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Antibiotics in WWTP discharge into the Chaobai River, Beijing

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Abstract: 22 representative antibiotics, including 8 quinolones (QNs), 9 sulfonamides (SAs), and 5 macrolides (MCs) were selected to investigate their occurrence and removal efficiencies in a Wastewater Treatment Plant (WWTP) and their distribution in the receiving water of the Chaobai River in Beijing, China. Water quality monitoring was performed in an integrated way at different selected points in the WWTP to explore the potential mechanism of antibiotics removal during wastewater treatment. Water quality of the Chaobai River was also analyzed to examine environmental distribution in a river ecosystem. The results showed that within all the 22 compounds examined, 10 antibiotics were quantified in wastewater influent, 10 in effluent, and 7 in river. Sulfadiazine (SDZ, 396 ng/L) and Sulfamethazine (SMZ, 382 ng/L) were the dominating antibiotics in the influent. Both the conventional treatment and advanced Biological Aerated Filter (BAF) system was important for the removal of antibiotics from the wastewater. And the concentrations of selected antibiotics were ranged from 0–41.8 ng/L in the effluent-receiving river. Despite the fact that the concentrations were reduced more than 50% compared to effluent concentrations, WWTP discharge was still regarded as a dominant point-source input of antibiotics into the Chaobai River.

Introduction

In recent years, antibiotics in the environment as a kind of emerging environmental contaminants under the category of pharmaceuticals and personal care products (PPCPs) have received an increasing attention due to their potential negative impacts on the human bodies and the aquatic organisms (Ziembinska-Buczynska et al. 2015, Zhang et al. 2013). Antibiotics, also named antibacterials, including quinolones, tetracyclines, sulfonamides and macrolides *etc.*, are used comprehensively all over the world for inhibiting and treating infectious diseases as well as promoting animal growing development in agriculture and aquaculture (Zhang et al. 2013, Sarmah et al. 2006).

Antibiotics are classified as part of PPCPs, which are usually regarded as "pseudopersistent" contaminants due to their continual introduction into the environment (Gulkowska et al. 2008). It has been reported that a multitude of antibiotics are detected in high levels from municipal sewage (Collado et al. 2014, Li et al. 2013, Watkinson et al. 2007) and drinking water (Figueira et al. 2011,Watkinson et al. 2009). They are even detected in the natural environment including surface water (Hedgespeth et al. 2008, Tien-his et al. 2012), groundwater (Loos et al. 2010, Stuart et al. 2014), and soil (Braschi et al. 2010, Micallef et al. 2012). Antibiotic residues in the environment can exhibit negative influence on aquatic and terrestrial organisms and some other non-target organisms, leading to a series of potential ecological hazards, such as the development of antibiotic resistance (Pruden et al. 2006).

One of the largest inputs of antibiotics into the environment results from the human ingestion and the subsequent excretion since only partially metabolized (up to 90%) and being excreted in its original, active form in urine and feces (Halling-Sørensen et al. 1998, Kümmerer 2009). Those residual antibiotics are then loaded into urban wastewater treatment plants (WWTPs), which have been generally considered to be a principal source of antibiotics in the environment (Watkinson et al. 2009), and finally discharged into the aquatic media with effluent. WWTPs are regarded as the major effective obstacle to antibiotics between wastewater and the environment (Al-Rifai et al. 2011). However, the reports on the removal efficiency of many antibiotics in WWTPs are usually incomplete (Zaleska-Radziwill et al. 2011), moreover, some of them even present the negative results (Behera et al. 2011, Reungoat et al. 2011). In Europe and America, some former studies have been conducted to certify this affirmation (Le-Minh et al. 2010, Rosal et al. 2010). However, only a few studies have been researched in China, which are on the fate and behavior of antibiotics during the wastewater treatment process and the subsequent discharge into the receiving rivers (Gulkowska et al. 2008, Li et al. 2013).

China, as a developing country with a huge population, is characterized by an enormous antibiotic production and a large number of consumption. It has been reported that the annual

usage of antibiotics in China is about 180,000 tons (including health and agricultural utilization), which is 10 times of annual per capita consumption compared with the United States (Zheng et al. 2016). This result indicated that in more opportunities the antibiotics would be exposed to comparative high levels in the environment.

Most WWTPs in China constitute only primary and secondary treatments, especially in large-scale plants. This guarantees the removal efficiency of the conventional pollutants, such as organic substances, oxides, sulfides and other toxic substances, but not of the antibiotics and other PPCPs (Caliman and Gavrilescu 2009). Therefore, advanced treatment technologies, such as membrane processes, ozone and sonolysis, have been studied for the elimination of PPCPs (De Witte et al. 2009, Hartmann et al. 2012). Yuan et al. (Yuan et al. 2009) examined the effect of UV radiation in the removal of antibiotics. Their results were not very satisfactory because of the poor removal efficiency. Other advanced treatments due to their significant expensive investment and running costs also need further investigation to confirm their necessity for the removal of antibiotics and other micropollutants (Lucas et al. 2010). Biological aerated filter (BAF) is a kind of immobilization reactor that has been widely employed all over the world due to its plentiful advantages, such as small footprint, low investment and running costs, and excellent performance. For example, Zhuang et al. (Zhang et al. 2014) applied BAF as an advanced treatment system for coal gasification wastewater. The system had high performance on the removal of NH_4^+-N and TN removal, especially under the high toxic loading.

In this study, the occurrence and removal of 22 antibiotics, including eight quinolones (QNs), nine sulfonamides (SAs) and five macrolides (MCs) (Table 1) were investigated in a WWTP (using a BAF system as advanced treatment) and the Chaobai River. The aim of the research was to estimate the removal efficiency for different antibiotics during different treatment steps and to assess the impact of selected antibiotics discharged into the receiving water body.

Materials and Methods

Chemicals

HPLC-grade methanol and acetonitrile were purchased from Fisher Scientific (Pittsburgh, PA, USA). Formic acid (98%) was purchased from Fluka. Ammonium formate (99%) and ammonium hydroxide (v/v, 50%) were purchased from Alfa Aesar. De-ionized (DI) water was prepared with the Milli-Q Advantage A10 system (Millipore, USA).

Norfloxacin (NOR, 99.9%), ciprofloxacin (CIP, 99.9%), sarafloxacin (SAR, 95.0%), Ofloxacin (OFL, 99.9%), fleroxacin (FLE, 99.5%), lomefloxacin (LOM, 98.0%), difloxacin (DIF, 98.0%), enrofloxacin (ENR, 99.9%), sulfadiazine (SDZ, 99.7%), sulfamerazine (SMR, 99.9%), sulfadimethoxine (SDM, 99.4%), sulfisoxazole (SIA, 99.0%), sulfamonomethoxine (SMM, 99.0%), erythromycin (ERY, 99.1%), roxithromycin (ROX, 90.0%), josamycin (JOS, 98.0%), tylosin (TYL, 82.4%), and spiramycin (SPI, 88.9%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Sulfamethoxazole (SMX, 99.0%), sulfathiazole (STZ, 99.0%), sulfapyridine (SPD, 99.0%), and

Table 1. Selected antibiotics and their properties[a]

Groups	Analytes	Acronym	MW (g/mol)	Log K_{ow}
Quinolones	Norfloxacin	NOR	319.3	-1.03
	Ciprofloxacin	CIP	331.3	0.3
	Difloxacin	DIF	399.4	-0.4
	Enrofloxacin	ENR	359.4	1.16
	Fleroxacin	FLE	369.4	0.24
	Ofloxacin	OFL	361.3	0.35
	Lomefloxacin	LOM	351.4	0.31
	Sarafloxacin	SAR	385.4	1.07
Sulfonamides	Sulfathiazole	STZ	277.3	0.72
	Sulfamethoxazole	SMX	253.3	0.9
	Sulfisoxazole	SIA	267.3	1.01
	Sulfapyridine	SPD	249.3	0.35
	Sulfadimethoxine	SDM	332.3	1.63
	Sulfamethazine	SMZ	278.3	0.89
	Sulfadiazine	SDZ	250.3	-0.09
	Sulfamerazine	SMR	286.3	0.14
	Sulfamonomethoxine	SMM	280.0	0.70
Macrolides	Spiramycin	SPI	842.4	na[b]
	Josamycin	JOS	827.3	na
	Tylosin	TYL	917.1	1.63
	Erythromycin	ERY	733.9	3.1
	Roxithromycin	ROX	836.4	2.75

[a] Verlicchi et al. (2012), Muñoz et al. (2008) and Zhou et al. (2013); [b] na: not available

sulfamethazine (SMZ, 99.0%) were purchased from KaSei Industry Co., Ltd. (Tokyo, Japan).

The following isotopically labelled compounds were used as surrogate standards at 100.0 µg/L in methanol. Norfloxacin-d_5 (NOR-d_5), ofloxacin-d_3 (OFL-d_3) and sarafloxacin-d_8 (SAR-d_8) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Sulfamethoxazole-d_4 (SMX-d_4), sulfamethazine-d_4 (SMZ-d_4), spiramycin I-d_3 (SPI I-d_3), and erythromycin-^{13}C, d_4 (ERY-^{13}C, d_4) were purchased from Toronto Research Chemicals (Oakville, ON, Canada).

Sample collection

Samples were all collected from Miyun WWTP in Beijing, China, during January 2014. The influent waters of Miyun WWTP include mainly domestic sewage and industrial wastewater (such as food, cosmetic, pharmacy and automotive manufacturing). This WWTP employs cyclic activated sludge technology, coupled with a subsequent biological aerated filter (BAF) for advanced treatment. BAF reactor was packed with light weight ceramists as biofilm carriers with a diameter of 2–6 cm and the media's depth was 150 cm. More information about the selected WWTP is provided in Table 2. The wastewater collected from the inlet and the outlet of each unit process including the influent and the effluent (final outlet) was sampled to understand the fate and behavior of antibiotics during wastewater treatment processes. The WWTP sampling points are indicated in Figure 1. In each unit, a 24 h composite sample was collected in a flow proportional mode. At equal time increments (2 h), samples were collected and composited with volume proportionally to the flow rate by an automatic device at each sampling point. Removal efficiencies during wastewater treatment were calculated on the basis of influent and effluent concentrations.

River water was collected about 0.5 m below the water surface of The Chaobai River, whose yearly average flow rate was 4.5 m^3/s approximately. 3 h composite samples were manually collected in the three different sites along the river: 200 m upstream (A), at the WWTP discharge point into the river (B) and 2 km downstream (C). Between sites B and C no other discharge is present and at the site B a homogeneous mixture of effluent water with river water was expected.

All water samples were collected to 500 mL amber glass bottles, which were washed with methanol and DI water before using. Immediately after delivery to the laboratory, they were filtered through 0.45 µm nylon membrane filters (Whatman, UK) to remove particles. All the samples were extracted within two weeks – those not extracted immediately were stored at 4ºC in the dark.

Sample extraction and analysis

Analytical procedures for the 22 antibiotics in wastewater were developed according to the published EPA Method 1694 (USEPA 2007), with some modifications. The procedures are described as following.

Water samples were pre-concentrated through solid phase extraction (SPE) with Oasis HLB cartridges (6 ml, 200 mg; Waters, USA). Before extraction, a total of 0.2 g Na_2EDTA and 20 ng surrogate standards (NOR-d_5, OFL-d_3, SAR-d_8, SDMD-d_4, SMX-d_4, ERY-^{13}C, d_4 and SPI I-d_3) were added to 200 ml water sample. The Oasis HLB cartridges were preconditioned with 5 ml methanol and 5 ml DI water. The samples were then loaded and passed through the cartridges at a flow rate of around 3ml/min. After that, cartridges were rinsed with 15 ml DI water, and then dried under nitrogen gas for 20 min. Finally, the analytes were eluted with 6 ml of ammonia-methanol solution (5:95, V/V). The eluate was concentrated to 1 ml or less with nitrogen gas at 35°C, and diluted with DI water to 1 ml. After centrifuged for 5 min at 12,000 rpm, the supernatant was filtered through a 0.22-µm

Table 2. Information of the Miyun Water Resource Recovery Facility

Daily flow ($m^3 d^{-1}$)	HRT[a] (h)	SRT[b] (d)	Parameter (mg/L, Mean)			
			COD[c]	NH_4^+-N	TN[d]	TPe
5000			Inf.[f] Eff.[g]	Inf. Eff.	Inf. Eff.	Inf. Eff.
	48	20	934.7 57.8	74.8 10.6	95.8 23.8	8.0 1.1

[a] HRT = hydraulic residence time. [b] SRT = solid residence time. [c] COD = chemical oxygen demand. [d] TN = total nitrogen. [e] TP = total phosphorus. [f] Inf. = Influent; [g] Eff. = Effluent

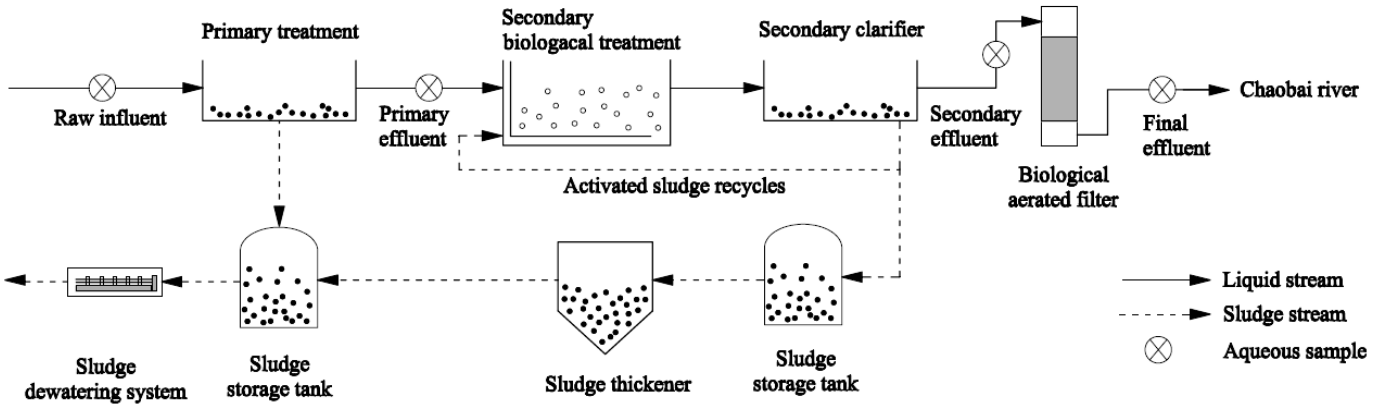

Fig. 1. Miyun WWTP scheme and sampling points

nylon membrane. An aliquot (15 μL) of the filtered supernatant was prepared for analysis.

High-performance liquid chromatography-electrospray ionization tandem mass spectrometry (HPLC-ESI MS/MS) was applied to analyze the target antibiotics. The LC system was Dionex Liquid Chromatography Ultimate 3000 (Sunnyvale, CA, USA). An XTerra MS C18 column (3 μm, 100 mm × 2 mm) was used as the analytical column at a flow rate of 0.20 mL/min. Methanol–acetonitrile (1:1, v/v) was used as a mobile phase A, and 0.3% formic acid in water (containing 0.1% ammonium formate, v/v, pH = 2.9) was used as a mobile phase B. The gradient program was as follows: the mobile phase starting conditions were 10% of A for 2.0 min, and A was increased to 70% in 10.0 min before being increased to 100% for 4.0 min; 100% of A for 3.0 min, followed by returning to the initial composition in 0.1 min, which was maintained for 13.9 min. The total run time was 33.0 min.

The MS system consisted of a triple-quadrupole mass spectrometer (API 3200; Applied Biosystems/MDS SCIEX, US) with electrospray ionization (ESI). The instrument was operated in the positive electrospray ionization and multiple reactions monitoring (MRM) mode. The MS/MS parameters were optimized as follows: curtain gas pressure, 0.14 MPa; collision gas pressure, 0.02 MPa; ion spray voltage, 5000 V; temperature, 600°C, gas 1, 0.38 MPa; and gas 2, 0.45 MPa. Other parameters of MS/MS and ion pair are listed in Table S1.

Table S1. Experimental conditions of electrospray tandem mass spectrometry

Analytes	Parent ion (m/z)	Daughter ion (m/z)	Declustering Potential/ V	Entrance Potential/ V	Collision cellent potential/ V	Collision Energy/ eV	Collision cell exit potential/ V
NOR	320.1	276.3	45	8.0	11	23	10
		302.2[a]	40	8.0	11	28	10
CIP	332.1	231.1	58	4.5	14	49	9.5
		314.3[a]	55	5.0	11	28	6.0
DIF	400.0	299.1	60	4.0	13	41	12
		356.2[a]	60	4.0	13	28	13
ENR	360.0	245.2	55	5.0	12	39	9.5
		316.2[a]	58	5.0	11	28	11
FLE	370.0	269.2	45	4.5	20	34	10
		326.2[a]	45	4.5	12	27	12
OFL	362.2	261.2	55	5.0	24	38	10
		318.2[a]	55	5.0	12	27	11
LOM	352.0	265.2[a]	53	5.0	12	34	10
		308.2	55	4.0	37	32	12
SAR	386.0	299.2	65	4.5	13	37	6.5
		368.2[a]	60	4.5	14	31	7.0
NOR-d_5	325.3	281.4	50	8.5	11	23	6.0
		307.3[a]	40	7.5	11	27	6.5
OFL-d_3	365.2	261.2	55	6	12	39	10
		321.2[a]	55	6	12	28	11.5
SAR-d_8	394.2	350.3	60	6	13	28	12
		376.2[a]	59	6	12	33	14
STZ	256.0	108.0	43	4.5	10	36	4.5
		156.0[a]	42	4.2	10	21	4.5
SMX	254.0	156.0[a]	45	4.0	9	23	5.2
		160.1	47	4.5	9	27	6.0
SIA	268.1	108.0	46	4.5	12	37	4.5
		156.0[a]	46	4.5	9	21	5.0
SPD	250.1	108.0	38	7.0	11	36	4.5
		156.0[a]	41	4.7	9	24	5.5
SDM	311.2	108.0	55	4.5	12	41	4.5
		156.1[a]	57	4.0	12	30	6.0
SMZ	279.2	156.0	47	4.5	9	27	6.0
		186.1[a]	49	4.0	10	25	6.5
SDZ	251.1	108.0	42	4.3	11	35	4.2
		156.0[a]	43	3.5	9	23	5.0
SMR	265.2	107.9[a]	47	4.5	11	37	4.5
		156.0	48	5.0	10	24	5.5

[a] quantitative ion

Quality assurance and quality control

Calibration curves of the target compounds were drawn across a wide range of concentrations (0.05–500 μg/L). The correlation coefficients (R^2) of the calibration curves were all over 0.99. All the concentrations were determined by an internal standard method. For each set of samples, procedure blank and independent check standard were operated separately in sequence followed by the background contamination and system performance examining each time later. Correlation coefficients and limits of quantity (LOQs) of the 22 antibiotics are listed in Table S2. LOQs were defined as the minimum detectable concentration that had a signal-to-noise ratio (S/N) of 10. LOQs of the analytes were in the range of 0.01–0.15 ng/L and their recoveries were in the range of 72.4–112.0% in water samples. All the samples were extracted 3 times and were analyzed. As duplicate samples were collected at each sampling site, mean concentrations were adopted. In most cases, deviations of duplicate samples were less than 20%.

Result and Discussion

Occurrence of antibiotics in the influent and effluent from WWTP

Influent

Table 3 presents concentrations of the selected antibiotics in the WWTP influent, secondary effluent and BAF effluent. Out of the 22 target compounds, 10 antibiotics including three quinolones (NOR, CIP, and OFL), 4 sulfonamides (SMX, SDM, SMZ, and SDZ) and 3 macrolides (SPI, ROX and ERY) were quantified in the influent samples. Other twelve antibiotics (DIF, ENR, FLE, LOM, SAR, STZ, SIA, SPD, SMR, SMM, JOS, and TYL) were detected below LOQs. The concentrations of detected quinolones, sulfonamides and macrolides in the influent were in the range of 214–320 ng/L, 1.20–396 ng/L and 6.52–30.6 ng/L, with the total concentration of 756 ng/L, 1083.2 ng/L and 47.98 ng/L, respectively. It is obvious that among the three groups of antibiotics detected in the influents, the total concentration of sulfonamides was higher compared with those of the other two in this study.

The highest antibiotic level of all the investigated antibiotics in the influent was 396 ng/L for SDZ, followed by SMZ, NOR, SMX, CIP and OFL. A similar concentration for OFL in influents was detected in the range of 80–368 ng/L from four WWTPs in the Pearl River Delta in southern China (Xu et al. 2007) but there was reported a higher OFL concentration (440–3100 ng/L, mean 1474 ng/L) in eight WWTPs in Beijing, China (Gao et al. 2012). The concentrations of other main selected antibiotics detected in this study were also not illustrated overall higher concentrations with respect to preciously studies of WWTP. For instance, Watkinson *et al*. reported that the concentrations of NOR, CIP and SMX in the influent were 170 ng/L, 3800 ng/L, and 360 ng/L respectively from a WWTP in Australia (Watkinson et al. 2007). Collado et al. observed that the concentrations of CIP, OFL and SMX were 392 ng/L, 128 ng/L, and 70 ng/L respectively from

Table S2. Correlation coefficients (r^2), linear range, recoveries (%) and limits of detection (LODs, S/N=3) of 22 antibiotics

Groups	Analytes	Surrogates	r^2	Linear range (μg /L)	Recovery (%)	LODs (ng/ L)
Quinolones	NOR	NOR-d_5	0.9974	0.1–500	87.5±7.4	0.1
	CIP	NOR-d_5	0.9987	0.05–500	82.7±11.4	0.1
	DIF	OFL-d_3	0.9985	0.05–500	74.3±10.3	0.1
	ENR	OFL-d_3	0.9990	0.05–500	97.4±8.9	0.1
	FLE	OFL-d_3	0.9984	0.1–500	97.6±6.8	0.15
	OFL	OFL-d_3	0.9988	0.1–500	104.0±8.5	0.2
	LOM	OFL-d_3	0.9967	0.05–500	72.4±3.3	0.1
	SAR	SAR-d_8	0.9992	0.05–200	95.9±4.6	0.1
Sulfonamides	STZ	SMX-d_4	0.9974	0.01–500	84.2±5.9	0.02
	SMX	SMX-d_4	0.9991	0.1–500	101.0±4.3	0.15
	SIA	SMX-d_4	0.9987	0.02–500	88.3±2.7	0.05
	SPD	SMZ-d_4	0.9985	0.02–500	98.0±5.3	0.04
	SDM	SMZ-d_4	0.9996	0.01–500	121.0±5.6	0.01
	SMZ	SMZ-d_4	0.9993	0.01–500	102.0±3.7	0.02
	SDZ	SMZ-d_4	0.9986	0.05–500	101.0±3.5	0.05
	SMR	SMZ-d_4	0.9977	0.02–500	107.0±7.1	0.05
	SMM	SMZ-d_4	0.9985	0.02–500	112.0±7.3	0.1
Macrolides	SPI	SPI I-d_3	0.9980	0.1–500	104.0±5.2	0.1
	JOS	SPI I-d_3	0.9934	0.05–200	84.4±5.6	0.05
	TYL	SPI I-d_3	0.9934	0.05–200	90.0±7.1	0.05
	ROX	SPI I-d_3	0.9905	0.05–500	101.0±6.1	0.1
	ERY	ERY-$^{13}C,d_4$	0.9992	0.1–500	109.0±5.3	0.15

a municipal WWTP in Catalonia, Spain (Collado et al. 2014). This indicates that the usage trends and consumption rates of antibiotics are similar in these regions.

Secondary Effluent

After the cyclic activated sludge treatment process, 10 antibiotics were still found in the secondary effluent samples and the quinolones were the dominating antibiotics among the three groups of antibiotics with a total concentration of 682.6 ng/L, while the total concentrations of sulfonamides and macrolides were 582 ng/L and 95.3 ng/L respectively. OFL was detected in the highest level in the secondary effluent, followed by NOR, SDZ, SMZ, CIP and SMX. Like the influent samples, the concentrations of the main antibiotics in this study also showed similarity to or a slight difference from the results in other researches. The concentrations of NOR in Hong Kong and Shenzhen, China, ranged from 85–320 ng/L and in Australia the concentrations of NOR, CIP and SMX were 145 ng/L, 600 ng/L and 185 ng/L (Gulkowska et al. 2008).

Advanced Treatment Effluent

After the advanced treatment of BAF system, the detected 10 antibiotics were still present in the final effluent. It was demonstrated that these antibiotics could not be effectively eliminated by BAF treatment. Among the three categories of antibiotics investigated in the tertiary effluent samples, the total concentrations of quinolones, sulfonamides and macrolides were 473 ng/L, 454 ng/L and 50 ng/L respectively. Quinolones and sulfonamides were still the major antibiotics which accounted for 48.4% and 46.5% of the overall antibiotics in the effluent, while macrolides accounted only for 5.1%. The concentration of NOR was 204 ng/L, and expressed the highest level among all the investigated antibiotics, followed by SMZ, OFL, SDZ, CIP and SMX.

Limited information is available regarding the presence of antibiotics in the tertiary effluents especially after the BAF system. Compared with some previous studies, the concentrations of CIP and SMX in our study were higher than those reported using ozone as advanced treatment in the USA (CIP, mean: 1 ng/L; SMX, mean: 80 ng/L) (Yang et al. 2011) and using UV-based as advanced treatment in Spain (CIP, mean: 137 ng/L; SMX, mean: 12 ng/L) (Collado et al. 2014).

Removal of antibiotics in wastewater treatment processes

Removal of antibiotics in conventional treatment

Table 4 shows the total concentrations of the three antibiotic groups and the proportion removed through each process during the whole wastewater treatment. The concentration of the targeted antibiotics was reduced by 27.94% in the aqueous phase while passing through the conventional treatment. The main contribution to the removal occurred during both primary and biological treatment with reduction in the concentrations of sulfonamides, which are the dominating antibiotics in the

Table 3. Concentrations of antibiotics in the facility influent, secondary effluent and BAF effluent

Groups	Compound	facility influent	secondary effluent	BAF effluent
		ng/L	ng/L	ng/L
Quinolones	NOR	320	240	204
	CIP	222	168.6	104.6
	DIF	na[a]	na	na
	ENR	na	na	na
	FLE	na	na	na
	OFL	214	274	164.4
	LOM	na	na	na
	SAR	na	na	na
Sulfonamides	STZ	na	na	na
	SMX	304	157.4	100.4
	SIA	na	na	na
	SPD	na	na	na
	SDM	1.20	0.65	0.864
	SMZ	382	202	202
	SDZ	396	222	151.2
	SMR	na	na	na
	SMM	na	na	na
Macrolides	SPI	6.52	9.7	3.6
	JOS	na	na	na
	TYL	na	na	na
	ERY	30.6	40.8	33.8
	ROX	10.86	44.8	12.5

[a] na: not available

raw wastewater. Previous research has reported relatively high removal efficiency of sulfonamides during biological treatment in activated sludge (Pérez et al. 2005). The removal of quinolones by the conventional treatment is very low in this study. However, previous studies have reported the results on quinolones, having significant removal efficiency (>85%) during wastewater treatment due to photochemical, thermal degradation and sorption, especially to soils and sludge (Watkinson et al. 2007). The total removal efficiency of macrolides by conventional treatment was negative in this study, which was very similar to that observed by others (Verlicchi et al. 2012). Most of macrolides were resistant to the processes carried out in WWTP. This was mainly due to the low adsorption potential of macrolides and it was reported that the sorption to sludge accounted for only minor contribution to the removal of major macrolides in sewage (Göbel et al. 2005). Additionally, biodegradation in activated sludge treatment units was of minor importance in the removal of macrolides.

The removal efficiency of individual antibiotics in various processes of WWTP is shown in Figure 2. Most antibiotics were not efficiently removed during the primary treatment except for SDM (47.7%) and SDZ (50.8%), indicating insignificant adsorption of investigated antibiotics to the particles eliminated in this stage. As shown in Table 1, all the 17 selected antibiotics have low log K_{ow} values that is less than 3.1 and are not expected to be adsorbed largely to the particles consequently.

During the secondary treatment, the removal efficiency for different antibiotics ranged from – 155% to 47.5% (Figure 2). SMX, SMZ and ERY had relatively high rates of removal efficiency of 47.5%, 37.3%, and 27.9% respectively. The removal rate of SMX in our study was lower compared to the reported range of 54–71% in the active sludge process in Spain , but the removal rate of SMZ was higher than the observed (SMZ: 16%) (García-Galán et al. 2011). Xu *et al*. have reported a similar reduction in ERY concentration by 26% during the secondary treatment (Xu et al. 2007). SMX has been proved to be efficiently biodegradable in previous literature (Yang et al. 2011). A secondary group of antibiotics including NOR, CIP, OFL, and SPI had lower removal rates by the secondary treatment of the WWTP. The removal efficiency of NOR was about 15.5% during the biological treatment process in the study, which was lower than that reported in Switzerland (NOR: 80–87%) (Golet et al. 2002). Vieno et al. reported that the elimination efficiencies of CIP and OFL were 84% and 83% in the biological units of WWTPs, which were much higher than the result (5.9% and 6.2%) (Vieno et al. 2007). Moreover, it is notable that removal efficiencies of SDM, SDZ and ROX during the secondary treatment were negative. This could ascribe to the presence of cleaving of conjugated microorganisms in wastewater sludge (Xu et al. 2007).

Removal of antibiotics in BAF system

The BAF system receives the treated effluent from the secondary treatment unit, where only a small portion of antibiotics have already been removed from the aqueous phase of wastewater. Residual antibiotics were more persistent in liquid, creating a challenge for removal. The advanced treatment process of BAF was then employed to examine the performance of further elimination of these compounds.

As shown in Table 4, the BAF stage of the WWTP removed approximately 28.1% of total antibiotics from the liquid phase. CIP, OFL, SMX, SDZ, SPI and ROX showed the relative high removal efficiencies ranging from 31.9–72.1%. But lower removal efficiency by BAF system was observed for NOR, SDM, SMZ and ERY with the removal efficiency in the range from – 32.9% to 15%.

In this study, the use of BAF as advanced treatment step to reduce emissions of antibiotics from WWTP secondary effluent exhibited the superior performance. Until now, a few studies have showed the removal efficiency of antibiotics by BAF system. Based on the former literature the potential removal mechanisms of organics in BAF could be attributed to microbial degradation and physical adsorption, whereas the synergy of the two effects could also prolong the operation cycle of biological filter bed (He et al. 2007, Mann et al. 1999). However, the removal rates of antibiotics by BAF can vary among different WWTPs and many factors, such as hydraulic loading, HRT and SRT, could affect the removal of target compounds. Further studies are still needed to examine if BAF could remove antibiotics from WWTP secondary effluent efficiently.

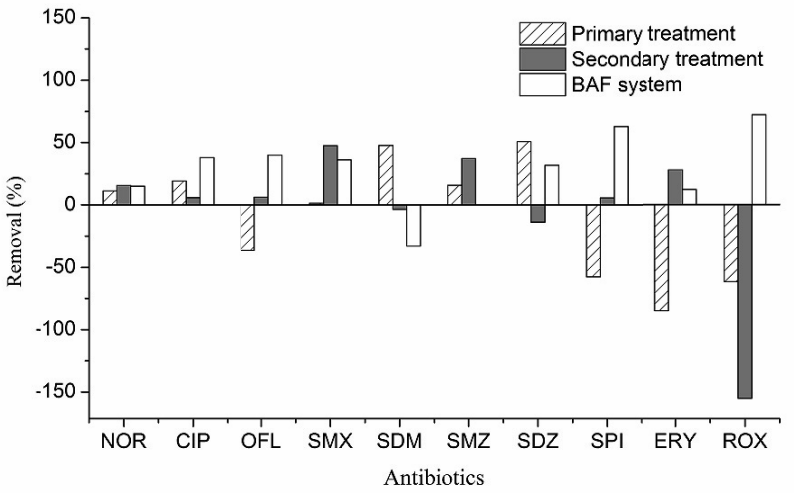

Fig. 2. The removal of detected antibiotics in various processes of WWTP

Antibiotics distribution in the Chaobai River

For the purpose of exploring the final fate of antibiotics after WWTP treatment, three samples from the effluent-receiving waters of the Chaobai River were monitored. The individual and total antibiotics concentrations detected in the river waters at different sampling sites are presented in Table 5.

Out of the 22 target antibiotics, just 7 were measured in river samples. Generally, nearly all the detected antibiotics concentrations were from 0.5 ng/L up to 40 ng/L or so, this result was in agreement with the previous study on other rivers in Beijing (Li et al. 2013). The highest concentration was detected for OFL at 41.8 ng/L in upstream and 94.6 ng/L in downstream. As regards OFL, other research reported the mean concentration of 9.9 ng/L in rivers (Zhang et al. 2012), which was much lower than in our study. The high level of OFL may be related to its relatively high medical consumption or its environmental behavior. In addition, the concentrations of antibiotics in downstream were clearly higher than those in upstream, indicating that WWTP discharge was a major point-source input of these antibiotics into the Chaobai River, although these concentrations were generally reduced by more than 50% compared to effluent concentrations.

Although the selected antibiotics were detected at low concentrations in the downstream of the river, the impact of their appearance in the river, particularly use as drinking water, on human and environmental health should not be ignored. Previous studies have reported that some antibiotics in the environmental levels could cause potential risks to the aquatic ecosystems and an adverse effect to some non-target organisms (Lindberg et al. 2005, Wilson et al. 2003). Li et al. observed that the risks of antibiotics could significantly decrease after the advanced treatment, comparing with conventional treatment methods (Li et al. 2013). However, more researches are urgently needed to evaluate the environmental risk of the occurrence of antibiotics in effluent-receiving rivers. Meanwhile, WWTPs with tertiary treatment, such as BAF system, are still needed to be investigated whether they are efficient in eliminating the release of other contaminants.

Conclusions

In this study 10 out of 22 selected target antibiotics were detected in WWTP influent and SDZ (396 ng/L) and SMZ (382 ng/L) were the dominating antibiotics in the influent. 4 antibiotics (SMX, SDZ, SMZ and SPI) showed significant removal efficiencies during the whole WWTP and they were removed mainly by the biological treatment process and BAF system. The removal efficiencies by the primary treatment were

Table 4. Total concentrations of the three antibiotic groups and removal proportion through each process during water resource recovery facility

	Influent	Primary treatment	Secondary treatment	BAF treatment	Overall
	ng/L	ng/L %	ng/L %	ng/L %	%
Quinolones	756	755.2 0.11%	682.6 9.6%	473 30.7%	37.4%
Sulfonamides	1083.2	817.6 24.5%	582 28.8%	454.5 21.9%	58.0%
Macrolides	48	84.4–76%	95.3–12.9%	49.9 47.6%	-4.0%
Overall	1887.2	1657.2 12.2%	1359.9 17.9%	977.4 28.1%	48.2%

Table 5. Detected antibiotics concentration (ng /L) in the Chaobai River at the three sampling positions[a]

Antibiotics	A	B	C	WWTP effluent
NOR	37.4	50.6	47.8	204
CIP	6.28	14	7.2	104.6
OFL	41.8	95.4	94.6	164.4
SMX	24	40.6	48.6	100.4
SDZ	0.55	51.8	4.94	151.2
SDM	0	0.42	0	0.86
SDZ	2.3	84.6	7.28	202
SPI	0	2	0.54	3.6
ROX	0	6.96	1.24	12.5
ERY	0.52	12.8	0.58	33.8
Quinolones	85.48	160	149.6	473
Sulfonamides	26.85	177.42	60.82	454.46
Macrolides	0.52	21.76	2.36	49.9
Overall	112.85	359.18	212.78	977.36

[a] Site A was 200 m upstream, site B at the facility discharge point and site C was 2 km downstream

poor and the BAF system was important for further removal of residual antibiotics from secondary effluent. It was also found that the concentrations of the selected antibiotics ranged from 0–41.8 ng/L in the effluent-receiving river. Despite that the concentrations were reduced by more than 50% compared to effluent concentrations, WWTP discharge was still regarded as a dominant point-source input of antibiotics into the Chaobai River. The environmental risk caused by the appearance of these antibiotics needs to be evaluated in further research.

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