the South-to-North Water Transfer Project (SNWTP), HR is currently an important water source for domestic and drinking water for millions of residents living in the basin and Northern China including Beijing and Tianjin (Ai et al., 2015). It is also one of the most important production bases of agriculture and aquaculture in the Yangtze River Basin (Wang et al., 2013). The water transfer project, high population density and intensive agricultural activities have significantly influenced the river (Sun et al., 2017; Wang et al., 2013). Until now, high levels of antibiotics have been reported in surface water from Lake Honghu and sediments in a small region of the Jianghan Plain (Tong et al., 2017; Wang et al., 2017), which are located in the downstream of HR. Thus, the investigation and risk assessment of antibiotics in HR should be carried out to guarantee safety of drinking water supply (Wang et al., 2014). The aim of this work was to study the occurrence of thirteen antibiotics in both surface water and sediments from HR, discuss the distribution and partition behavior in these two phases, and evaluate the individual and mixture ecological risks of antibiotics to aquatic organisms in both surface water and sediments.

2. Materials and methods

2.1. Standards and chemicals

The target compounds belong to 4 families: (1) SAs, including sulfameter (SME), sulfamethoxazole (SMX), sulfadiazine (SDZ), sulfamethazine (SMZ); (2) TETs, including chlortetracycline (CTC), tetracycline (TC), oxytetracycline (OTC), doxycycline (DC); (3) FQs, including ciprofloxacin (CIP), norfloxacin (NOR), enrofloxacin (ENR), ofloxacin (OFL); and (4) diaminopyrimidine, including trimethoprim (TMP). Because the TMP is often prescribed in combination with SAs and has similar properties to SAs, it is usually grouped with SAs in discussion (Jiang et al., 2014). The target compounds were obtained from Sigma-Aldrich Co. (St. Louis, USA). Citric acid, disodium hydrogen phosphate and disodium ethylenediamine tetraacetate (Na_2EDTA) were of analytical grade. Methanol, acetonitrile, acetic acid and ammonium acetate were of HPLC grade.

2.2. Sampling

Two sampling events were conducted in the HR including Danjiangkou Reservoir (DJKR) in November 2014 (winter) and June 2015 (summer) (Fig. 1). The DJKR is located in the middle reach of HR, and it contains two subreservoirs, the Han Reservoir and the Dan Reservoir. Water sample 0.5 m below the surface was collected from each sampling site using an amber glass bottle that has been pre-cleaned with methanol and ultrapure water. All water samples were kept at 4 °C until analyzed within 24 h after collection. Sediment samples (0–10 cm depth) were obtained using a stainless steel grab, wrapped in aluminum foil and placed into polyethylene plastic bags. Then they were stored at − 20 °C in the dark until extraction.

2.3. Extraction and analysis

All samples were pretreated and analyzed according to a previously described analytical method (Jiang et al., 2011; Yang et al., 2016) and based on solid-phase extraction (SPE) coupled to high performance liquid chromatograph-electrospray ionization tandem mass spectrometry (HPLC-ESI-MS-MS) operating in positive mode. Briefly, water samples were filtered using 0.45 μm filters and acidified to pH 3.0 before extraction. Na_2EDTA and the surrogate standards were added to one liter of water sample. Then the water sample passed through an Oasis hydrophilic-lipophilic balance (HLB) cartridge (6 ml, 500 mg, Waters) that has been pretreated with methanol and deionized water. The target compounds was eluted with methanol and concentrated to 1 ml under a gentle nitrogen stream. Final extracts were then analyzed by HPLC-ESI-MS-MS.

For sediments, approximately 5.0 g of homogenized and freeze-dried sample was extracted using solution mixture (5 ml Na_2EDTA, 15 ml methanol and 10 ml citrate buffer at pH 5.0). The extract was centrifuged three times at 4000 *g* for 5 min. The supernatant was collected and the final volume was adjusted to 500 ml with deionized water. Then HLB cartridges and Strata strong anion exchanger (SAX) cartridges (3 ml, 200 mg, Thermo, USA) were used to extract target antibiotics from the samples. The SPE procedure was the same as that used for treating water sample.

A total organic carbon analyzer (Elementar, Germany) with a solid sampler was used to detect dissolved organic carbon (DOC) in water and total organic carbon (TOC) in sediments. The limit of detection was 0.02 mg/l for DOC and 0.01% for TOC.

2.4. Quality control and quality assurance (QC/QA)

In order to monitor procedural performance and matrix effects, each sample was spiked with the surrogate compounds. A procedural blank, a solvent blank, and a matrix spike were processed for every 10 samples. The limits of quantification (LOQs), defined as the concentrations corresponding to the signal-to-noise (S/N) ratio of 10 was 0.2–1.3 ng/l for water and 0.1–0.5 ng/g dry weight for sediments. The recoveries for the antibiotics were in the range of 65–124%. All the samples were analyzed in triplicates, and the relative standard deviations (RSD) were lower than 10%. The target antibiotics were not detected in the procedural blanks. The residue levels of antibiotics in all samples were corrected based on the recovery of the surrogates.

2.5. Ecological risk assessment

To estimate the ecological risks of antibiotics to the aquatic ecosystems, the hazard quotient (HQ) approach was used in the present study. According to the European Chemicals Agency Guideline (ECA, 2008) and European Commission Technical Guidance Document (EC, 2003), the HQ is assessed by comparing the measured environmental concentration (MEC) with the predicted no effect concentration (PNEC), as presented in:

$$HQ = MEC/PNEC \quad (1)$$

In this study, the PNEC values for OTC and ENR with sufficient toxicity data were calculated by using species sensitivity distribution (SSD) method (Table S2 and Fig. S1) as follows:

$$PNEC = 5\%SSD\ (50\%c.\ i.)/AF \quad (2)$$

where 5%SSD (50%*c.i.*) is 5th percentile effect concentration according to the curve of SSD with a 50% confidence interval (*c.i.*); AF is the assessment factor.

For the other antibiotics, the PNEC values were calculated by assessment factor method using the following formula:

$$PNEC = (NOEC \text{ or } EC50)/AF \quad (3)$$

where NOEC is the no observed effect concentration; EC50 is the median effective concentration. The values of NOEC and EC50 were obtained from the published literature. If more than one value was available for the same species, the lowest value was used.

Due to few toxicity data of antibiotics in sediments, the risk assessment was performed by converting the antibiotic concentrations in sediments into their corresponding pore water concentrations (Rico