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Occurrence and fate of antibiotics in a wastewater treatment plant and their biological effects on receiving waters in Guizhou

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ABSTRACT

Wastewater treatment plants (WWTPs) are not designed for the removal of antibiotics. Thus, several studies have been conducted to evaluate the fate of antibiotics in wastewater treatment processes. However, most of these investigations did not consider the antibiotic contamination in the receiving waters. This study investigated the occurrence and fate of antibiotics in a wastewater treatment plant and the ecological risks posed by surface water receiving the effluent discharge. The results indicated that the levels of 18 antibiotics in the influent ranged from 37.21 ng L^{-1} to 2935.40 ng L^{-1}, and sulfamethizole (SMZ) was the major component among the 18 antibiotics; SMZ occurred most frequently and at the highest concentrations. Mass balance analysis was performed to explore the mechanisms of antibiotic removal, and the findings indicated that biotic and abiotic degradation are the major removal mechanisms; however, removal of quinolones is primarily ascribed to sludge adsorption. Because activated sludge consists of negatively charged colloidal particles, it is more inclined to adsorb quinolones, which contain positively charged nitrogen atoms. The resulting loading of antibiotics from WWTP effluent discharge into the receiving water of the Yangjie River may result in their uptake by aquatic organisms and thus poses a risk to human health.

1. Introduction

Antibiotics are organic metabolic products generated from biological processes in microorganisms, plants, and animals and from biological activities (Zhou et al., 2013). In the past century, antibiotics have been widely used to prevent and treat various diseases in humans and animals. Approximately 5460 and 3465 tons of antibiotics are used for humans and animals, respectively, each year in the European Union and Switzerland combined (Mao et al., 2015). China appears to severely abuse the use of antibiotics; China consumes 180,000 tons per year, which is approximately 10 times the annual consumption of America (Jiang et al., 2014). Antibiotics are mainly present from humans and animals in the form of the original drugs and their metabolites via faeces and urine (Di Cesare et al., 2016). Antibiotic residues can cause resis-

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tance to pathogens; thus, the declining ability of antibiotics to treat diseases has become a global concern (Li et al., 2013).

Antibiotics can selectively inhibit or affect secondary metabolites of other species, as well as the derivatives of these metabolites, even at very low concentrations (Michael et al., 2013). Given that antibiotics are not completely consumed and degraded in human and animal bodies, a large number of antimicrobial compounds (Dong et al., 2016), their metabolites and their transformation products enter urban wastewater treatment plants (WWTPs) (Birošová et al., 2014; Sun et al., 2017). However, antibiotics are not completely biodegraded in conventional wastewater treatment processes (Mulla et al., 2017), so when treated wastewater is discharge to the receiving water, any remaining antibiotics may become secondary pollutants and could be further modified in the receiving water; this may lead to their pseudo-persistence in aquatic environments and to serious ecological impacts on aquatic organisms (Ashfaq et al., 2017; Segura et al., 2018; Wu et al., 2016). The high detection frequency of antibiotics in receiving waters is mainly attributed to the extensive use, low human metabolic capability, and low removal efficiency of highly toxic antibiotics (Cardinal et al., 2014).

The Yangjie River, which is situated in Weining County in northwestern Guizhou and adjacent to Caohai Wetland, is a valuable state reserve for migrant birds. With the influx of antibiotics, the risk of antibiotic exposure to migrant birds and aquatic organisms is inevitable (Tang et al., 2016). In addition, the populations of organisms living within the vicinity of WWTPs often consume fish and shrimp obtained from the Yangjie River. The antibiotic residues could eventually enter and accumulate in the water, sediment, or food chain through effluent discharge and reuse of wastewater and sludge for agricultural applications, and such accumulation may be detrimental to humans and animals. Exposure of humans to these chemicals in the environment is a critical concern and has unknown long-term impacts. Thus, this study analysed the occurrence and levels of selected antibiotics in a WWTP and in the receiving water in Weining County. Moreover, this study compared the ecological risks that these antibiotics pose to aquatic organisms in influent, effluent, and receiving waters.

2. Materials and methods

2.1. Chemicals and reagents

Fourteen of the antibiotic standards, namely, sulfamethazine (SM2, 99.0%), sulfamonomethoxine (SMM, 99.0%), sulfamethizole (SMZ, 99.0%), sulfaquinoxaline (SQ, 99.0%), sulfadimethoxine (SDM, 99.4%), chlortetracycline (CTE, 93%), doxycycline (DOX, 99.0%), enrofloxacin (ENR, 99.9%), sarafloxacin (SAR, 99.0%), ofloxacin (OFX, 99.9%), norfloxacin (NOR, 99.9%), erythromycin (ERY, 99.0%), roxithromycin (ROX, 90.0%), and azithromycin (AZM, 99.0%), were purchased from Dr. Ehrenstorfer GmbH (Germany). Oxytetracycline (OTC, 96.5%), tetracycline (TCY, 97.0%), clarithromycin (CLA, 98.0%), and ciprofloxacin (CIP, 99.9%) were purchased from KaSei Industry Co., Ltd. (Tokyo, Japan). The internal standard $^{13}C_3$-trimethylxanthine was purchased from Cambridge Isotope Laboratories. the surrogate standard $^{13}C_6$-sulfamethylthiadizaole was procured from Toronto Research Chemicals Inc. (North York, UN, Canada). Formic acid, acetonitrile, and Na_2EDTA were purchased from J.T. Baker Co., Ltd. (USA).

The following instruments were used: Agilent 1260-6460 LC-MS (USA, Agilent), 12-port vacuum rack solid-phase extraction apparatus (Waters; USA), nitrogen evaporation instrument EYELA MG-2200 (Rikakikai; Japan), Allegra X-22R table-top centrifuge (Backman Coulter; USA), Q-POD MILLI-Q Ultra-pure water purifier (Millipore; Germany), ZORBAX C18 chromatography column (4.6 mm × 150 mm × 0.5 μm), and Oasis HLB SPE Cartridge (500 mg/6 mL; Waters; USA).

2.2. Sampling

The plant selected for this study is a secondary WWTP that uses a conventional activated sludge process with an average daily flow of 10,000 m^3 and serves a population of 200,000 in the northern part of Guizhou, southwest China. The treated effluent is discharged into the Yangjie River.

We collected water samples from the influent, effluent, and activated sludge of the WWTP, as well as from the receiving water in the Yangjie River from April to June in 2016 (sample was collected every other week for a total of four samples from each location). Fig. 1 shows the specific sampling locations. The Yangjie River is 113 km long, and its average flow is 310 $m^3\,s^{-1}$. Sampling sites were located both upstream and downstream from the treatment plant.

Collected surface water and wastewater samples were placed in clean, 1 L amber glass bottles. A water grab sampler was used to collect surface water from three points at each site. In particular, the three points at each sampling site in the Yangjie River were approximately 0.5 m below the surface and 1 m apart from each other. Each bottle was pre-rinsed with Milli-Q water in the laboratory and then rinsed twice with the sample water prior to sample collection. All the samples were stored in a shaded place at 4 °C and analysed within 7 days to minimize degradation. The mean concentration of the three collected samples was calculated for each sampling location.

2.3. Sample pretreatment and analytical methods

Sample extraction and instrumental analyses were performed as previously described (Wu et al., 2016; Xu et al., 2009). A water sample (0.5 L) was collected and adjusted to pH 3.0, and a 0.45 μm fibre ultrafiltration membrane was used to remove suspended particles (or 5 g of solid sample was suspended in 30 mL of methanol for extraction; the extract was concentrated to 10 mL and then added to 0.5 L of ultrapure water). The surrogate standard (50.0 μL) and Na_2EDTA (0.4 g) were added, and the solution was mixed thoroughly. The Oasis HLB SPE columns were preconditioned sequentially with 4 mL each of methanol, ultra-pure water, and 2 $g\,L^{-1}$ Na_2EDTA. Water samples were passed through the OASIS HLB SPE columns at 3–5 $mL\,min^{-1}$. After sample enrichment, the columns were flushed with 4 mL of ultra-pure water and then with 4 mL of methanol (10%) and dried for 1 h. The column was subsequently eluted with 8 mL of methanol into 10 mL nitrogen blowpipes, and the volume of the sample was reduced under flowing nitrogen to approximately 0.2 mL. The final volume of methanol was adjusted to 1 mL.

The following chromatographic conditions were used. The chromatographic column was a ZORBAX C18 chromatography column (4.6 mm × 150 mm × 0.5 μm). The column temperature was 30 °C, the flow rate was 0.30 $mL\,min^{-1}$, and the sample volume was 10 μL. The mobile phase consisted of (A) acetonitrile and (B) water with 10% formic acid. The gradient was set up as follows: 0–8 min, 10% A; 8–16 min, 10%–40% A; 16–24 min, 40%–90% A; 24–27 min, 90%–100% A; and 27–32 min, 100% A.

The analytical methods described by Wu et al. (2016) were employed in this study. An Agilent 6460 Triple Quadrupole spectrometer equipped with and electrospray ionization source and operated in the positive ion mode was used in mass spectrometric analyses. Qualitative and quantitative analyses of each of the selected antibiotics were performed in multiple reaction monitoring mode. The MS conditions were as follows: capillary voltage, 4.5 kV; drying gas temperature, 350 °C; neb-