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Research article

Occurrence and removal of antibiotics in ecological and conventional wastewater treatment processes: A field study

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ABSTRACT

The occurrence and removal of 19 antibiotics (including four macrolides, eight sulfonamides, three fluoroquinolones, three tetracyclines, and trimethoprim) were investigated in two ecological (constructed wetland (CW) and stabilization pond (SP)) and two conventional wastewater treatment processes (activated sludge (AS) and micro-power biofilm (MP)) in a county of eastern China. All target antibiotics were detected in the influent and effluent samples with detection frequencies of >90%. Clarithromycin, ofloxacin, roxithromycin and erythromycin-H_2O were the dominant antibiotics with maximum concentrations reaching up to 6524, 5411, 964 and 957 ng/L, respectively; while the concentrations of tiamulin, sulfamerazine, sulfathiazole, sulfamethazine, sulfamethizole and sulfisoxazole were below 10 ng/L. Although the mean effluent concentrations of target antibiotics were obviously lower than the influent ones (except ciprofloxacin), their removals were usually incomplete. Principal component analysis showed that the AS and CW outperformed the MP and SP processes and the AS performed better than the CW process in terms of antibiotics removal. Both the AS and CW processes exhibited higher removal efficiencies in summer than in winter, indicating biological degradation could play an important role in antibiotics removal. Because of the incomplete removal, the total concentration of detected antibiotics increased in the mixing and downstream sections of a local river receiving the effluent from a typical wastewater treatment facility practicing AS process. Nowadays, ecological wastewater treatment processes are being rapidly planned and constructed in rural areas of China; however, the discharge of residual antibiotics to the aquatic environment may highlight a necessity for optimizing or upgrading their design and operation.

1. Introduction

Due to the extensive human and veterinary utilization and the potentials to cause the selective proliferation of antibiotic resistant bacteria, antibiotics have raised increasing concerns recently (Pontes et al., 2009; Wilkinson et al., 2016). Antibiotics, including their parent compounds and transformation products, are being continuously discharged into the environment during manufacturing, consumption and disposal (Daughton and Ternes, 1999; Lin et al., 2010; Sharma et al., 2016). Among different pathways by which antibiotics enter the aquatic environment, effluents from various wastewater treatment facilities (WWTFs) have been considered as an important pollution source (Kim et al., 2007; Massey et al., 2010). As WWTFs are designed to remove organic materials, nitrogen and phosphate from wastewater, the removal of micro-pollutants (e.g. pharmaceuticals and personal care products, estrogens, etc.) is generally incomplete (Joss et al., 2006; Sponza and Celebi, 2012). The removal of antibiotics in WWTFs is affected by many factors including the physicochemical properties of antibiotics, specific treatment process employed, sludge retention time (SRT), hydraulic retention time (HRT) and environmental temperature, which make the removal efficiencies of antibiotics vary to a large extent (Cizmas et al., 2015; Gao et al., 2012a).

Although the ecological wastewater treatment processes usually have a high surface to equivalent-inhabitant ratio, relatively low cost, simple operation and maintenance, favorable environmental appearance and other ecosystem service benefits make them being widely planned and constructed as the secondary and/or tertiary treatment processes for wastewater in rural areas of China, where wastewater collection is often difficult because of the dispersed

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Abbreviations

AS	activated sludge
CIP	ciprofloxacin
CLA	clarithromycin
COD_{Cr}	chemical oxygen demand
CTC	chlortetracycline
CW	constructed wetland
ERY-H_2O	erythromycin-H_2O
ESI	electrospray ionization
HRT	hydraulic retention time
LOQ	limit of quantification
MRM	multiple reaction monitoring
MP	micro-power biofilm
NH_3–N	ammonia nitrogen
NOR	norfloxacin
OFL	ofloxacin
OTC	oxytetracycline
PCA	principal component analysis
PE	population equivalent
ROX	roxithromycin
SDM	sulfadimethoxine
SDZ	sulfadiazine
SFX	sulfisoxazole
SML	Sulfamethizole
SMN	sulfamethazine
SMR	sulfamerazine
SMX	sulfamethoxazole
SP	stabilization pond
SPE	solid phase extraction
SRT	sludge retention time
STZ	sulfathiazole
TCN	tetracycline
TIA	tiamulin
TMP	trimethoprim
TSS	total suspended solids
UPLC-MS/MS	ultra performance liquid chromatography and tandem mass spectrometry
WWTF	wastewater treatment facility
WWTP	wastewater treatment plant

layout, small scale and diverse geographic situations (Hijosa-Valsero et al., 2010). Continued efforts have been made on the occurrence and removal of antibiotics in wastewater treatment processes. However, the majority of past studies focused on large-scale wastewater treatment plants (WWTPs) that usually employ an activated sludge (AS) process while the occurrence and removal of antibiotics in ecological wastewater treatment processes remain largely unknown (Andreozzi et al., 2003; Brown et al., 2006; Lindberg et al., 2005).

In this study, the occurrence and removal of 19 antibiotics were investigated in 20 WWTFs located in a county of eastern China, which adopted either an ecological (such as constructed wetland (CW) and stabilization pond (SP)) or a conventional treatment process (such as AS and micro-power biofilm (MP)). The target antibiotics comprised five groups: macrolides, including roxithromycin (ROX), clarithromycin (CLA), tiamulin (TIA) and erythromycin-H_2O (ERY-H_2O); sulfonamides, including sulfadiazine (SDZ), sulfamerazine (SMR), sulfathiazole (STZ), sulfamethazine (SMN), sulfamethizole (SML), sulfamethoxazole (SMX), sulfisoxazole (SFX) and sulfadimethoxine (SDM); fluoroquinolones, including ciprofloxacin (CIP), ofloxacin (OFL) and norfloxacin (NOR); tetracylines, including tetracycline (TCN), oxytetracycline (OTC) and chlortetracycline (CTC); and a miscellaneous one, trimethoprim (TMP). Meanwhile, the seasonal variations in antibiotics removal were compared between the AS and CW processes. To assess the impact of the effluent discharged from a typical WWTF on local water quality, the antibiotic concentrations in the upstream, mixing (i.e., outfall), and downstream sections of a receiving river were examined. This study would provide useful information for optimizing or updating the ecological wastewater treatment processes, so as to reduce the potential risks associated with the antibiotics released to the aquatic environment in rural areas.

2. Materials and methods

2.1. Wastewater treatment processes selected

The 20 WWTFs surveyed in this study were classified into four wastewater treatment processes: the centralized AS process and the decentralized CW, MP and SP processes. The detailed information on each WWTF, such as the inhabitants served, HRT, SRT, and engineering commissioning is provided in Table 1. The CW, SP and MP processes had a treatment capacity ranging from 200 to 1200 population equivalent (PE), while the AS process had a much larger treatment capacity of 8000–60 000 PE. The 20 WWTFs were constructed between 2001 and 2008 and the HRT of ecological and conventional processes ranged from 24 to 240 h and from 10 to 24 h, respectively.

2.2. Sample collection

Seasonal sampling campaigns were carried out in summer and winter, each of which lasted for two weeks. Because of the discontinuity of the influent flow rate in rural areas, sampling acquisition method was adopted which spread over a certain period of time to eliminate the high variation in influent flux. The samples were collected three times per day (i.e., morning, noon and evening) to make a mixed sample. Note that during the sampling campaigns, there were no rainfalls and the daily hydraulic loading rates of the test WWTFs were nearly constant. The collected samples were stored in pre-cleaned amber glass bottles and preserved in cool boxes (ca. 4 °C). Immediately after delivery to the laboratory, the samples were filtered through prebaked glass microfiber filters (GF/C, Whatman) and analyzed within three days.

2.3. Chemicals and analytical methods

STZ, SMR, SFX, SMX, SML, SDM, SDZ, TMP, OFL, NOR, CIP, TIA and ERY, all with a purity of 99.0%, were purchased from Sigma-Aldrich (St. Louis, USA). ROX (97.0%), TCN (97.0%), OTC (96.5%) and CTC (93.0%) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). CLA (98.0%), the internal standard (simatone) and SMN (99.0%) were obtained from TCI (Tokyo, Japan), Accu Standard (New Haven, USA) and Acros Organics (New Jersey, USA), respectively. The detailed structures of the investigated antibiotics are listed in Table S1 (Supplementary material, SM). The stock solutions of individual antibiotics were prepared by dissolving each compound in methanol at a concentration of 100 mg/L (Ben et al., 2008). Because the dehydration product (ERY-H_2O) was the predominant form of ERY in water (Hirsch et al., 1999), ERY-H_2O was prepared and determined according to the method proposed by Lindberg et al.