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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

concentrations in the samples. To make up for the experimental losses, the isotope-labeled (sulfapyridine-D4, sulfachlorpyridazine-$^{13}C_6$, levofloxacin-D8, enrofloxacin-D5, erythromycin-D7 and chloramphenicol-D5), which are not present in the collected samples, were used as the surrogate standards. Although the single-labeled surrogate used is a possible limitation, due to the investigated antibiotics possessed different properties and chemical structure as compared with these surrogate, in this study all the data obtained were carried out under the strict quality control procedures. To monitor the procedural recoveries, surrogate standards were spiked into all samples. Based on the calibration curve for each antibiotic, quantification was carried out using the internal standard method. The correlation coefficient (R^2) for each antibiotic was > 0.99. The limits of detection (LODs) were the minimum detectable quantity of each antibiotic standard in spiked environmental matrix extract in MRM mode with a signal-to-noise ratio of 3, respectively. Signal-to-noise ratios were calculated using Masslynx software (Waters, Xevo TQ, USA) and obtained using the data from the recovery experiments with the lowest spiked level for each antibiotic. LODs of the target compounds ranged from 0.02 to 2.27 ng L^{-1} and 1.36–4.05 ng g^{-1} in water and sludge samples, respectively. Recovery tests were carried out by spiking sludge samples, pure water, and surface water with standard solutions. For water samples, each antibiotic (200 ng) and surrogate (100 ng) were used to spike water (1 L), and the samples spiked were extracted with SPE cartridge. For sludge samples, each antibiotic (200 ng) and surrogate (200 ng) were used to spike sludge (2 g), and then these samples were extracted after ultrasonic and rotary evaporation. Recoveries of 21 antibiotics ranged from 74% to 115%, 68–113% and 61–96% in pure water, surface water, and sludge samples, respectively. All the data are listed in detail in the Table S4.

2.6. Human health risk evaluation

Risk of drinking water-mediated exposure of humans at different life stages from antibiotics was assessed using risk quotients (RQs) according to methods described in previously reported reference (Gaffney et al., 2015). More details description about the calculation are provided in the SI. RQ values ≥1 were defined as posing a potential risk to exposed humans through the intake of drinking water.

3. Results and discussion

3.1. Antibiotics distribution pattern in drinking water and related risk for human health

3.1.1. Antibiotics concentrations

The wet and dry seasonal variation of different groups of antibiotics in drinking water source, i.e. the river location that supplies the water for Plant D and Plant Y DWTPs (named as site D1 and site Y1) is provided in Fig. 1. The levels of the total antibiotics during the dry season (3.3×10^2 ng L^{-1}, D1; 1.3×10^2 ng L^{-1}, Y1) were much higher than in the wet season (1.0×10^2 ng L^{-1}, D1; 61 ng L^{-1}, Y1) in the dissolved phase in both DWTPs (Fig. 1a). This means that either the water source had alternative antibiotic inputs during the dry season, or the amount of antibiotics was constant across both the dry and wet seasons but the rain may dilute the contaminants during the wet season. Among the four antibiotic groups, no CHLOs were found in dissolved phase of any water source during both the dry and wet seasons. This is a reasonable conclusion, as they are not frequently used to treat any infectious disease nowadays (Fraunfelder and Fraunfelder, 2013). Only SAs and FQs (the main component, accounting for 95.7% of the total antibiotics) were detected during the dry season. Comparatively, MLs and SAs presented in both water sources and FQs were only detected in site D1 during the wet season (Fig. S4). Similarly, conclusion was obtained that SAs (sulfamethoxazole, 78.38 ng L^{-1}) and MLs (erythromycin, 174.73 ng L^{-1}) were also detected in a Spanish river (Giusy et al., 2017; López-Serna et al., 2010). And approximately 25 and 30 ng L^{-1} of sulfamethoxazole was also found in the surface waters in France and Germany, respectively, but no sulfamethoxazole was found in the surface waters in Austria (Voulvoulis et al., 2015). Nevertheless, our detection of MLs obtained only during the wet season is a very interesting finding as the water solubility of all the investigated MLs, including erythromycin and roxithromycin, is extremely low probability and typically only detected at the adsorbed particulate or sediments (Sassman et al., 2007). MLs were detected mainly due to new dissolved source of MLs jointed into the aquatic environment during the wet season or because MLs adsorbed onto particulate were re-dissolved into water through precipitation during the wet season.

Among 11 SAs (Fig. S5), sulfamethazine was detected in both seasons and in two drinking water sources, particular during the dry season. Comparatively, three other SAs (sulfadiazine, sulfachlorpyridazine, and sulfisoxazole) were also detected during the wet season with relatively similar concentrations in both drinking water sources. These results agreed with a previous study that relatively high concentrations of sulfamethazine were found in the Pearl River, South China (Peng et al., 2011). Compared with other studies, the antibiotics found in this study were different. For instance, sulfamethoxazole was frequently detected across USA public source waters (Benotti et al., 2009; Schaider et al., 2014; Ye et al., 2007), but not in our study. This difference was unexpected since sulfamethoxazole is commonly used in China (Leung et al., 2012). Among seven FQs (Fig. S6), enoxacin was found in all investigated sites and seasons except at site Y1 during the wet season. During the dry season, a very small portion of nadifloxacin (≤2.1%) was also found in both drinking water sources. It needs to be pointed out that at site D1 during the dry season, > 50% of detected FQs were norfloxacin; while approximately one fifth of FQs were obtained as enrofloxacin at site D1 during the wet season. Comparatively, in the US, low concentrations of ciprofloxacin (0.03 μg L^{-1}) were found in drinking water sources in 25 states and Puerto Rico (Focazio et al., 2008), whereas enoxacin was not found because it has been largely discontinued in the US (http://en.wikipedia.org/wiki/Enoxacin).

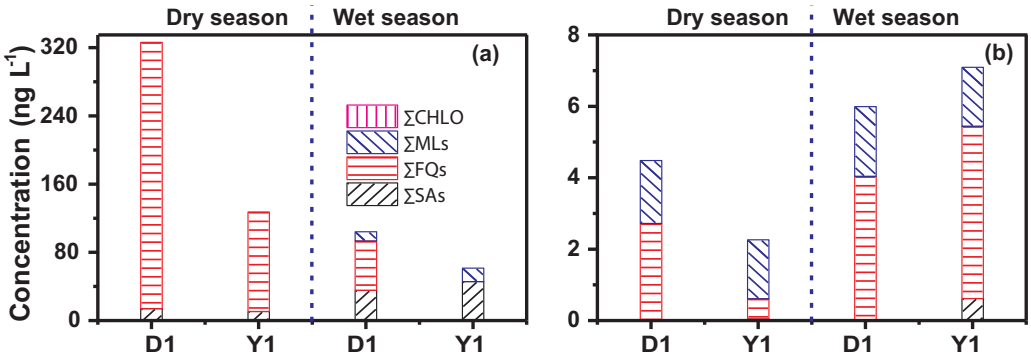

Fig. 1. The wet and dry season variation of different antibiotics groups in source of drinking water in (a) dissolved and (b) particulate phase.

In particulate phase (Fig. 1b), the total concentrations of antibiotics were very low ($\leq$7.1 ng L^{-1}), especial at site Y1 during the dry season (2.3 ng L^{-1}). This is likely because most of the antibiotics investigated have limited water solubility. Nevertheless, unlike the pollution profile in dissolved phase, the total antibiotic concentrations were much lower during the dry season than that during the wet season, particularly at site Y1. In general, airborne particles wet deposition and soils or dusts inflow will lead to the new inputs of antibiotics. Furthermore, similar to the dissolved phase, no CHLOs were found in both water sources during both seasons. However, as expected due to their low water solubilities, 1.7–2.0 ng L^{-1} of MLs were found in all particulate phase samples. FQs were the main contributors to all antibiotic contamination (accounting for 60.7–68.0% of total antibiotics), except at site Y1 during the dry season where MLs were the dominant species (accounting for 73.0% of total antibiotics) (Fig. S7).

The diversity of antibiotics detected was much lower in particulate phase than the dissolved phase. For instance, no SAs were detected at site D1 during both seasons; and only one kind of SA was found at site D1 during dry (sulfachinoxalin: 4.0×10^{-2} ng L^{-1}) and wet (sulfamethoxazole: 6.2×10^{-1} ng L^{-1}) seasons. For MLs, only erythromycin was found in both drinking water sources and during both seasons. Nevertheless, the diversity of FQs group during the wet season was slightly richer than the other antibiotic groups. As shown in Fig. S8, levofloxacin was found to be the predominant contributor to total antibiotic contamination during the dry season in both drinking water sources, but more than three kinds of antibiotics were found in both drinking water sources during the wet season.

3.1.2. Distribution of antibiotics in dissolved and particulate phase

The relative distributions of four groups of antibiotics in dissolved and particulate phases during both seasons were also investigated. During the dry season (Figs. S9a and b), the relative distribution of the four antibiotic groups at both drinking water sources was very similar. That is, SAs and FQs were predominantly found in dissolved phase (99.1–100%), whereas 100% of MLs were found in particulate phase. The reason is similar as mentioned above, e.g. SAs and FQs are more hydrophilic, whereas MLs are more hydrophobic. Like the dry season, SAs were also dominant in dissolved phase (98.7–100%) during the wet season (Figs. S9c and d). Nevertheless, the relative distribution of MLs and FQs was dramatically different during the wet season than the dry season. That is, FQs were mainly detected in dissolved and particulate phases at sites D1 and Y1, respectively. Interestingly, most of MLs were detected in dissolved phase during the wet season. The reason for this might be that during the wet season, there was some new input of these antibiotics into the sites or because the rain disturbed the sediment, leading to redissolution of the antibiotics in the aquatic system.

3.1.3. Risk assessment in drinking water source

Risk of antibiotics to human being at different life stages via water drinking was assessed. The RQs were estimated for the antibiotics using Acceptable Daily Intake (ADI) values (Table S1), and RQ values of individual antibiotics were summed from both dissolved and particulate phases. As shown in Fig. 2 and S10, all RQ values of antibiotics investigated were < 1, suggesting that these antibiotic contaminants posed no risk to humans by consuming drinking water from drinking water sources during both seasons according to the standard used in the reference (Gaffney et al., 2015). In addition, the RQ values decreased gradually as people's ages were increased, indicating that antibiotics posed a higher risk to people at earlier life stages. These results are well agreed with a previous study (Gaffney et al., 2015).

Risk quotient values were much higher during the wet season than the dry season at both drinking water sources. These risk results conflicted with antibiotic concentrations, which were much higher during the dry season (3.3×10^{2} ng L^{-1}, site D1; 1.1×10^{2} ng L^{-1}, site Y1) than the wet season (1.3×10^{2} ng L^{-1}, site D1; 69 ng L^{-1}, site Y1). This phenomenon may occur due to two reasons. First, some of the antibiotics detected in the drinking water sources (levofloxacin, nadifloxacin, enoxacin) were not included when calculating the RQ values during the dry season, because of they had no available ADIs. Second, some different antibiotic such as enrofloxacin and erythromycin-H_2O were detected in both Plant D and Plant Y source waters, respectively, during the wet season. Although their concentrations of both antibiotic were not very high, their contributions to the RQ values were relatively high, since their ADI values are very low (with 0.15 and 0.7 μg/kg bw/day, respectively). Indeed, during the wet season, the RQ of enrofloxacin (1.7×10^{-2}) accounts for approximately 78.9% of the total RQ in Plant D source water, and erythromycin-H_2O (4.9×10^{-3}) accounts for approximately 50.3% of total RQ in the Plant Y source water.

3.2. Removal of antibiotics and reduction in human health risk through drinking water treatment processes

3.2.1. Removal of antibiotics in dissolved phase

As shown in Figs. S1 and S2, the water from drinking water sources at Plant Y and D DWTPs were underwent different water treatment processes. In the dissolved phase, the levels of overall antibiotics were decreased in the finished drinking water during both seasons and in both DWTPs, except in Plant Y DWTP during the dry season, although their removal efficiencies fluctuated widely during treatment processes (Fig. S11a). This fluctuation trend can be vividly presented through the removal efficiencies at each treatment step. As shown in Fig. 3, in Plant D DWTP, the overall removal efficiencies were > 57% no matter what kind of technology was used or what season was. Nevertheless, negative removal efficiencies were observed in some treatment steps, such as step site D3 (both seasons), site D3′ (the wet season) and site D4 (the dry season). In Plant Y DWTP, the overall removal efficiencies were 52.3% and −49.6% during the wet and dry season, respectively. Similarly, negative removal efficiencies were also observed for some steps at site Y2 (the dry season) and site Y4 (the wet season). These negative removal efficiencies might be because the antibiotics had bound to the particulate or sludge was re-dissolved in water. Similar phenomena also occurred in WWTP, that is, even higher levels of some pharmaceuticals were found in the finished drinking water than the drinking water source (Gao et al., 2012; Jelic et al., 2011).

In Fig. S11a, the predominant antibiotics during the dry season were obtained as the FQs. That is, the removal efficiency of FQs were very low during the water treatment processes. Overall 55.8% and −63.0% of FQs were removed in Plant D and Plant Y DWTPs, respectively (Fig. S12). Comparatively, more than 96.8% of SAs was removed after the water treatment processes, although some of SAs might re-dissolve into water from adsorbed particulate (Fig. S12). High removal efficiencies of SAs were also observed during the wet season in both DWTPs using three different treatment processes. Nevertheless, FQs removal were almost equivalent to SAs during the wet season in Plant D DWTP, and a small amount of re-dissolved FQs was also removed in Plant Y DWTP. Higher removal efficiencies of FQs during the wet season are probably due to lower concentrations of FQ in drinking water sources during the wet season (Fig. 1a), and too high antibiotics concentration in the inlet water became overloaded. In addition, as mentioned, during the wet season, MLs were found in the drinking water sources for both DWTPs, but only less than half were removed (Fig. S12).

During the drinking water treatment processes, the changes in concentration and the removal of individual antibiotics were also analyzed in detail. For SAs (Fig. S13), the sum concentration of all investigated SAs was much higher during the wet than the dry season. Only approximately 80% of SAs could be removed in finished drinking water during the wet season due to the extremely high contaminant input level (e.g. high concentrations overwhelm removal capacity). Among SAs, during the wet season, sulfadiazine (7.9% removal) and sulfisoxazole (0% removal) were very persistent. In contrast, all other SAs species could be fully removed during treatment process in Plant D and Plant Y DWTP, respectively, which can also be seen in Fig. 4.

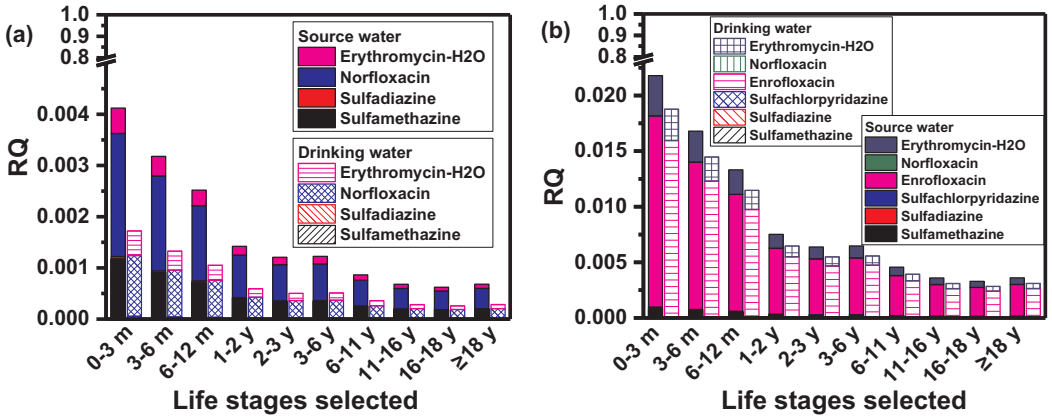

Fig. 2. Human Health Risk Quotients for the quantified antibiotics in the water at various life stages selected in D plant during the (a) dry and (b) wet season.

During the dry season, sulfamethazine and sulfadiazine were the main SAs components, and were also very persistent during first four water treatment steps. However, almost all other SAs were efficiently removed during the chlorination step. Chlorination is commonly used in water disinfection as it can effectively remove antibiotics from water via two general mechanisms: chorine substitution and chlorine radical oxidization (Li and Zhang, 2012). Similar to SAs, ML concentrations were higher during the wet than the dry season (< LOD) during the entire treatment processes (Fig. S14). Nevertheless, the removal efficiencies of erythromycin (the main component) were less than 50% (Fig. 4), but the re-dissolved high level of erythromycin (68 ng L^{-1}) in D3′ step could be fully removed in the subsequent filtration step. FQ concentrations in the dry season were much higher for the entire treatment process (Fig. S15). During the wet season, approximately 12 ng L^{-1} enrofloxacin was found in the finished drinking water from both DWTPs, although enrofloxacin was not found in the drinking water sources of Plant Y DWTP. Comparatively, during the dry season, enoxacin was also presented and retained in both DWTPs, especially in Plant Y DWTP, during treatment process. Nevertheless, no norfloxacin was found in Plant Y DWTP, but both norfloxacin and enoxacin were detected in the finished drinking water in both DWTPs. We hypothesize that the newly detected antibiotics during treatment processes are from the flocs or sludge, where they were previously absorbed, as flocs or sludge are major sinks for various organic pollutants in water (Martinez, 2009; Sukul and Spiteller, 2007).

Comparatively, the total concentrations of antibiotics found in this study were higher than other places. For example, only trace amounts of antibiotics (SAs: sulfamethoxazole, < 3.4 ng L^{-1}; MLs: erythromycin, < 4.9 ng L^{-1}) were detected in the finished drinking water in USA (Benotti et al., 2009; Ye et al., 2007), Macao (Yiruhan et al., 2010) and South Korea (Kim et al., 2007). Nevertheless, the total levels of antibiotics detected in this work were lower than those previously detected in Guangzhou (1.0–679.7 ng L^{-1}) (Yiruhan et al., 2010).

Overall, in the dissolved phase, the removal capacity of the combination technologies (flocculation → horizontal flow sedimentation → V type filtration → liquid Cl_2 chlorination) used in Plant D DWTP was much higher than Plant Y DWTP, and the SAs were the most easily removed antibiotic group.

3.2.2. *Removal of antibiotics in particulate phase*

The overall concentrations of antibiotics in the particulate phase during both seasons (Fig. S11b) were much lower than in the dissolved phase (Fig. S11a) during the entire treatment process. Similarly, the total concentrations detected antibiotics fluctuated widely during the drinking water treatment processes. For instance, during the dry season, all of antibiotics in step D3′ and most of antibiotics in step D3 were removed and then partial of antibiotics adsorbed onto the sludge were re-dissolved and reabsorbed onto particulate phase in water, leading to the increase of antibiotics levels in the following steps, although the total antibiotic concentrations were much lower in finished drinking water than the drinking water sources. However, a different trend was observed for antibiotics detected during the water treatment process at Plant Y DWTP during the dry season. That is, the total antibiotic concentrations first increased, peaked at step Y3, and then gradually dropped during treatment processes. However, the sum concentration was slightly higher in finished drinking water than the drinking water source. Compared with the dry season, the total antibiotic concentrations in the particulate phase were slightly higher during the wet season during treatment processes, and about half antibiotics were removed in both DWTPs in finished drinking water. All these results can be clearly observed in Fig. 5. That is, in Plant D DWTP, the overall removal

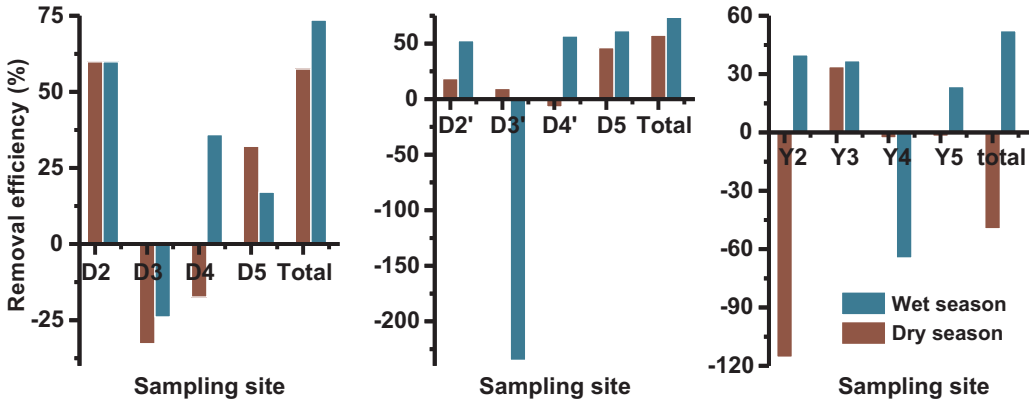

Fig. 3. Overall removal efficiency of total antibiotics during drinking water treatment processes in dissolved phase during both seasons.

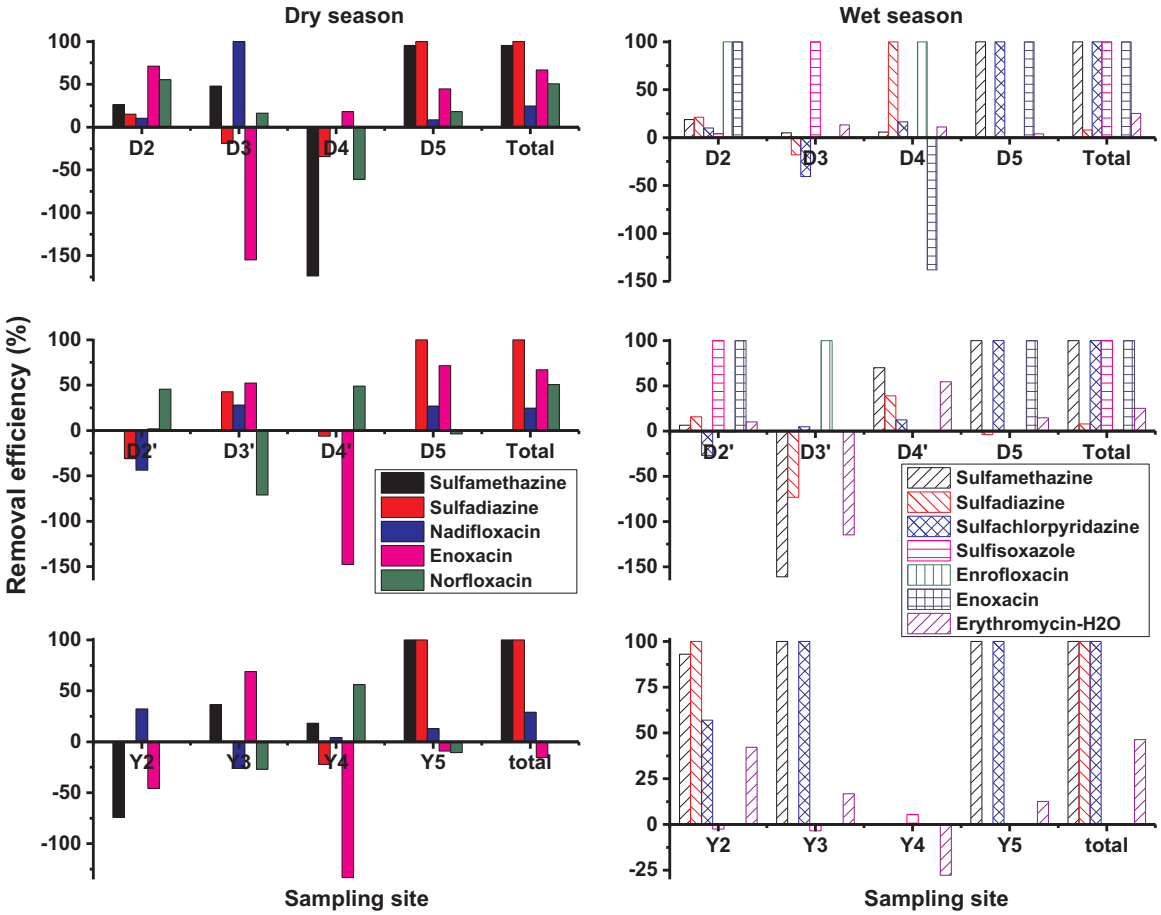

Fig. 4. Removal efficiency of individual antibiotics during drinking water treatment process in dissolved phase during both seasons.

efficiencies were approximately 50% no matter what kind of techniques were used or what the season was, although the removal efficiencies were −313.1% (the dry season) and −238.1% (the wet season) in particulate phase in D4 step. This is likely partially due to the redissolution and reabsorption of MLs (erythromycin, the dry season) and FQs (enrofloxacin and lomefloxacin, the wet season) onto particulates in the water samples (Figs. S16-S18). Although some SAs (sulfachinoxalin in site D4, the wet season; sulfathiazole in site D2′, the dry season) were re-dissolved and reabsorbed onto particulates during treatment processes, they were completely removed from particulate phase in the subsequent steps in Plant D DWTP using different techniques (Fig. S19).

In Plant Y DWTP, the overall removal efficiencies in particulate phase were approximately −15.5% (the dry season) and 44.3% (the wet season) in the water after whole treatment processes. This is likely due to the redissolution and reabsorption of some of the antibiotics (e.g. MLs (erythromycin, site Y2 to site Y4, the wet season; site Y2 to site Y5, the dry season) and FQs (norfloxacin, site Y4 and site Y5, the wet season; levofloxacin, Y2 step, and enrofloxacin, Y4 step, the dry season)) from the sludge onto the particulate phase during the water treatment processes (Figs. S16-S18). Similar results were found for the SA antibiotic group. That is, some SA antibiotics (e.g. sulfamethazine in Y3, the dry season) were re-dissolved, reabsorbed onto particulate phase, and then could be completely removed from the particulate phase in the subsequent steps in the Plant Y DWTP treatment process (Fig. S19).

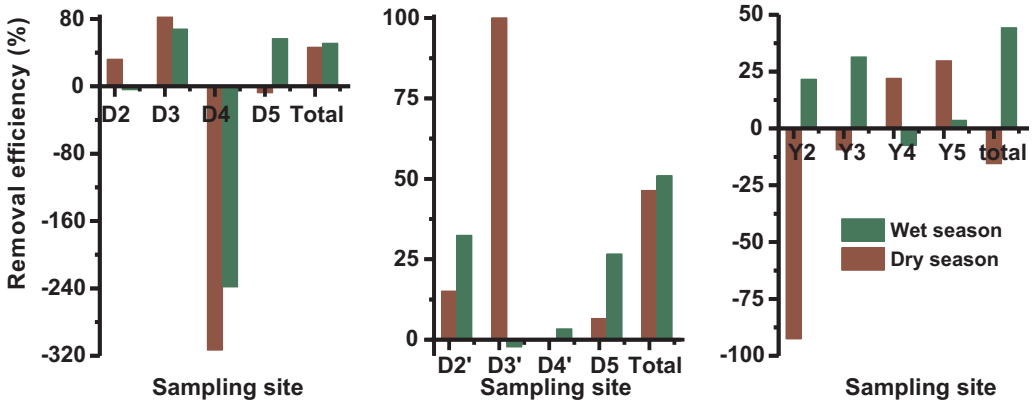

Fig. 5. Overall removal efficiency of total antibiotics during drinking water treatment process in particulate phase during both seasons.

Overall, the removal of antibiotics from particulate phase in these plants was very limited, especially in Plant Y DWTP. This is understandable, as most of DWTPs were not mainly built to remove antibiotics, but rather for traditional compounds and microorganisms. This kind of phenomenon has also been recorded to occur in other WWTPs (Gao et al., 2012; Jelic et al., 2011).

3.2.3. Antibiotics occurrence in sludge during drinking water treatment processes

During sedimentation, part of the antibiotics bound onto particulate phase would be deposited as sludge. As shown in Fig. S20, during the dry season, the total concentrations of antibiotics varied greatly in both DWTPs, even in same DWTP using different techniques. The total concentrations of antibiotics at site DII (5.1×10^2 ng g^{-1}) were approximately 3.9 and 26.6 times higher than at sites DI and YI, respectively. However, the distribution of antibiotics in each group was very similar and FQs was the main contributor (> 93.6%) at both sites DI and DII, except that there were slightly more SAs in site DI (1.6%). In contrast, the main contributors to antibiotic contamination at site YI sludge was MLs (Fig. S21). The similar distribution profile of antibiotics between site DI and DII is likely because they have the same source water. Higher antibiotic concentrations in the DII site sludge indicates that whirling flocculation was better than grille flocculation for antibiotic removal, which could be clearly seen by the antibiotic removal in the dissolved phase (Fig. 3). The different distribution profiles in sludge between the two DWTPs were due to the differences in source water. For instance, during the dry season, FQs were the main contributors to antibiotic contamination in both the dissolved (95.7%) and particulate phases (60.7%) in Plant D DWTP (Figs. S4 and S7). After flocculation and sedimentation, particulate adsorbed a significant amount of FQs from both phases could be deposited as sludge. In addition, low concentrations of SAs in the dissolved phase and MLs in the particulate phase could also be removed by these two techniques (Fig. S21). Similar phenomena could also be observed in Plant Y DWTP during the dry season. Higher percentage of MLs in sludge was due to their low water solubility (Sassman et al., 2007), which could be clearly observed in Figs. S4 and S7.

Comparatively, during the wet season, the total concentrations of antibiotics were roughly the same (40–44 ng g^{-1}) (Fig. 3) and mainly composed of FQs (66.3–84.4%) and MLs (15.6–29.1%) (Fig. S22). Antibiotics with high water solubility values (e.g. SAs) were difficult to remove via flocculation and sedimentation technologies, which could also be clearly seen in Fig. S11a.

Individual antibiotics of each group were also analyzed during drinking water treatment process in sludge. As seen in Fig. S23, from the MLs group, erythromycin was found in both seasons, while roxithromycin was only detected at site DI and YI during the wet season. Low concentrations of roxithromycin both in source water and water from the treatment process are probably due to the fact that erythromycin was a first generation (i.e. widely applied) antibiotic and roxithromycin is a new generation MLs (primarily used for bacterial infection treatment). Therefore, erythromycin has likely been currently and historically more widely used specie than roxithromycin (Taninaka et al., 2000). The distribution of SAs was very simple in the sludge, with only sulfisoxazole being detected in site DI during the dry season and sulfamethoxazole being detected in site DI and YI during the wet season. The presence of sulfisoxazole in sludge might be from the dissolved phase in source water and presence of sulfamethoxazole might from the drinking water treatment system, where it was adsorbed previously, since sulfisoxazole could only be found in dissolved phase and no sulfamethoxazole was detected in the drinking water source. Comparatively, the pollution profile of FQs, especially during the dry season in sludge was more abundant and their concentrations were much higher (except in site YI). During the dry season, the main contributors to FQ contamination were norfloxacin (51.6%), enoxacin (67.6%), and nadifloxacin (100%), in site DI, DII, and YI, respectively. During the wet season, FQs contamination was very similar amongst the three sludge samples, in which levofloxacin and enrofloxacin were the dominant FQ components.

3.2.4. Human health risk reduction

The human health risk of antibiotic exposure via consumption of finished drinking water was assessed for people from infant to adult stages (Fig. 2 and S10). It can be found that in both DWTPs, after water treatments, the human health risk decreased during both seasons except in Plant Y DWTP during the wet season. The largest reduction in RQ value was much higher during the dry season, especially in Plant D DWTP (58.2% removal). It worth noting that the RQ values were increased (more than 3 times higher than in the source water) rather than decreased in Plant Y DWTP during the wet season after treatment. Nevertheless, the total RQ value of all antibiotics in Plant Y DWTP during the wet season after treatment was < 1, indicating that the consumption of the finished drinking water posed no risk to humans (Gaffney et al., 2015). The risk was increased in Plant Y DWTP during the wet season after treatment, primarily due to the significant increase of enrofloxacin level from 0 to 12 ng L^{-1} after the filtration (Siphon) step. This might be due to re-dissolution of antibiotics into water from sludge. This can also be confirmed by the high proportion of enrofloxacin (accounting for 29.2% of the total antibiotics) detected in site YI sludge during the wet season. From these results, it can be further proved that the treatment techniques used in Plant D DWTP were much better for not only antibiotic removal, but also for reduction of the risk antibiotic residuals posed to human health.

4. Conclusion

Four groups of target antibiotics (total 21) were detected in two DWTPs with different treatment technologies frequently used in Southern China. In drinking water sources (dissolved phase), the total concentrations of all antibiotics were much higher in the dry season than the wet season. Among the four antibiotic groups, no CHLOs were detected at any time. FQs were the predominate antibiotic groups during the dry season, while low concentrations of SAs were found in the wet season in both drinking water sources. In the particulate phase, the total concentrations of antibiotics were very low, especially at site Y1 during the dry season. FQs and MLs were the main antibiotic groups. After the treatment with combination techniques, although the overall concentrations of antibiotics as well as human health risk of antibiotics were decreased in finished drinking water in both seasons at both DWTPs, antibiotics are still very high especial in the dissolved phase. As such, new treatment technologies should be developed to ensure the safety of drinking water in the near future.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ecoenv.2018.04.019.

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