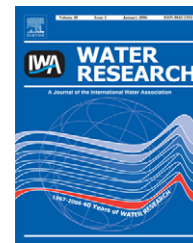


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Occurrence and elimination of antibiotics at four sewage treatment plants in the Pearl River Delta (PRD), South China

Weihai Xu^{a,b,d}, Gan Zhang^{a,*}, Xiangdong Li^b, Shichun Zou^c, Ping Li^a, Zhaohui Hu^a, Jun Li^a

^aState Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

^bDepartment of Civil and Structural Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

^cSchool of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou 510250, China

^dLED, South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510250, China

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ABSTRACT

In this paper, the occurrence and elimination of eight selected antibiotics mainly for human use, including chloramphenicol, fluoroquinolone, sulfonamide and macrolide groups, were investigated at four sewage treatment plants (STPs) in the Pearl River Delta (PRD), South China. The most frequently detected antibiotics in the present study were ofloxacin, norfloxacin, roxithromycin, erythromycin-H₂O (the main degradation product of erythromycin) and sulfamethoxazole. The concentrations of these compounds in raw influents and final effluents at the four STPs ranged from 10 to 1978 ngL⁻¹ and from 9 to 2054 ngL⁻¹, respectively. The other analytes were detected only in a few samples from the four STPs. Antibiotics could not be eliminated completely at the four STPs, with the highest elimination efficiency reaching to 81%. Analysis of the dissolved daily mass flow showed that fluoroquinolones were mostly eliminated from the sewage, and high concentrations of these compounds were found in secondary sludge. Therefore, it can be concluded that the observed elimination of fluoroquinolones in the STPs was due to their sorption to the sludge, but not biodegradation. Macrolides, especially erythromycin-H₂O, were stable in sewage during the treatment process, and in fact even higher concentrations were found in the final effluents than in the raw sewages. Sulfamethoxazole was also found in raw influent and final effluent, indicating that it could withstand different treatment processes in the STPs. Remarkable differences in the daily environmental loads (the sum of the amounts in the final effluent and sludge) of the five most frequently detected antibiotic compounds were found in the range of 0.5–828 g at the four STPs.

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1. Introduction

The occurrence and impacts of pharmaceuticals for human and veterinary use in the environment are emerging environmental issues. The concern with pharmaceutical residues in the environment is regarding their potential function toward the widespread resistance of bacterial pathogens, and post-

therapeutic effects. Several studies have proclaimed widespread antibiotic resistance in the Rio Grande (Sternes, 1999) and wild Canada geese (Eichorst et al., 1999). The presence of pharmaceuticals in the environment generally results from human and veterinary excretion of metabolized or unmetabolized drug passing into sewage systems, and subsequent discharge of sewage effluents. Many pharmaceuticals can be

*Corresponding author. Tel.: +86 20 8529 0178; fax: +86 20 8529 0706.

E-mail address: zhanggan@gig.ac.cn (G. Zhang).

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degraded in human and veterinary body after use, but others excreted or not fully absorbed can leave the body in their active forms. Among a wide variety of pharmaceuticals, antibiotics assume special significances due to their extensive use in human therapy, veterinary medicine, as well as in promoting the growth of the animals in livestock production.

Extensive investigation on the occurrence of antibiotics in the environment began in the 1990s. Since Watts et al. (1983) first reported the occurrence of several selected antibiotics in river water samples, the past decade witnessed more investigations related to antibiotics, resulting in many publications documenting their presence in ground and surface waters, landfill leachate and wastewater. Antibiotics have been detected in sewage water (Mcardell et al., 2003; Hernando et al., 2006), river water and sediment (Hirsch et al., 1998; Golet et al., 2002), hospital wastewater (Lindberg et al., 2004) and even ground water (Sacher et al., 2001). The concentrations of antibiotics in the environment were generally low (ngL^{-1} level). However, their impact cannot be neglected.

Sewage treatment plants (STPs) play an important role in the life cycle of antibiotics in modern society. The main transport pathways of antibiotics into the ambient environment are via STPs, where they may be only partially eliminated. However, studies focusing on sewage treatment systems for the occurrence and elimination of antibiotics are somewhat limited. More data are available from Europe. The concentrations of antibiotics in the influent/effluent from the STPs ranged from several hundred ngL^{-1} to several μgL^{-1} . While Hirsch et al. (1999) and Mcardell et al. (2003) reported on the presence of antibiotics in sewage effluents in Germany and Switzerland, respectively, in Sweden, several hundred ngL^{-1} was measured in the effluents (Lindberg et al., 2005). More than 14 antibiotics were detected, with the maximum concentration of tetracycline reaching to $0.977 \mu\text{gL}^{-1}$ in the effluents in Canada (Miao et al., 2004). In many previous studies, the eliminations of antibiotics in STPs have been proved to be incomplete. Vieno et al. (2007) reported the elimination of eight pharmaceuticals, including fluoroquinolones antibiotic (ciprofloxacin, norfloxacin (NOR), ofloxacin (OFL)), in 12 STPs in Finland. The results show that fluoroquinolones were eliminated by $>80\%$. Similar results (88–91%) were obtained in the studies performed in other STPs (Golet et al., 2002, 2003). In Spanish plants, an overall elimination rate of 60% for sulfamethoxazole (SMX) was observed by Carballa et al. (2004). It should be noted that the elimination process of antibiotics in STPs is rather complex. Antibiotics may have different elimination mechanisms and rates in various STPs with different treatment technologies. The fates of sulfonamides, macrolides and trimethoprim were investigated in different wastewater treatment technologies in Switzerland (Göbel et al., 2007). The compounds were eliminated up to 50% at the solid retention time (SRT) of 16 and 33 days. However, a higher elimination of up to 90% was obtained at an SRT of 60–80 days.

The antibiotics, fluoroquinolone, macrolide and sulfonamide groups, selected in our study were the most frequently used antibiotics in China, contributing to approximately 15%, 20% and 12% of the total amount of antibiotics used for human and livestock purposes, respectively. The Pearl River

Delta (PRD), located in South China with typical subtropical climate, is one of the fastest developing and most highly urbanized regions in China. A total of eight antibiotics have been detected in the aquatic environment in the PRD, with the maximum concentration close to μgL^{-1} level (Xu et al., 2007). It is supposed that the occurrence and fate of pharmaceuticals in the aquatic environment of the PRD deserve great concern (Richardson et al., 2005). However, there are very few data available from China at the moment. Besides, the behaviors of individual compounds during wastewater treatment processes are still largely unknown. In particular, there have been no researches on the occurrence and fate of antibiotics in domestic sewage in China.

Previously, the antibiotics selected in the present study were frequently detected in the Pearl River and Victoria Harbour receiving STP effluents. The purpose of the current research was, therefore, to determine the occurrence of selected antibiotics in the influent to and effluent from sewage treatment systems in the PRD, South China. A specific objective was to investigate the efficiency of various sewage treatment processes to remove antibiotics from the aquatic phase. The data obtained in this study were used to assess the impacts of antibiotics in the aquatic environment of the PRD from the effluent discharge of the selected STPs.

2. Materials and methods

2.1. Sample location and collection

Sewage water and secondary sludge samples were collected at four different STPs in South China, two in Guangzhou and two in Hong Kong. The sampling campaign in Guangzhou was carried out in October 2005. For Hong Kong plants, the samples were collected in May 2006. The STPs have primary treatment processes which consist of a screen, an aerated grit-removal tank and a primary clarifier. The primary effluents of Kaifau (STP A) and New Territory (STP C) STPs are directed to the activated sludge system for denitrification and nitrification. For Liede (STP B) STP, biological treatment was conducted before the sewage water entered the oxidation ditch. Different from other STPs, the major treatment processes of Kowloon STP (STP D) are chemically enhanced. After the primary clarifier, ferric chloride and polymer were added to the sewage water to remove suspended solids and microorganisms from the water. These STPs have different treatment capacities (average daily flow from 0.03 to $1.377 \text{ million m}^3/\text{day}^{-1}$). Detailed information on the four STPs is summarized in Table 1.

Sewage samples were collected as “grab samples” from the two STPs in Guangzhou (STP A and STP B). For the grab sampling program, the raw sewage influents and the final effluents from the STPs were sampled in sequence according to the hydraulic retention of the sewage water treatment. Replicate samples (early in the morning, six in 30 min apart for 3 h) were collected for laboratory analysis. Raw sewage influents and effluents of other two STPs in Hong Kong (STP C and STP D) were collected as 24-h composite samples (from 7 am to 7 am the next day, six combined samples were analyzed). During the sample collection, the sampling bottles

Table 1 – Descriptive data of the four investigated STPs

STPs/location	STPs ^a ID	Inhabitant served $\times 10^3$	Hydraulic retention (h)	Solid retention (h)	Daily flow ($m^3 \times 10^3$)	Daily discharge sludge ^b (t/d)	Disinfection method	Major treatment method	Discharge point/location
Kaifuq/Guangzhou	A	80	22	4.5–6	30	25	Chlorine	Activated sludge	Pearl River
Liede/Guangzhou	B	1050	12–18	na ^c	400	300	UV	Oxidation ditch	Pearl River
New Territory/Hong Kong	C	300	15–22	5.6–8.2	95	70	na	Activated sludge	Tolo Harbour
Kowloon/Hong Kong	D	3500	8–12	3–4	1377	900	Chlorine	Chemically enhanced	Victoria Harbour

^a Note that all STPs were given ID codes for purposes of reporting of the data.

^b Wet weight with 90% of water.

^c Data not available.

were rinsed with sample three times before a final sample was collected. All samples were kept in the dark at -18°C until analysis. All secondary sludge samples were collected every 3 h in a 12-h cycle for analysis. As for the secondary sludge, all samples were collected from the final settling tanks at the STPs.

2.2. Chemicals and standards

Eight antibiotic standards, OFL, NOR, roxithromycin (RTM), erythromycin (ETM), sulfadiazine (SD), sulfadimidine (SM2), SMX and chloramphenicol (CAP), were purchased from Sigma-Aldrich Co. $^{13}\text{C}_3$ -caffeine solution was obtained from Cambridge Isotope Labs (1 mg mL⁻¹ in methanol, USA). All the antibiotics were dissolved in methanol and stored in a freezer. ETM–H₂O, a major degradation of ETM, was obtained by acidification from ETM using the method described by Mcardell et al. (2003). Methanol and acetonitrile (HPLC grade) were obtained from Merck (Darmstadt, Germany). Ultra-pure water was prepared with a Milli-Q water purification system (Millipore, Bedford, MA, USA). Unless otherwise indicated, chemicals used in the analysis were purer than the analytical grade.

2.3. Sampling preparation for sewage water

Antibiotics in sewage water (1000 mL) were concentrated through a solid phase extraction (SPE) using the method of Xu et al. (2007).

2.4. Sampling preparation for sludge

2.4.1. Extraction

The sludge samples were air dried and sieved to $<0.4\text{ mm}$. Approximately 5 g sludge samples were accurately weighed (200 ng $^{13}\text{C}_3$ -caffeine being added as surrogate), and then placed into 50-mL polypropylene centrifuge tubes. About 10 mL of extraction buffer was added. The extraction buffer consisted of a 2:1:1 mixture of methanol, 0.1 M citric acid buffer with pH adjusted to 4.0 with NaOH and 10 mM Na₂EDTA buffer with pH adjusted to 4.0 with H₂SO₄. The tubes were vortex mixed for 1 min and then placed into an ultrasonic bath for 15 min (water temperature $<40^\circ\text{C}$), then the tubes were centrifuged (Eppendorf Centrifuge 5810 R) for 10 min at 3000g. The supernatant was decanted into a 500 mL glass bottle, and the sediment residue was extracted once more. The supernatant was combined, diluted to approximately 500 mL with ultra-pure water, and then the pH adjusted to approximately 3.0.

2.4.2. SPE clean-up

SAX-HLB SPE cartridges were set up in the tandem, which was pre-conditioned sequentially with 6.0 mL of methanol, 6.0 mL of ultrapure water and 6.0 mL of 10 mM Na₂EDTA buffer (pH 3.0). The samples were passed through the SPE columns at a flow rate of approximately 10 mL min⁻¹. The SAX cartridges were then removed and the HLB cartridges washed with ultra-pure water (10 mL, pH 3.0) before being dried with a flow of nitrogen gas for 1 h. After that, each cartridge was eluted with three 2-mL tubes of methanol. The analytes were

Table 2 – Recoveries and limits of quantification of the analytes in sewage water and sludge

Compound	Recovery \pm SD ^a (%)		LOQ ^b	
	Sewage water	Sludge	Sewage water (ngL ⁻¹)	Sludge (ngg ⁻¹)
Ofloxacin	65 \pm 13	45 \pm 4	10	50
Norfloxacin	68 \pm 15	51 \pm 5	10	50
Roxithromycin	70 \pm 8	63 \pm 10	5	20
Erythromycin-H ₂ O	78 \pm 10	64 \pm 13	5	20
Sulfadiazine	81 \pm 7	61 \pm 5	1	10
Sulfadimidine	65 \pm 9	64 \pm 11	1	10
Sulfamethoxazole	81 \pm 9	70 \pm 8	1	10
Chloramphenicol	69 \pm 6	65 \pm 12	5	50
¹³ C ₃ -caffeine	80 \pm 11	72 \pm 10	1	20

^a n = 6.
^b Limits of quantification.

collected in 10 mL brown glass vials, concentrated under a flow of N₂ gas to about 20 μ L and then dissolved in 40% aqueous methanol to a final volume of 1.0 mL.

2.5. Analysis of the antibiotics

The extracted antibiotics were analyzed using high-performance liquid chromatography–electrospray ionization tandem mass spectrometry with multiple reaction monitoring (MRM) described in our previous study (Xu et al., 2007). Quantitative analysis of each compound was performed using LC-ESI-MS/MS, with the MRM mode using the two highest characteristic precursor ion/product ion transitions. For the sewage water and sludge samples, limits of quantification (LOQs) were difficult to determine because the samples already contained some of the selected analytes and thus the matrix interference was serious. Therefore, LOQs in the sewage water and sludge samples were defined as signal-to-noise (S/N) ratios of 10. The recovery rates of sewage water and sludge are shown in Table 2. The mean recoveries for these spiked antibiotics in sewage water and sludge ranged from 65% to 81% and from 45% to 70%, respectively. LOQ for each compound in sewage and sludge are from 1 to 10 ngL⁻¹ and from 10 to 50 ngg⁻¹, respectively.

3. Results and discussion

3.1. Occurrence of the selected antibiotics at the four STPs

Table 3 presents the concentrations of the selected antibiotics in sewage water and sludge at the four STPs. A total of five antibiotics, among the eight antibiotics selected in the current study, were detected in all the influent and effluent samples from the four STPs, including two fluoroquinolones (OFL and NOR), two macrolides (RTM and ETM–H₂O) and one sulfonamide (SMX). The other three antibiotics were only detected in some STPs in the aquatic phase. All fluoroquinolone and macrolide antibiotics were detected in the final sludge samples at the four STPs. However, for other anti-

biotics, only lower concentrations of SM2 and SMX were detected in the STP B.

Fluoroquinolones were one of the most frequently detected antibiotics at the four STPs. OFL and NOR were detected in all the samples, including sewage and sludge samples from these STPs. The concentrations of OFL and NOR in the influents of the four STPs ranged from 80 to 368 ngL⁻¹ and from 54 to 263 ngL⁻¹, respectively. Brown et al. (2006) reported similar concentrations of OFL in two STPs in Albuquerque (470 ngL⁻¹) and Hagerman (400 ngL⁻¹), USA. The concentration of NOR was below the LOQs in all STPs. Lindberg et al. (2005) investigated the concentrations of OFL and NOR in five STPs in Sweden, and the results showed that OFL concentrations in two STPs were below LOQs in the raw sewage, and the concentration ranged from 7 to 213 ngL⁻¹ in the other three STPs. For NOR, the concentrations ranged from 72 to 155 ngL⁻¹ in the five STPs. The concentrations of fluoroquinolones in the sludge samples in the four STPs were higher than those of other compounds, while the concentrations of fluoroquinolones in the sewage water were not the highest among the detected antibiotics in some STPs.

Macrolides were another group of the most frequently detected antibiotics at the four STPs. It should be noted that ETM was determined in the form of its dehydration product, ETM–H₂O. Hirsch et al. (1998) and Mcardell et al. (2003) showed that ETM–H₂O was the predominant form of ETM in the aquatic environment. At the four investigated STPs, macrolides were detected in raw sewage, with ETM–H₂O being the most abundant compound. The maximum concentration of ETM–H₂O reached 1978 ngL⁻¹ in the influent from the STP B. The high concentrations of ETM–H₂O in the present study may be due to the high consumption of this compound in the study area. Maximum concentrations in raw influents were recorded as 199 ngL⁻¹ (Mcardell et al., 2003) and 190 ngL⁻¹ (Gobel et al., 2005) in Switzerland, 838 ngL⁻¹ in Canada (Miao et al., 2004) and 1200 ngL⁻¹ in the US (Karthikeyan and Meyer, 2006). SMX was the most commonly detected sulfonamide in the current study, and presented in 79% of the analyzed samples, with concentrations ranging from 16 to 118 ngL⁻¹. The corresponding occurrences for SD and SM2 were 14% and 43%, respectively. The maximum

Table 3 – Concentrations of antibiotics determined in the investigated STPs in 2005 and 2006

STPs ID	Sample type	Fluoroquinolones		Macrolides		Sulfonamides			Chloramphenicol
		OFL	NOR	RTM	ETM	SD	SM ₂	SMX	CAP
A-Raw influent ^a	Grab	137 ± 58 ^b	229 ± 42	102 ± 32	751 ± 109	nd ^c	25 ± 12	16 ± 5	nd
A-Prime effluent	Grab	65 ± 20	44 ± 22	45 ± 32	737 ± 138	nd	19 ± 8	14 ± 4	nd
A-Final effluent	Grab	41 ± 8	44 ± 19	36 ± 21	430 ± 73	nd	12 ± 6	16 ± 7	nd
A-Sludge ^d	Grab	227 ± 46	301 ± 89	40 ± 23	76 ± 25	nd	nd	nd	nd
B-Raw influent	Grab	359 ± 52	179 ± 41	164 ± 31	1978 ± 233	72 ± 22	696 ± 212	118 ± 17	31 ± 16
B-Final effluent	Grab	137 ± 28	62 ± 13	278 ± 46	2054 ± 386	36 ± 13	346 ± 54	78 ± 13	17 ± 10
B-Sludge	Grab	886 ± 222	40 ± 165	64 ± 16	195 ± 56	nd	31 ± 12	20 ± 10	nd
C-Raw influent	24-h	80 ± 12	54 ± 10	75 ± 14	253 ± 22	nd	nd	10 ± 3	nd
C-Prime effluent	Composite 24-h	77 ± 9	33 ± 8	40 ± 11	226 ± 18	nd	nd	10 ± 2	nd
C-Final effluent	Composite 24-h	48 ± 7	27 ± 6	35 ± 8	216 ± 34	nd	nd	12 ± 3	nd
C-Sludge	Grab	165 ± 71	187 ± 38	32 ± 9	38 ± 14	nd	nd	nd	nd
D-Raw influent	24-h	368 ± 23	263 ± 36	156 ± 29	469 ± 38	nd	nd	25 ± 7	nd
D-Final effluent	Composite 24-h	165 ± 15	85 ± 12	37 ± 11	259 ± 20	nd	nd	9 ± 4	nd
D-Sludge	Grab	835 ± 186	372 ± 97	44 ± 10	62 ± 24	nd	nd	nd	nd

^a ngL⁻¹.

^b Values are means ± standard deviation (n = 6 and 4 for sewage and sludge samples, respectively).

^c Not detected.

^d ng g⁻¹.

concentration of SMX in raw influents was reported to be 580 ngL⁻¹ in Spain (Carballa et al., 2004) and 520 ngL⁻¹ in the United States (Yang and Carlson, 2004).

CAP was only detected in the raw influents of STP B, with a low concentration at 31 ngL⁻¹. The lower detection frequency of CAP was probably due to the fact that it had been forbidden for use in food and aquaculture in China.

3.2. Elimination of antibiotics in the treatment processes

The elimination rates of the detected antibiotics between the raw sewage and final effluent from the four STPs are given in Fig. 1.

In general, the mean elimination rate of OFL was 57% at the four STPs with maximum of 70%. For NOR, the mean and maximum elimination rates were 66% and 81%, respectively. Castiglioni et al. (2006) reported similar elimination rates (~60%) for OFL. In Switzerland, the mean elimination rate of NOR in the largest STP was 88% (Golet et al., 2003). In Lindberg's investigation in Sweden (2005), the mean degrees of elimination of NOR and OFL were estimated to be 87% and 86%, respectively. It should be noted that sorption to the sludge and biodegradation function were carried out simultaneously during the treatment process in these plants. In our study, higher concentrations of OFL and NOR were found in the secondary sludge with the maximum up to 886 and

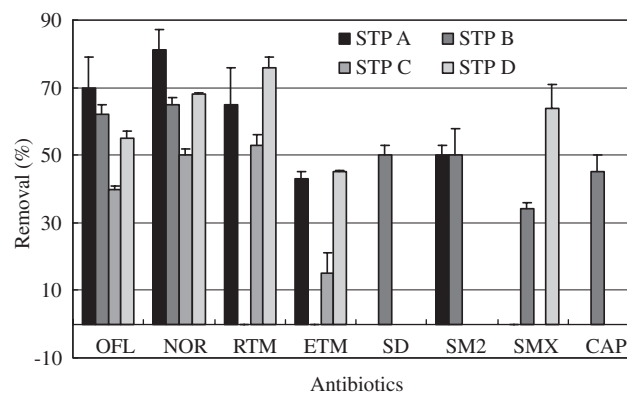


Fig. 1 – Removal efficiencies of selected antibiotics at the four STPs.

372 ng g⁻¹, respectively. Therefore, for fluoroquinolones, although being very hydrophilic compounds, sorption to the sludge is the main elimination process in the STPs. Similar results have been obtained in the Golet et al. (2002, 2003) and Lindberg et al. (2005) studies. This sorption of fluoroquinolones may be conducted via possible electrostatic interactions with the cell membranes of the micro-organisms.

Compared with fluoroquinolones, lower elimination rates were measured for the macrolide group, with 48% for RTM

and 26% for ETM–H₂O. Karthikeyan and Meyer (2006) reported 49–80% elimination rates for RTM and ETM–H₂O in several STPs in the USA. For RTM and ETM–H₂O compounds analyzed at the STP B, there was an observed increase between the raw influent and the final effluent. This kind of increase has also been noted in previous studies (Lindberg et al., 2005). In our experimental conditions, this increase might be because of not including the particulate matter with sizes greater than 0.45 μm in the analysis, which may result in the underestimation of the total content entering the STPs. Furthermore, this may be due to the deconjugation of conjugated metabolites during the treatment process, or signal suppression of the MS/MS detector in raw effluent samples due to high concentrations of organic matter (Miao et al., 2002; Heberer, 2002; Petrović et al., 2005).

Elimination rates from 0 to 64% for SMX were obtained in our study. Carballa et al. (2004) reported higher removal efficiency (60%) of SMX in an STP in Spain. Except for STP B (only 20 ng g⁻¹), SMX was not detected in the secondary sludge in the other three STPs. The elimination rate of SMX from the raw sewage was lower than for other compounds. Therefore, it seemed that SMX can undergo the treatment processes from the selected STPs. SD and SM2 were detected only in two STPs with elimination rates of 50%.

CAP was detected only in the sewage of STP B with lower concentration and the elimination rate for this compound was 45%.

3.3. Elimination of antibiotics at various STPs

The elimination of antibiotics at various STPs is a complex process with many possible mechanisms. The difference between elimination rates in various STPs probably results from many factors, such as the type of the treatment process, the hydraulic retention time (HRT), solids retention time (Clara et al., 2005), temperature (Vieno et al., 2005) and even the rainwater input (Tauxe-Wuersch et al., 2005). Therefore, elimination rates can vary significantly from one plant to another, and at different time periods in any one plant.

Obviously, the type of the treatment process is the dominant factor which can influence the elimination rate. In our study, STP A and STP C are the two secondary treatment plants with activated sludge treatment process, while STP B and STP D have oxidation ditch and chemical enhanced treatment, respectively. The present study results showed that the elimination rates of fluoroquinolones in STP A were higher than those in the other three plants. The possible reason is that the fluoroquinolones have higher tendency to be adsorbed by sludge. However, the elimination rates of fluoroquinolones in STP C were lower than others, despite the fact that activated sludge was also added in the treatment process. Besides, the elimination rates of other compounds in STP C, such as RTM, were still lower than in other STPs. The possible explanation is that STP C has no special disinfection method, such as UV or chlorine. In addition, the differences in sampling can also result in this change. Commonly, the plants with secondary treatment could get higher removal efficiency for compounds than primary treatment plants. However, it should be noted that STP D had relatively higher removal efficiencies for some compounds despite using primary treatment in this plant.

Most drugs are designed in a stable condition so that they can retain their chemical structure long enough to do their therapeutic function (Ternes et al., 2004). The STP D has chemical enhanced treatment, which may destroy the chemical chain of many pharmaceuticals and produce high removal efficiency in the process. However, the use of grab or even 24 h composite samples in the present study had limitations in revealing the changes during the treatment processes. Using these methods, the samples collected only represent a few hours or 1 day, and may not mimic the continuous exposure of these antibiotics during the treatment processes.

HRT and SRT are the other two key factors which can affect the elimination efficiencies of compounds in the STPs. Previous studies showed that some compounds were better eliminated in STPs with high HRT or SRT (Clara et al., 2005; Kreuzinger et al., 2004; Tauxe-Wuersch et al., 2005). Kim et al. (2005) examined the influence of HRT and SRT on the removal of tetracycline in the activated sludge processes. The results showed that the removal efficiency is more sensitive to SRT than to HRT. In our study, since the changes of elimination rates in different HRTs or SRTs were not investigated, the influence of HRT and SRT on the elimination rate could not be assessed from the selected STPs.

The samples in our study including the sewage and secondary sludge were not collected in different seasons; therefore, the effect of temperature on the elimination rate of the antibiotics cannot be fully assessed.

3.4. Dissolved daily mass fluxes of the antibiotics at the STPs

The dissolved daily mass fluxes for the most frequently detected antibiotics, fluoroquinolones, macrolides and sulfonamides, are shown in Fig. 2. The dissolved daily mass fluxes can vary significantly among different STPs. The dissolved daily mass fluxes of antibiotics in STP B and STP D were much higher than those in the other two plants. The dominant factors may include the nature of the two STPs, which were larger with higher treatment capacity. Compared with other antibiotics, the dissolved mass fluxes of fluoroquinolones clearly showed that they had a high tendency to be adsorbed to sludge. SMX was the only compound that showed relatively equal mass flow between the raw influent and the final effluent, suggesting that this antibiotic has not been adsorbed to sludge. On the other hand, the partial removal of SMX in the STPs could be attributed to biodegradation. By calculation, the daily environmental loads (sum of the amounts in the final effluent and sludge) of the five most frequently detected antibiotic compounds at the four STPs were found to be in the range of 0.5–828 g. The data showed that the total amounts of antibiotics entering the surface water environment via the municipal STPs was at considerable levels.

3.5. Concentrations and impacts of antibiotics in the receiving water

Large amounts of antibiotics are transported to the aquatic environment via STPs. Although the elimination of antibiotics in STPs may be optimized through increased sludge retention time and/or an additional tertiary treatment step, the overall elimination of antibiotics in STPs is still incomplete.

Therefore, residual amounts of these compounds are continuously discharged to receiving surface waters. In addition, little knowledge of the environmental risk assessment for these compounds is available at the moment.

In the present study, STP B and STP D are two major STPs in Guangzhou and Hong Kong. The Pearl River and Victoria Harbour are the two major receiving water bodies for STP effluents. By calculation, the total amount of the studied

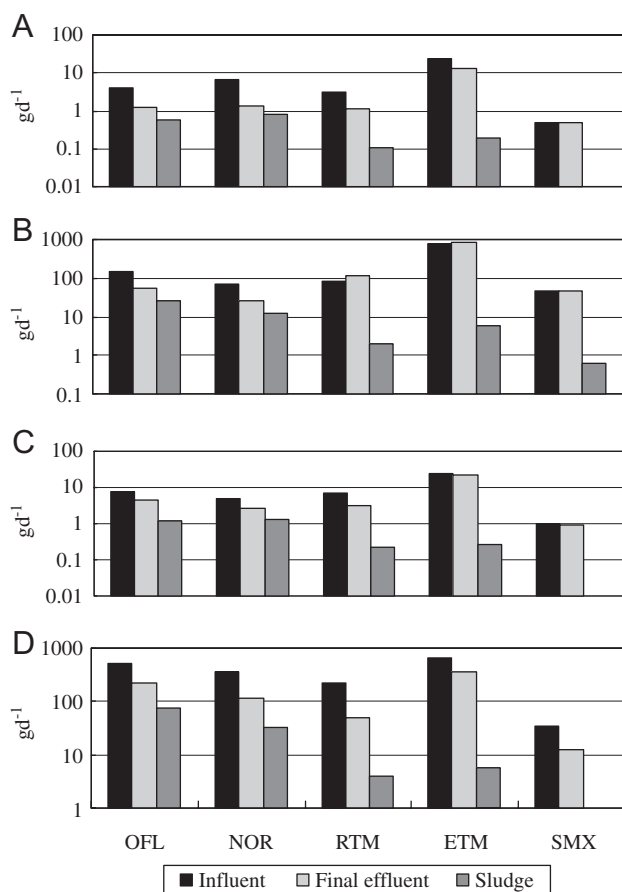


Fig. 2 – Daily dissolved mass fluxes of five antibiotics at the four STPs.

antibiotics being discharged into the receiving waters from STP B and STP D was up to 1824 g. A dilution factor of 1:10 recommended by the US Federal Drug Administration can be used to estimate the maximum expected concentrations in receiving water from the two STPs' effluent data (USFDA, 1998). The maximum expected concentrations of the most frequently detected antibiotics in this study for the Pearl River and Victoria Harbour are shown in Table 4. In addition, the measured concentrations (mean) in the two receiving waters from Xu et al. (2007) are also shown in Table 4. The calculated concentrations of the selected antibiotics in Victoria Harbour were very close to the measured concentration, except for ETM-H₂O. It is also worthy to note that the sampling sites are close to a large fish farming area with a lot of seafood restaurants along the coast. Therefore, the extra ETM+H₂O may be from fish farming at the east side of the harbor. However, for the Pearl River, the measured concentrations were about 2–25 times higher than the calculated concentrations. Therefore, there may be untreated wastewater with higher concentrations of antibiotics, such as the hospital and aquaculture zone effluents, flowing into the Pearl River. In Guangzhou, the treatment ratio for domestic sewage was only 61.7% in 2005, but in Hong Kong the figure was about 100%. The selected antibiotics in the two receiving water bodies were detected at the ngL⁻¹ range. Generally, it is unlikely for the antibiotics in the environment to have acute effects on aquatic organisms. It is reported that the lethal concentrations of antibiotics to fish and invertebrates are in the high milligrams per liter range (Boxall et al., 2004). Therefore, the antibiotics in the Pearl River and Victoria Harbour near the sewage discharge points were unlikely to induce lethal toxicity to aquatic organisms or to have a significant impact on the growth of plants and bacteria. However, there are not enough data to assess the long-term influences caused by continuous discharge of hundreds of antibiotics into the aquatic environment. Moreover, antibiotics can be accumulated in the organisms and can reach higher concentrations (Bebak-Williams et al., 2002). Another important issue that should be paid more attention is that antibiotics residues in the environment with ngL⁻¹ level can contribute to the widespread resistance of bacterial pathogens and post-therapeutic effects.

Table 4 – Calculated and detected concentrations of antibiotics in the Pearl River and Victoria Harbour/ngL⁻¹

Compound	Concentrations in the Pearl River ^a		Concentrations in the Victoria Harbour ^a	
	Calculated	Detected ^b	Calculated	Detected ^c
Ofloxacin	14	74 ± 15 ^d	17	8 ± 5
Norfloraxin	6	166 ± 42	9	11 ± 7
Roxithromycin	30	70 ± 41	4	10 ± 3
Erythromycin-H ₂ O	205	489 ± 70	26	3 ± 2
Sulfamethoxazole	8	143 ± 21	1	n.d ^e

^a Data from Xu et al. (2007).

^b n = 12.

^c n = 5.

^d Values are means ± standard deviation.

^e Not detected.

4. Conclusions

A total of five antibiotics, including two fluoroquinolones, two macrolides and one sulfonamide, were detected in the raw influents and effluents at the four selected STPs in Guangzhou and Hong Kong, with the concentrations ranging from 9 to 2054 ngL⁻¹ in the effluents. The elimination of antibiotics in the four STPs was generally incomplete. It was found that, in the studied compounds, fluoroquinolones were easy to be removed from the aquatic phase. However, for macrolides, the elimination rate was lower, there was even no elimination in a certain treatment plant. Fluoroquinolones were easily adsorbed to sludge during the treatment process. The total amount of antibiotics being discharged into the receiving waters from STP B and STP D was up to 1824 g each day. The antibiotics in the Pearl River and Victoria Harbour were detected at the ngL⁻¹ level, not reaching the acute level (milligrams per liter). Therefore, it is unlikely to induce lethal toxicity to aquatic organisms or to have a significant impact on the growth of plants and bacteria. However, the antibiotics residues in the environment with ngL⁻¹ level may contribute to the widespread resistance of bacterial pathogens and post-therapeutic effects.

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