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Occurrence, fate and interrelation of selected antibiotics in sewage treatment plants and their receiving surface water

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ABSTRACT

The occurrence and fate of 12 commonly used antibiotics, two fluoroquinolones (FQs), three sulfonamides (SAs), three macrolides (MLs), two β-lactams and two tetracyclines (TCs), were studied in four sewage treatment plants (STPs) and their receiving water, the Huangpu River, Shanghai. The levels of selected antibiotics in the STPs ranged from ng L^{-1} to μg L^{-1}, while ofloxacin (OFL) was predominant (reach up to 2936.94 ng L^{-1}). The highest and lowest proportions were of FQs (STP 1, STP 2 and STP 3) and TCs (in four STPs) respectively in both influents and effluents. And the second-highest proportion was of FQs in STP 4 (only 2% lower than the highest). What could be inferred was that the usage of TCs were extremely low while the usage of FQs were larger than other antibiotics in our study area. The elimination of antibiotics through these STPs was incomplete and a wide range of removal efficiencies (−442.8% to 100%) during the treatment was observed. Based on the mass loadings as well as the per-capita mass loadings of target antibiotics in four STPs, OFL was considered the primary contaminant herein. In the Huangpu River, 3 antibiotics were not detected in any water samples, while the detection frequencies of 4 antibiotics were 100%. The highest concentration detected in the river was 53.91 ng L^{-1} of sulfapyridine (SD). The Spearman correlation analysis of antibiotics in STPs and the nearby water samples suggests that the antibiotics discharged from some STPs might influence the receiving water to some extent. Moreover, most of the hazard quotient (HQ) values in STP effluents were one order magnitude higher than those in their receiving water. However, there is no imminent significant ecotoxicological risk caused by any single compound in the effluents and receiving waters.

1. Introduction

During the last several decades, the production and consumption of antibiotics have increased rapidly with the development of society. From 2000 to 2010, consumption of antibiotic drugs in 71 countries increased by 36% (from 54,083,964,813 standard units in 2000 to 73,620,748,816 standard units in 2010) (Van Boeckel et al., 2014). China's usage of antibiotics was estimated as more than 25,000 t every year (Jiang et al., 2011). Having been consumed, these antibiotics were discharged into the environment through medical waste, industrial wastewater, animal waste discharge and sewage effluent, mostly in their original form (Kummerer, 2009). Multifarious antibiotics have been frequently detected in groundwater (Barnes et al., 2008; Batt et al., 2006), drinking water (Benotti et al., 2008), surface water (Hirsch et al., 1999; Yan et al., 2013; Yang et al., 2011), sediment (Zhou et al., 2011) and agricultural lands (Hu et al., 2010; Karci and Balcioglu, 2009). Besides, the occurrence of antibiotics in sewage effluents, which are considered one of the main 'hotspots' for antibiotics spread into the environment, has been extensively investigated and well documented in several countries (Andreozzi et al., 2004; Fatta-Kassinos et al., 2011; Gulkowska et al., 2008; Jones et al., 2001; Leung et al., 2012; Miao et al., 2004). Since sewage treatment plants (STPs) were not originally designed to deal with pharmaceutical contaminants, these structures have a limited capability for removing antibiotics from municipal wastewaters. As a result, treated wastewater containing antibiotics is always discharged into natural water bodies or recycled into irrigation.

The Huangpu River exists as one of the most important waterways in Shanghai, China, because it provides about 80% of their raw drinking water (6,300,000 t d^{-1}) (Jiang et al., 2011). The discharged antibiotics remaining in the river potentially

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threatens the aquatic environment and eventually the residents (Chen and Zhou, 2014).

Nowadays, most studies focus on the determination of antibiotics in natural water bodies or removal efficiencies in STPs, respectively (Chen and Zhou, 2014; Jiang et al., 2011; Shi et al., 2009; Wang et al., 2014). Few studies combined STPs with their receiving water (He et al., 2015; Rodriguez-Mozaz et al., 2015; Xu et al., 2015; Zhang et al., 2013). To date, no studies along the Huangpu River have entirely focused on the occurrence, mass loading, environmental risk assessment and interrelationship of antibiotics between STPs and their receiving water. However, such significant information is urgently needed, since Shanghai continues to increase in population, annual antibiotics consumption, and inadequate STPs.

The investigation is aimed to determine and monitor the occurrence of selected antibiotics in Shanghai, including STP influents/effluents and their receiving water, and to study the removal of these substances in STPs. In addition, we estimate the mass loading, per-capita mass loading as well as interrelationship of targeted antibiotics between STP effluents and the Huangpu River. Furthermore, we assessed the potential ecological risk caused by the target antibiotics on aquatic species based on calculated hazard quotients (HQs). The results will provide important background data on the contamination control of antibiotics in the aquatic environment of this area.

2. Materials and methods

2.1. Materials and reagents

Five categories of antibiotic standards, fluoroquinolones (ofloxacin (OFL), enrofloxacin (ENR)), sulfonamides (sulfadiazine (SD), sulfamethoxazole (SMX), sulfamethazine (SMZ)), macrolides (erythromycin (ERY), roxithromycin (ROX), spiramycin (SPI)), β-lactams (cefalexin (CFX), amoxicillin (AMOX)) and tetracyclines (tetracycline (TC), oxytetracycline (OTC)), were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Isotope-labeled $^{13}C_3$-caffeine as surrogate standard was obtained from Cerilliant (Austin, TX, USA). Oasis Hydrophilic-Lipophilic Balanced (HLB, 6 cc, 500 mg) cartridges were purchased from Waters (Milford, MA, USA). HPLC grade methanol and acetonitrile were purchased from Merck (Darmstadt, Germany). All the ultra-pure water used in this study was produced by a Milli-Q water purification system.

2.2. Sample collection

Water samples were collected from influents and effluents of four STPs, as well as their receiving water, the Huangpu River of Shanghai in November, 2014. Information about the selected STPs is provided in Table S1. No precipitation occurred in the week prior before sampling and it was cloudy on the day. The specific sampling locations are depicted in Fig. 1. 16 sampling points are georeferenced in Table S2. The Huangpu River, whose average flow rate and lengths are 319 $m^3 s^{-1}$ and 113 km, originates in the Dianshan Lake and flows into the Yangtze River. The remaining wastewater and effluents are directly discharged into this river each day. Sampling sites are distributed through the river from top to bottom; significantly, the samples from the sites where there is a tributary afflux into the Huangpu River are all collected (Fig. 1).

Surface and sewage water samples were collected in clean amber glass bottles. The influent and effluent samples (4 L) of STPs were collected as 24-h composite samples using automatic samplers according to the residence time of each STP, while the surface water was collected from three points on one site using a water grab sampler. Specifically, the three points in the river were about 0.5 m below the surface and 1 m apart from each other. Each bottle was entirely pre-rinsed with Milli-Q water at the lab and then, rinsed twice with the sample water before sample collection. All the samples were kept in shade place at 4 °C and analyzed within seven days to minimize the degradation. Three repetitions of each analysis were performed and the results reported referred to the mean values.

2.3. Method of analysis

After transportation to the laboratory, collected water samples were passed through neutral filter papers and 0.7 μm glass fiber filters (Whatman, Maidstone, England) pre-baked in a furnace for six hours.

Sample extraction and instrumental analysis used in this study was improved based on previous studies (Xu et al., 2009, 2007b). 200 mL water samples of STPs and 300 mL of river samples were acidified to about pH 3.0 by adding H_2SO_4, followed by an additional 0.1 g disodium ethylenediamine tetraacetate (Na_2EDTA). Before the samples were subjected to extraction, 100 ng $^{13}C_3$-caffeine was added to each as a surrogate to monitor the recovery. Each Oasis HLB cartridge (6 mL, 500 mg, Waters) used for the solid-phase extraction (SPE) was preconditioned sequentially with 6 mL of methanol, 6 mL of ultra-pure water and 6 mL of 10 mmol L^{-1} Na_2EDTA buffer (pH 3.0). Thereafter, the samples were passed through the SPE columns at a flow rate of approximately 10 mL min^{-1}. The HLB column was then rinsed with 10 mL of ultra-pure water (pH 3.0) and dried for 1 h. After drying, each cartridge was eluted with 6 mL of methanol. The analytes were collected in 10 mL nitrogen blowpipes, volume-reduced under nitrogen purge to about 0.2 mL, and then methanol was added to a final volume of 1 mL.

All target antibiotics were monitored by high performance liquid chromatography–tandem mass spectrometry (HPLC–MS/MS). The HPLC separation was performed using an Agilent 1260 series equipped with an Agilent Poroshell 120 EC-C18 reversed-phase column (3 × 100 mm, 2.7 μm, Agilent). The column was maintained at 40 °C during the sample analysis. The injection volume was 5 μL and flow rate was kept at 0.4 mL min^{-1}. Mobile phase consisted of A: acetonitrile; B: water with 0.2% (v/v) formic acid and 5 mmol L^{-1} ammonium acetate. The gradient was set up as follows: 0–5 min, 0–13% A; 5–10 min, 13–20% A; 10–32 min, 20–90% A; with a post time of 5 min. Mass spectrometric analyses were performed in an Agilent 6460 triple quadrupole mass spectrometer equipped with an electrospray ionization (ESI) source that operated in the positive ionization mode. The data acquisition was performed in the multiple reaction monitoring (MRM) mode. The MS conditions were as follows: capillary voltage, 4.5 kV; nebuliser pressure, 45 psi; drying gas temperature, 350 °C; source gas flow, 10 L min^{-1}; and drying gas flow, 3 L min^{-1}. Detailed instrumental analysis data about 12 antibiotics and 1 surrogate standard is shown in Table S3.

In this study, external standard method was used due to the low commercial availability of corresponding internal standards for each analyte. We used $^{13}C_3$-caffeine as the surrogate standard to all samples prior to enrichment to avoid possible losses during the analytical procedure. The regression coefficients (R^2) of the calibration curves were greater than 0.999. A spike and recovery study was performed to determine the efficiency and reproducibility. Quality control also included at least one distilled water blank sample at every sixth sample. And the procedural blanks were also run to check for background contamination and system performance of the analysis procedure. The recovery percent of all samples in the complete method is from 66% to 99%. The quality parameters of the method (including extraction and LC-MS) for each compound can be found in Table S4.