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Antibiotics elimination and risk reduction at two drinking water treatment plants by using different conventional treatment techniques

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ABSTRACT

Safe drinking water is essential for the wellbeing of people around the world. In this work, the occurrence, distribution, and elimination of four groups of antibiotics including fluoroquinolones, sulfonamides, chloramphenicols and macrolides (21 antibiotics total), were studied in two drinking water treatment plants during the wet and dry seasons. In the drinking water source (river), the most abundant group was fluoroquinolones. In contrast, chloramphenicols were all under the limitation of detection. Total concentration of all investigated antibiotics was higher in dissolved phase (62–3.3 × 10^2 ng L^{-1}) than in particulate phase (2.3–7.1 ng L^{-1}) during both wet and dry seasons in two plants. With the treatment process of flocculation → horizontal flow sedimentation → V type filtration → liquid Cl_2 chlorination, approximately 57.5% (the dry season) and 73.6% (the wet season) of total antibiotics in dissolved phase, and 46.3% (the dry season) and 51.0% (the wet season) in particulate phase were removed. In contrast, the removal efficiencies of total antibiotics were obtained as −49.6% (the dry season) and 52.3% (the wet season) in dissolved phase, and −15.5% (the dry season) and 44.3% (the wet season) in particulate phase, during the process of grille flocculation→ tube settler sedimentation → siphon filtration → ClO_2 chlorination. Sulfonamides were found to be typically easily removed antibiotics from the dissolved and particulate phases during both seasons. Through a human health risk assessment, we found that the former treatment technologies were much better than the later for risk reduction. Overall, it can be concluded that the treatment processes currently used should be modified to increase emerging contaminant elimination efficiency and ensure maintenance of proper water quality.

1. Introduction

Some antibiotics for human and veterinary use are poorly absorbed by human beings and animals after intake. Typically, approximately 75% of consumed antibiotics enter raw sewage via feces and urine (in the parent form or as metabolites) and finally reach wastewater treatment plants (WWTP) (Kummerer, 2009). In addition, other sources like unintentional discharged wastewaters from hospitals (Szekeres et al., 2017; Tuc et al., 2017; Verlicchi and Zambello, 2016) and pharmaceutical manufacturers (Creusot et al., 2014; Larsson, 2014) may also contribute to the antibiotic loading in WWTP effluents. Thus, WWTP effluent has been identified as one of the major sources of antibiotics in receiving rivers, as conventional technologies currently used in WWTP are considered to be inefficient to remove emerging contaminants (Afonso-Olivares et al., 2017; Guo et al., 2017; Roberts et al., 2016; Zhang et al., 2017b). Typically, surface waters like rivers provide a substantial part of total potable water supply for a community (Gracia-Lor et al., 2011). Due to current inefficient WWTP techniques, sources of drinking water are more and more being affected by the discharges of the upriver WWTP. This is important to address because water security strategies currently developed was employed to purify recycled wastewater as a dependable potable water source that can increase the water supply capacity of communities, especially in big cities and in situations where there is water scarcity due to climate change (Chen et al., 2017; Gu et al., 2017).

Indeed, antibiotics occur ubiquitously in drinking water sources (e.g. rivers), drinking water treatment plants (DWTP), and even in drinking waters (Li et al., 2017; Simazaki et al., 2015; Wang et al., 2016). Thus, the exposure of aquatic biota and human beings to trace levels of antibiotics is possible (Wang et al., 2017, 2016). As antibiotics are originally devised to kill the target species at trace levels, the presence of low levels of antibiotics in water environment has been prompted a noticed public and mass media interest because they have high biological activity and can cause various undesirable outcomes on

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the nontarget species (Arnnok et al., 2017; Gonzalez-Rey et al., 2014; Grabicova et al., 2017). Furthermore, these antibiotics could have indirect effects, for example the creation of antibiotic-resistance bacteria (Jiang et al., 2013; Zhang et al., 2016) and a superbug gene in drinking water (Walsh et al., 2011).

Antibiotics in the aquatic environment are not a new issue. However, unlike other organic pollutants, the environmental effects and fate of antibiotics are not well characterized, leading to ubiquitous presence of them in various aquatic environments around the world (Creusot et al., 2014; Guo et al., 2017; Li et al., 2018; Liang et al., 2013; Schaider et al., 2014; Song et al., 2017; Zhang et al., 2017a). The detection of antibiotics in drinking water is not well reported, as most municipal DWTPs as well as government are unaware of the necessity of routine chemical testing or do not have the capability to detect these new emerging contaminants (mainly due to very low concentrations) (Touraud et al., 2011). Nevertheless, surveillance and removal of the antibiotics from drinking water is very important for the human beings' health, since the antibiotics in such low-level concentrations whose effects to humans and domestic animals are still unknown (Padhye et al., 2014).

Therefore, two typical DWTPs techniques (dominantly in used in China) using different water treatment combination processes were chosen to investigate the removal ability to a variety of antibiotic contaminants (4 groups of total 21 antibiotics, Table S1). The removal efficiencies of these antibiotic contaminants by two different techniques including conventional flocculation, sedimentation, filtration, and chlorination technology was also compared. This work also answers the question of whether the pollution of these antibiotic contaminants can be resolved safely and the occurrence of antibiotics residues pose a risk to human beings by calculating the human health risk via consumption of water at different life stages. Obtained results provide basic data for risk evaluation and regulation of antibiotics in water environment.

2. Material and methods

2.1. Materials and chemicals

Four different groups of total 21 antibiotic standards, fluoroquinolones (FQs), sulfonamides (SAs), chloramphenicols (CHLOs), and macrolides (MLs) were purchased from either Sigma–Aldrich (St. Louis MO, USA) or Dr. Ehrenstorfer GmbH (Germany). Erythromycin-H_2O was prepared as the method reported in reference (Xu et al., 2007). Six isotope-labeled internal standards (sulfachlorpyridazine-$^{13}C_6$, levofloxacin-D_8, sulfapyridine-D_4, enrofloxacin-D_5, erythromycin-D_7 and chloramphenicol-D_5) were obtained from Toronto Research Chemicals (North York, ON, Canada). Detailed information about other reagents and materials used are listed in detail in Supplementary information (SI).

2.2. Drinking water treatment technique and sample collection

The chosen water treatment plants, situated in Southern China, serve a population of 700,000 and an area of 160 km^2. Among the six plants in this area, two of them with different treatment techniques (Plants Y and D) were chosen. The schemes for Plants Y and D can be found in Figs. S1 and S2, respectively. Detailed information about the differences in the two plants can be found in SI.

Using pre-cleaned glass bottles, samples were collected from Plants Y and D. Both water (approximately 10 L, depth 0.5 m) and sludge samples (500 g) were collected from the end of each treatment process during the dry (April 2013) and wet seasons (September 2013). After collection, all the samples were added with sodium azide, transported to the laboratory and stored at 4 °C. Prior analysis, sludge was freeze-dried, sieved (0.5 mm pore size), and then stored in the dark at −20 °C until the extraction.

2.3. Pretreatment and analysis

2.3.1. Water samples extraction

The procedures of the sample pretreatment were performed according to methods used in a previous work (Zhou et al., 2012). Briefly, to protect the solid-phase extracted (SPE) cartridges, the surface water was first filtered through glass fiber filters (Whatman GF/F, 0.7 μm, UK), removing particle matters. The obtained water was optimized to pH 3 and then the internal standards (100 ng) were added. To prevent the chelation of metal cations with the antibiotics, Na_2EDTA (0.2 g) was putted into each water sample. SPE cartridges were pre-treated with methanol (10 mL) and high purity deionized water (Millipore Corp., 18 MΩ cm) in turn. Water samples were then passed through the cartridges with a flow rate of less than 5 mL min^{-1}. Afterward, the cartridges were washed with 10 mL of high purity deionized water and incubated for 30 min under a vacuum to remove redundant water. The antibiotics kept in cartridges were eluted with methanol (10 mL), and concentrated to near dryness under a gentle nitrogen stream, re-dissolved in of methanol (1 mL), and then kept at −20 °C. Just prior to analysis, sample extracts were evaporated and then re-dissolved in a mixed solvent (methanol, 2 mM ammonium acetate, and 0.2% formic acid, 10:90, v/v). Particulates were firstly removed using a 0.22 μm filter, and the final extract was moved into an amber vial (1.5 mL).

2.3.2. Solid sample extraction

Twenty microliters of internal standard (10 μg L^{-1}) was added into 2 g (wet weight) of each sludge sample, then mixed and incubated at 4 °C for 12 h. Afterward, citric acid buffer (pH = 3, 10 mL) and acetonitrile (10 mL) were added into the sludge solution, mixed with a vortex mixer for 4 min, and incubated in an ultrasonator for 40 min in turn. The sample was then centrifuged at 1370 rpm for 10 min. This extraction process was replicated in triplicate. Combined supernatants were concentrated in a rotary evaporator (bath temperature ≤40 °C), and diluted to 250 mL with high purity deionized water to ensure less than 5% of organic solvent in solution. A strong anion exchange (SAX) cartridge (500 mg, 6 mL) was placed on the top of HLB cartridge (500 mg, 6 mL) in tandem to clean up and enrich the solutions of the sludge extracts. Sludge extracts were handled in the same manner as water extracts. After extraction and removal of the SAX cartridge, the HLB cartridge was washed with high purity deionized water (10 mL).

2.4. Instrument analysis

Target antibiotics were analyzed via UPLC–MS/MS (ultra-high-performance liquid chromatography-tandem mass spectrometry, Waters, Xevo TQ, USA) in multiple-reaction monitoring (MRM) mode. The Zorbax Eclipse XDB C18 column (50 mm × 2.1 mm, i.d 1.8 μm, Agilent, USA) was kept at 25 °C with 0.2 mL min^{-1} flow rate. Eluent A was 2 mM NH_4Ac buffer and H_2O with formic acid (0.2%, v/v), while eluent B was methanol. The separation of target antibiotics was started at 10% eluent B (for 2 min), was brought to 80% eluent B (in 5 min) and then held constant (for 2 min). The cycle of the analysis was finished by returning the eluent B to 10% over 2 min and keeping at 10% for 4 min. A 10 μL of the sample was injected, and the analyses were carried out (chloramphenicol, negative mode; the other compounds, positive mode). The drying and collision gas were nitrogen gas. The MS parameters were listed in Table S2. The optimization of the MS conditions uses an Optimizer (Waters, Xevo TQ, USA) for cone voltage, collision energy, and MRM transitions for the antibiotics are as listed in Table S3. UPLC–MS/MS chromatograms for antibiotics in the standard solution (100 ng L^{-1}) and in the surface water spiked with antibiotics (10 ng L^{-1}) are presented in Fig. S3.

2.5. Quality control

Internal standard method was used to quantify the antibiotics