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RESEARCH ARTICLE

Occurrence, removal, and environmental risks of pharmaceuticals in wastewater treatment plants in south China

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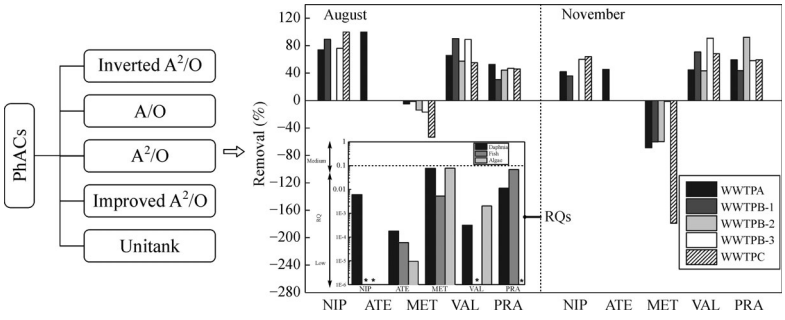
HIGHLIGHTS

- Five pharmaceuticals were detected in wastewater treatment plants in southern China.
- Biological treatment was the most effective process for PhACs removal.
- Metoprolol showed negative removal during secondary treatment process.
- The pharmaceuticals studied posed a low environmental risk to aquatic ecosystems.

GRAPHIC ABSTRACT



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ABSTRACT

Pharmaceutically active compounds in wastewater released from human consumption have received considerable attention because of their possible risks for aquatic environments. In this study, the occurrence and removal of 10 pharmaceuticals in three municipal wastewater treatment plants in southern China were investigated and the environmental risks they posed were assessed. Nifedipine, atenolol, metoprolol, valsartan and pravastatin were detected in the influent wastewater. The highest average concentration in the influents was observed for metoprolol (164.6 ng/L), followed by valsartan (120.3 ng/L) in August, while median concentrations were higher in November than in August. The total average daily mass loadings of the pharmaceuticals in the three plants were 289.52 μg/d/person, 430.46 μg/d/person and 368.67 μg/d/person, respectively. Elimination in the treatment plants studied was incomplete, with metoprolol levels increasing during biological treatment. Biological treatment was the most effective step for PhACs removal in all of the plants studied. Moreover, the removal of PhACs was observed with higher efficiencies in August than in November. The WWTP equipped with an Unitank process exhibited similar removals of most PhACs as other WWTPs equipped with an anoxic/oxic (A/O) process or various anaerobic-anoxic-oxic (A^2/O) process. The environmental risk assessment concluded that all of the single PhAC in the effluents displayed a low risk ($RQ < 0.1$) to the aquatic environments.

1 Introduction

Pharmaceutically active compounds (PhACs) including antihypertensive drugs and lipid regulators have been recognized as emerging "pseudo-persistent" contaminants due to their continuous input to ecosystems and their potential negative effects on human health (Hernando et al., 2006). Antihypertensive drugs and lipid regulators

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have been detected at concentrations ranging from ng/L to μg/L in wastewater, surface water, ground water and even drinking water (Khan and Ongerth, 2002; Huerta-Fontela et al., 2011; Verlicchi et al., 2012; Peng et al., 2014). This has generated particular concern on antihypertensive drugs and lipid regulators in recent years. Humans cannot completely metabolize anti-hypertension drugs and lipid regulators, so they are excreted through urine and feces as parent compounds, metabolites or conjugates and finally delivered to wastewater treatment plants (WWTPs) (Yan et al., 2014a). The wastewater treatment facilities are not specifically designed for the removal of PhACs, but with the aim to eliminate biodegradable carbon, nitrogen, phosphorus and pathogens (Yan et al., 2014a). Therefore, antihypertensive drugs and lipid regulators are most likely eliminated only partially in the WWTPs (Behera et al., 2011; Yuan et al., 2015). Thus, the effluent of WWTPs is regarded as the primary source of PhACs pollution of aquatic environments.

Previous studies have investigated the occurrence and fate of some antihypertensive drugs and lipid regulators in WWTPs in some developed countries such as Greece, Australia and Spain, as well as in Chongqing and Xiamen cities, in China (Verlicchi et al., 2010; Kosma et al., 2014; Sun et al., 2014; Yan et al., 2014a; Roberts et al., 2016). Their occurrence varies depending on different consumption patterns, demographics and climatic conditions (Vieno et al., 2007; Verlicchi et al., 2012). Meanwhile, the removal efficiencies of PhACs in WWTPs differ depending on the compounds' properties and the treatment processes applied (Yuan et al., 2015). The Pearl River Delta (PRD) is a rapidly developing and densely urbanized region in southern China, where the average prevalence rate of hypertension has been reported to be in excess of 20.5% (Wang et al., 2014). This may result in significant occurrence and the wide distribution of antihypertensive drugs in sewer systems in the PRD area. However, data on the occurrence, fate and environmental risk of antihypertensive drugs and lipid regulators in wastewater in the PRD area remain insufficient (Huang et al., 2011). Several different biological treatment systems are employed in WWTPs in the PRD area, while the fate of the PhACs in Unitank systems are rarely reported. Other external factors such as seasonal variations in usage patterns, demographic changes in the region and weather conditions such as heavy rain or drought might result in temporary variations in levels of PhACs (Sun et al., 2014).

In this study, the occurrence and removal of five antihypertensive drugs and five lipid regulators were surveyed in August and November in three municipal full-scale WWTPs equipped with five different treatment processes located in the PRD area, southern China. The average daily mass loadings were documented to evaluate the drugs' consumption patterns. Risk quotients (RQs) for the residual PhACs in effluents were estimated to assess the risk to aquatic ecosystems. The results were then compared to those from related studies conducted in some developed countries such as the USA and Spain, as well as in other regions in China such as Wuxi, Chongqing and Xiamen city. The study was designed to enhance knowledge of the presence and fate of PhACs in WWTPs.

2 Materials and methods

2.1 Chemicals and reagents

Five antihypertensive drugs — amlodipine (AML), nifedipine (NIP), atenolol (ATE), metoprolol (MET), valsartan (VAL) and five lipid regulators — atorvastatin (ATO), simvastatin (SIM), bezafibrate (BZB), gemfibrozil (GEF), pravastatin (PRA) were investigated in this study. They were selected based on the high consumption levels in China and their environmental relevance. Further information of these PhACs in detailed is in Table S1 (See it in Supplementary material).

All pharmaceuticals standard were of a high purity grade (>97%). The AML was obtained from China's National Research Center for Certified Reference Material. The BEZ and MET were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The ATE, NIP, GEF and VAL were purchased from CNW Technologies GmbH (Duesseldorf, Germany). The PRA and SIM were purchased from Tokyo Chemical Industry Ltd. (Tokyo, Japan). The ATE was obtained from Adamas Pharmaceuticals (Schaffhausen, Switzerland). Oasis hydrophilic–lipophilic balanced cartridges (HLB, 6cc, 500mg) were purchased from Waters Corporation (Milford, USA). Methanol and formic acid (HPLC grade) were obtained from Merck (Darmstadt, Germany). Stock solutions of all of the PhACs with the exception of AML were prepared individually at a concentration of 1000 mg/L in methanol. The AML stock solution was prepared at a concentration of 100 mg/L due to its low solubility. Standard mixtures were prepared by appropriate dilution of the individual stock solutions. Fresh stock solutions were prepared every three months and stored at −20°C in the dark.

2.2 Sampling approaches

Three WWTPs labeled as WWTPA, WWTPB and WWTPC, located in Guangzhou and Foshan were studied. WWTPA employs an inverted anaerobic-anoxic-oxic (A^2/O) process; WWTPB has three treatment lines labeled as WWTPB-1, WWTPB-2 and WWTPB-3, which employ an anaerobic-oxic (A/O) process, an A^2/O process and an improved A^2/O process, respectively; WWTPC utilizes the Unitank process. The schematic diagrams and properties of the studied WWTPs are presented in detail in Fig. 1 and Table S2. Wastewater samples were collected from the influent streams, the effluent from the treatment units and the final effluent based on the hydraulic retention times in

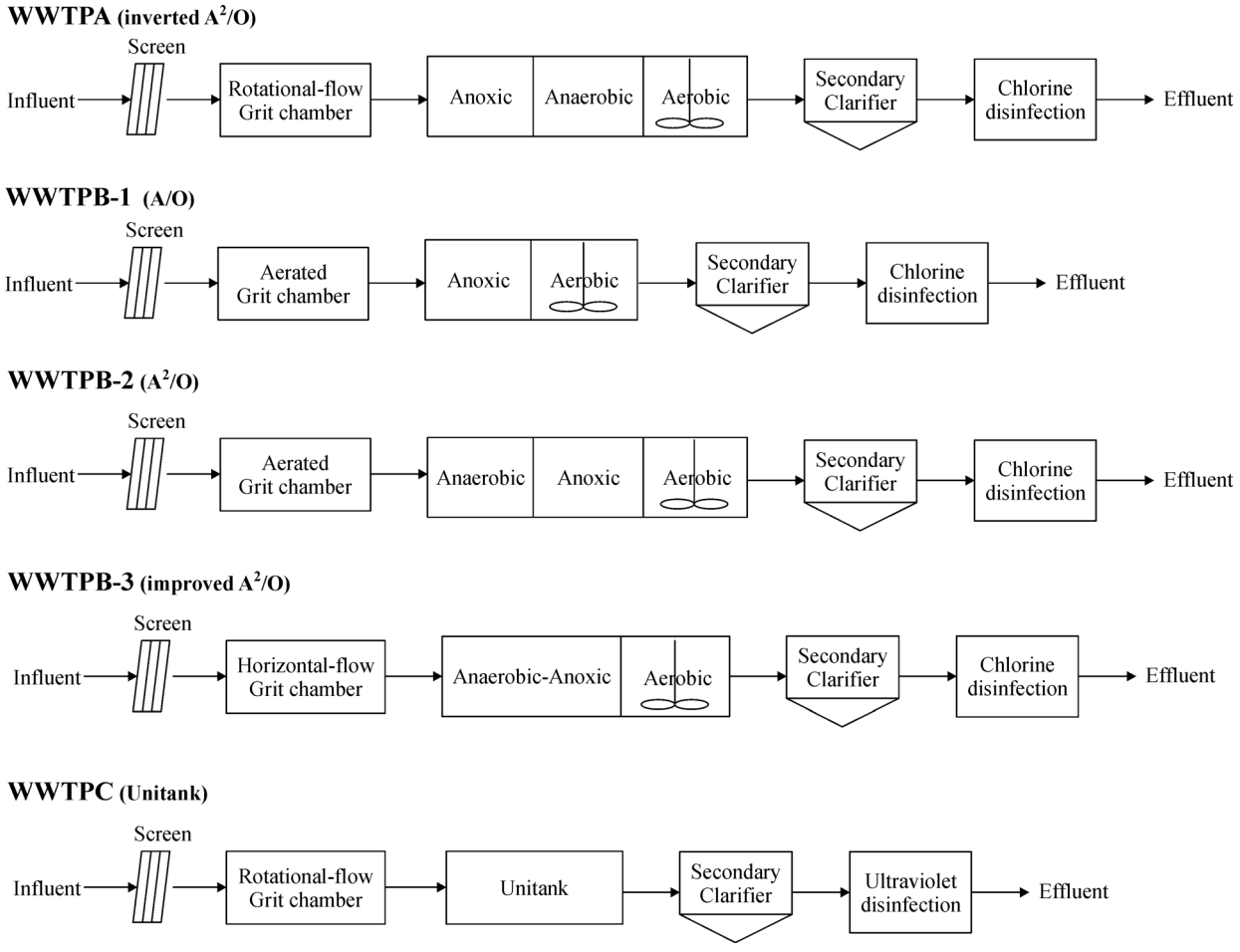

Fig. 1 Schematic diagrams of the WWTPs studied

each WWTP. They were collected in August and November 2015 (the average temperatures were 27°C–35°C and 18°C–24°C, respectively). All of the samples were immediately transferred to the laboratory in polyethylene containers. Sodium azide (NaN_3) was added at 0.5 g/L to suppress any further biological activity. The samples were vacuum filtered using a 0.45 μm mixed cellulose filter to eliminate suspended solids and bacteria, and then stored at 4°C until being extracted.

2.3 Analytical methods

The PhACs analysis was developed base on the EPA Method 1694 (USEPA, 2007) with some modifications (USEPA 2007; Yan et al., 2014a). Samples were extracted in a solid phase extraction (SPE) system equipped with an Oasis HLB cartridge (6cc; 500 mg; Waters Corp). Prior to extraction,the pH was adjusted to 4 by adding hydrochloric acid since most of the 10 PhACs being investigated had exhibited relatively high recoveries at pH 4 in preliminary experiments (Fig. S1). Then 0.4 g/L cleating reagent (Na_2EDTA) was added to the samples. The Oasis HLB cartridge was pre-conditioned with 6mL of methanol and 6mL of ultrapure water passed through by gravity, and then loaded with 500mL of the sample at a flow rate of 1mL/min. Any analytes retained in the cartridge were eluted with 8 mL methanol for 4 times. The cartridge was rinsed with 10 mL of ultrapure water and vacuum-dried for 20 min. The extracts were concentrated with a nitrogen stream and dissolved in 50% aqueous methanol to a final volume of 1mL. The resulting solution was stored at −20°C until analysis.

PhACs analysis was performed using high-performance liquid chromatography in tandem with mass spectrometry (HPLC-MS/MS) equipped with an electrospray ion source (ESI) (Agilent, Wilmington, USA). Chromatographic separation was performed using an Agilent ZORBAX Eclipse Plus C18 column (3.0 mm × 150 mm, 3.5 μm; Agilent, Wilmington, USA). The column temperature was maintained at 30°C. The injected volume was 20 μL. The mobile phase consisted of methanol (phase A) and 0.1% formic acid in water (phase B). The gradient elution program (time in minutes, percentage of mobile phase A) was set as follows: (0, 10), (2, 10), (10, 90), and (25, 90). Based on their physicochemical properties, VAL and BEF were analyzed at negative ionization mode while the other

residual PhACs were analyzed in positive ionization mode. The mass spectrometer was operated in multiple-reaction monitoring (MRM) mode detecting two selected ions. The fragment ions and retention times are summarized in Table S3. The drying gas flowed at 10 L/min at 350°C. The capillary voltage was 4500 V and the nebulizing gas pressure was 40 psi. Triplicate analyses yielded a standard deviation of 6% for these determinations. The correlation coefficients (r^2), limits of detection (LODs) and recoveries are presented in Table S4. The recoveries for all PhACs except AML ranged from 20% to 128%, which were similar to the recoveries reported in previous studies (Kosma et al., 2014; Sun et al., 2014; Yan et al., 2014a; Subedi and Kannan, 2015; Yuan et al., 2015; Papageorgiou et al., 2016). AML could not be assessed due to its low recovery. The reported concentrations in the samples were corrected for recovery using the recovery estimates from recovery trials.

2.4 Risk assessment

The potential ecological risk of antihypertensive drugs and lipid regulators in effluent was assessed based on the RQ as suggested in the European Commission's Technical Guidance Document (Yuan et al., 2015). The RQ value for an aquatic ecosystem relates the maximum measured environmental concentration (MEC) with the predicted no-effect concentration (PNEC) using Equations (1) and (2).

$$RQ = MEC/PNEC, \tag{1}$$

$$PNEC = (EC_{50} \text{ or } LC_{50})/AF. \tag{2}$$

Here, MEC was the maximum concentration of each PhACs observed in the final effluent samples, EC_{50} or LC_{50} is the lowest median concentration to aquatic organisms at different trophic levels of ecosystem: Daphnia, algae, and fish, which was collected from the literatures (Table S5). AF is the safety factor set at 1000 following the guidelines of Water Framework Directive (Directive 2000/60/EC) (Yuan et al., 2015). A commonly-used risk ranking takes an $RQ \geqslant 1$ as indicating that the corresponding chemical constitutes a high risk to the environment, $0.1 \leqslant RQ < 1$ represents a medium risk, and $RQ < 0.1$ means a low risk (Yuan et al., 2015).

3 Results and discussion

3.1 Occurrence of PhACs in the influents

Figure 2 presents the concentrations of ten pharmaceuticals observed in the influent streams of the three WWTPs in August and November. Only four of the antihypertensive drugs and one of lipid regulator were detected in the influent. MET and VAL were found to be the predominant compounds with maximum concentrations of 386.8 and 222.0 ng/L in August and 497.0 and 587.2 ng/L in November, respectively. VAL has rarely been detected in wastewater in prior studies, though concentrations ranging from 132.0 to 5388.0 ng/L have been reported in the influents of two WWTPs in South Wales, UK (Kasprzyk-Hordern et al., 2009). Verlicchi et al. have reviewed concentrations of MET in various influents ranging from around 10 ng/L to more than 1000 ng/L (Verlicchi et al., 2012). The MET concentrations observed in this study ranged from 49.5 to 382.6 ng/L in the influents of the three WWTPs. That is comparable with the levels reported from Wuxi in eastern China (Yuan et al., 2015), but higher than those in Chongqing in the south-west (Yan et al., 2014b). NIP was detected at concentrations ranging from 7.0 to 87.0 ng/L, which was not detected in a WWTP in Voles, Greece (Papageorgiou et al., 2016). The ATE concentra-

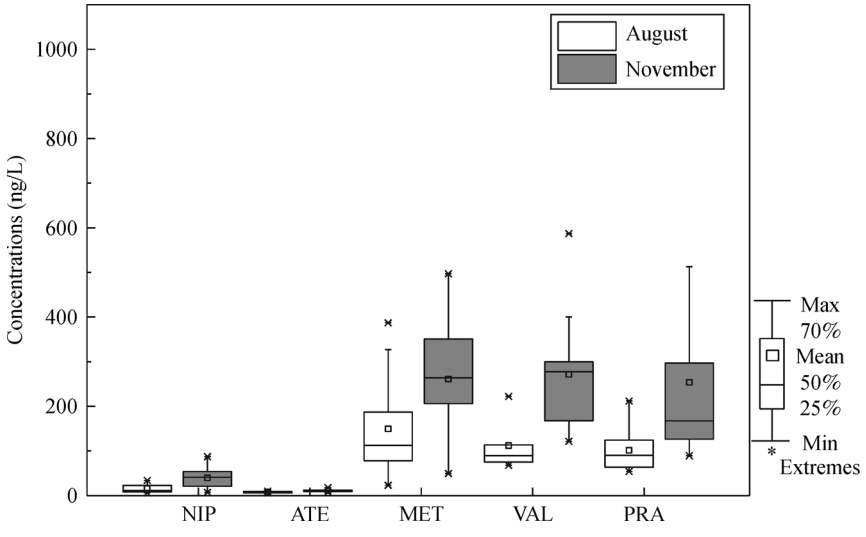

Fig. 2 Concentration ranges of PhACs in the influents of three WWTPs in the PRD area

tions were the lowest among the four antihypertensive drugs detected in this work, mean levels were 10.0 ng/L in August and 12.3 ng/L in November. Those concentrations are comparable to those measured in Wuxi (Yuan et al., 2015), but an order of magnitude lower than those measured in Madrid, Spain and New York, USA (Rosal et al., 2010; Subedi and Kannan, 2015).

Among the 5 lipid regulators, PRA was detected at an average concentration of 99.3 ng/L in August and 235.8 ng/L in November. Traces of the other liquid regulators were observed at concentrations below their LODs. Papageorgiou and Kosma also found concentrations of BZB, GEF and ATO in Voles, Greece were below the LOD or of only a few ng/L (Papageorgiou et al., 2016). Similar results have also been reported for GEF and ATO in the influents of four WWTPs in Chongqing, China, though BZB levels were higher (Yan et al., 2014a). However, prior studies have reported that PRA are observed with a mean concentration of 490.0 ng/L and BZB and GEF are detected at concentrations ranging from 10ng/L up to 30 μg/L (Verlicchi et al., 2012). For SIM, lower concentrations around the LOD have been observed in the influents of two WWTPs in South Wales, UK (Kasprzyk-Hordern et al., 2009), while higher concentrations up to hundred ng/L levels have been reported from in Voles, Greece and Chongqing, China, respectively (Yan et al., 2014a; Papageorgiou et al., 2016). In general, the concentrations of PhACs measured in this study were lower than those reported from developed countries such as the UK and the USA, with the exception of NIP. However, the concentrations of antihypertensive drugs were generally higher than those reported from other cities of China. The use of PhACs apparently varies between countries and regions, which is probably due to the different consumption of medicine as well as various economic and demographic level. Indeed, traditional medical care is widely used in China instead of Western medicine.

The influent concentrations of all of the PhACs were higher in November than in August. This agrees with reports that the morbidity of blood pressure and blood lipid in humans are higher in winter than in summer (Brennan et al., 1982; Sui et al., 2011). Thus, the consumption of antihypertensive drugs and lipid regulators in winter was found to be slightly higher in Beijing, China (Sui et al., 2011). In addition, the PRD has a subtropical monsoon climate with high temperature year-round and heavy rain in summer. The increased rainfall in August might lead to dilution and lower concentrations of the PhACs. Previous studies have also reported that the detection frequencies and concentrations of PhACs were lower in wet-season due to rainfall dilution (Lv et al., 2014; Lolić et al., 2015). Therefore, the discrepant variation of PhACs in the PRD could be accounted to the extensive therapeutic usage in November and abundant rainfall dilution in subtropical cities in August.

Three WWTPs serving different drainage regions showed diverse distributions of PhACs in their influents even though they are located in the same delta region. The concentration ranges handled by each WWTP in August and November are reported in Fig. S2. In general, both the mean concentrations and the detection frequency were in the order of WWTPA>WWTPB>WWTPC. ATE was detected at concentrations around 10ng/L with a detection frequency of 83% both in August and November and only in the influent of WWTPA. It could not be detected in the influents of WWTPB and WWTPC which are located in Foshan, near Guangzhou. The concentrations of all PhACs in WWTPB's influent were similar except for NIP. The concentration ranges were relatively large, which probably could be attributed to three treatment lines with different drainage regions for WWTPB. However, the highest concentration and detection frequency in WWTPC was MET, further indicating that occurrence patterns of PhACs vary from region to region.

3.2 Mass loads of PhACs in the influents

The mass loadings of antihypertensive drugs and lipid regulators were calculated based on the mean concentrations of PhACs in influent of each WWTP in two sampling months. The average daily mass load per person (L_i, μg/d/person) of the target pharmaceuticals in influents was calculated as following equation:

$$L_i = (C \times Q)/SP \quad (3)$$

where C (ng/L) is the average concentrations of a PhAC in the influent; Q (m^3/d) is the daily wastewater flow rate and SP is population served by the corresponding WWTPs (Table S2).

The average daily mass loadings of all PhACs in influents of three plants in August and November are shown in Fig. 3. The average values of all PhACs together were estimated to be 289.52 μg/d/person at plant A, 430.46 μg/d/person at plant B and 368.67 μg/d/person at plant C. The highest average mass loadings in three WWTPs were observed for MET, suggesting high consumption of MET in two cities. Similar to the concentrations, the daily mass loadings were higher in November than in August.

The average mass loadings of MET were between 122.79 and 143.18 μg/d/person in all WWTPs. This is higher than has been reported from other Chinese cities such as Chongqing (25.22 μg/d/person) and Wuxi (66.15 μg/d/person) (Yan et al., 2014b; Yuan et al., 2015). It is also higher than the loadings observed in Greece (53.3 μg/d/person) and Spain (3.6 μg/d/person) (Rosal et al., 2010; Papageorgiou et al., 2016), but lower than in Finland (405±123 μg/d/person) (Vieno et al., 2007). ATE was detected only in WWTPA's influent with an average daily mass loading of 3.49 μg/d/person. That is close to the loading observed in Wuxi, China (7.24 μg/d/person) but significantly lower than that estimated in several cities of

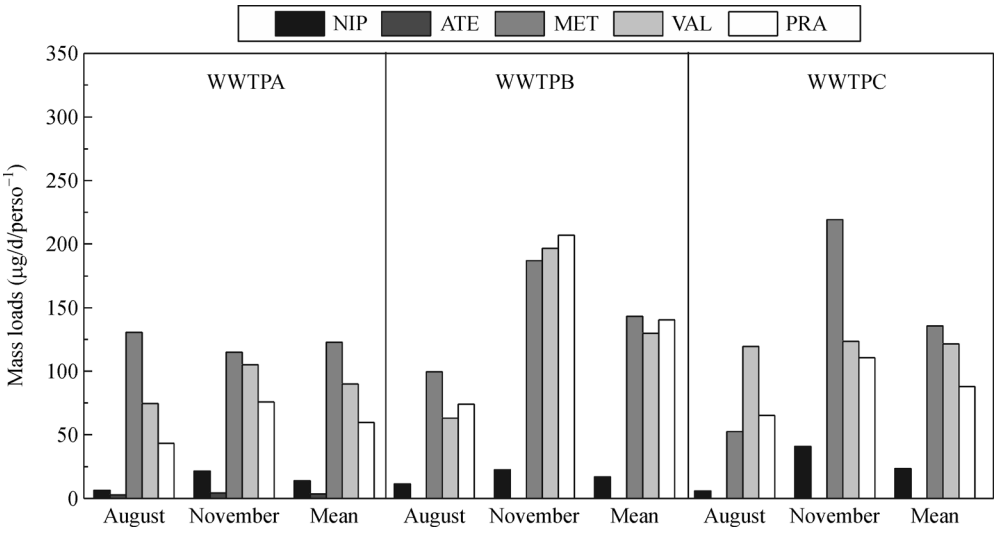

Fig. 3 Average daily mass loadings of target PhACs in three WWTPs

developed countries such as the USA (347μg/d/person), Greece (407 μg/d/person) and Finland (290.0±78μg/d/person) (Vieno et al., 2007; Subedi and Kamnan, 2015; Papageorgiou et al., 2016). In general, the daily mass loadings evaluated in this study were the same as or higher than those reported in Chongqing and Wuxi, but lower than those in some developed countries such as Finland.

3.3 Removal of PhACs in WWTPs

To evaluate the PhACs removal efficiencies of the three WWTPs, six to 12 samples were collected at 2h intervals a day based on the hydraulic retention time of the various treatment units. Samples were collected from each WWTP in both August and November 2015. The average concentrations of the PhACs in each WWTP's effluent of different units are summarized in Table 1. The overall removal and the removal efficiency for each PhAC during the primary, secondary treatment and the disinfection in each WWTP treatment process are compiled in Fig. 4 and Table 2.

Figure 4 shows that the removal efficiencies presented clear variation, ranging from "negative removal" to almost complete removal. NIP showed high removal in five treatment processes in August (73.9%–89.3%); its removal efficiencies varied more widely in November (36.0%–64.0%). VAL and PRA showed removal efficiencies of 55.1% to 90.4% and 30.6%–52.7% respectively in August. The corresponding values in November were 43.3% to 91.1% and 43.8% to 92.3%. Comparable removal efficiencies were reported for VAL in two British WWTPs (40 to 80%) (Kasprzyk-Hordern et al., 2009) and for PRA in two Spanish WWTPs (60 to 90%) (Radjenović et al., 2009). The removal efficiency of ATE was only observed in WWTPA, where it was 100% in August and 45.3% in November. The removal efficiency of ATE in two WWTPs in Wuxi, China has been estimated as 89.9–94.3% (Yuan et al., 2015). MET showed negative removal ranging from −1.1% to −179.10% in both August and November in all of the WWTPs, which agreed with observations in previous investigations (Yan et al., 2014a; Papageorgiou et al., 2016). The negative removal efficiencies were probably a result of glucuronide and conjugated metabolites being converted back to their parent compounds through enzymatic processes during the treatment (Göbel et al., 2005; Radjenović et al., 2009; Yan et al., 2014b; Papageorgiou et al., 2016). Moreover, the lack of MET-degrading microbial community and the release of PhACs adsorbed on particles might lead to higher concentration in the effluents.

PhACs removal is affected by many factors such as the treatment process, the operating conditions, the physico-chemical properties of the PhACs and weather conditions (Yan et al., 2014a; Yuan et al., 2015; Papageorgiou et al., 2016). Table 2 shows that the removal during secondary treatment was generally higher than the primary step and disinfection. Except for MET, secondary treatment generally accounted for more than 50% of the total removal and as much as 93%. The removal of these PhACs from WWTPs depends mainly on biological treatment processes, which is consistent with those of previous studies (Kasprzyk-Hordern et al., 2009; Behera et al., 2011; Yan et al., 2014b; Yuan et al., 2015). However, the removal of these PhACs through biological treatment does not indicate that they are necessarily biodegradable. They may have been partitioned from the wastewater into the sludge without mineralization (Kasprzyk-Hordern et al., 2009). Further study involving analysis of both the wastewater and the sludge is needed to evaluate these pharmaceuticals' biodegradability. However, ATE was biodegraded effectively due to the low proportions detected in both the effluent and in the sludge (Yuan et

Table 1 Average PhACs concentrations (ng/L) in the effluents from various treatment units of three WWTPs

PhAC	August																			
	WWTPA				WWTPB-1				WWTPB-2				WWTPB-3				WWTPC			
	Influent	Primary effluent	Secondary effluent	Final effluent	Influent	Primary effluent	Secondary effluent	Final effluent	Influent	Primary effluent	Secondary effluent	Final effluent	Influent	Primary effluent	Secondary effluent	Final effluent	Influent	Primary effluent	Secondary effluent	Final effluent
NIP	23.0	19.0	9.0	6.0	29.8	25.6	18.7	3.2	–	–	–	–	11.4	9.0	4.8	2.7	6.8	6.0	5.4	0
ATE	10.0	8.0	4.9	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
MET	386.8	300.0	415.9	405	96.6	80.7	97.6	97.6	221.5	198.9	252.4	252.2	169.7	150.5	198.5	198.3	78	74.2	141.6	119.6
VAL	211.0	198.0	98.0	72.0	87.4	73.0	12.2	8.4	96.4	93.1	46.8	41.0	96.5	80.3	13.4	10.5	200.9	192.2	101.6	90.1
PRA	112.0	108.0	64.0	53.0	67.9	61.9	47.5	47.1	123.9	122.8	85.8	68.8	54.6	54.1	32.6	28.9	98.3	94.6	62.3	52.9
PhAC	November																			
	WWTPA				WWTPB-1				WWTPB-2				WWTPB-3				WWTPC			
	Influent	Primary effluent	Secondary effluent	Final effluent	Influent	Primary effluent	Secondary effluent	Final effluent	Influent	Primary effluent	Secondary effluent	Final effluent	Influent	Primary effluent	Secondary effluent	Final effluent	Influent	Primary effluent	Secondary effluent	Final effluent
NIP	34.3	31.1	21.3	19.8	32.0	28.8	25.3	20.5	–	–	–	–	18.1	16.1	8.8	7.2	48.6	43.3	19.4	17.5
ATE	12.3	10.6	7.7	6.73	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
MET	116.8	116.5	171.7	197.1	382.6	376.5	615.3	613.2	206.0	208.8	330.4	329.3	119.7	115.2	126.1	121.0	49.5	43.4	145.7	138.1
VAL	278.2	253.2	180.5	153.9	587.2	500.9	253.7	171.3	132.7	113.5	86.1	75.2	280.5	267.9	31.3	25.1	146.5	113.5	51.7	46.3
PRA	180.5	165.3	96.9	72.9	131.9	97.6	94.6	74.2	594.1	316.8	77.8	45.8	158.3	117.9	75.5	66.3	144.3	113.8	65.6	58.4

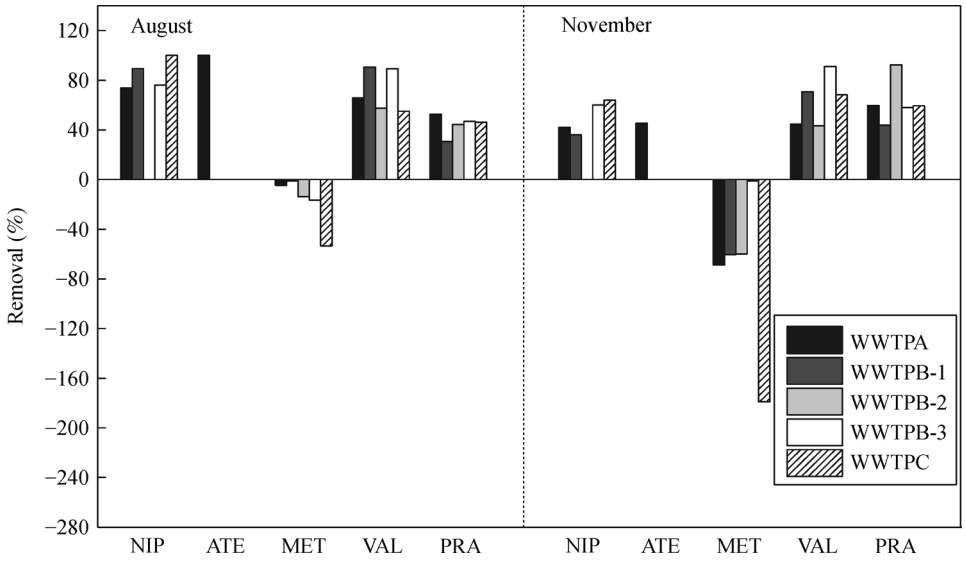

Fig. 4 Overall PhACs removal efficiencies of various treatment processes in three WWTPs (Missing values were undetectable in the influent or effluent samples)

al., 2015). The negative removal of MET was also attributed to the secondary treatment step, further indicating that conversion of metabolites into MET through enzymatic processes may take place during biological treatment (Göbel et al., 2005; Radjenović et al., 2009).

Compared to A/O process in WWTPA and the various A^2/O process in WWTPB, the Unitank process combined with secondary clarification in WWTPC showed similar results with all of the PhACs with the exception of MET. The removal efficiencies by secondary treatment were generally higher in August than in November, which was probably due to greater microbial activity at higher temperatures. The removal efficiencies in primary treatment were relatively low in general (Table 2), indicating that PhACs cannot be eliminated through adsorption onto suspended particles because of low log Kow[a]. The horizontal-flow grit chamber in WWTPB-3 showed the best removal efficiency for all WWTPs in both seasons, which was consistent with the findings of a previous study (Yuan et al., 2015). The removal of most PhACs in the disinfection processes was negligible, except a few cases (Table 2). Meanwhile, the UV disinfection in WWTPC presented similar removal efficiencies to that achieved through chlorine disinfection in the other WWTPs. This could be because the disinfection processes were designed to eliminate microorganisms but not trace levels of PhACs (Yuan et al., 2015).

3.4 Ecological risk assessment of PhACs in effluents

The effluents of all WWTPs were discharged into aquifers thus reaching downstream lakes or rivers, so all of the chemical compounds investigated could have the potential to cause advert impacts on the ecosystem. The RQs of the PhACs in the effluents were estimated to assess an ecological risk. The EC50 values for daphnia, fish and algae for acute toxicity were collected from the literatures, and the corresponding RQ values were calculated and summarized in Table S5 and Fig. 5.

Although each aquatic organism exhibited different susceptibilities to different PhACs, all of the RQ estimates are less than 0.1, indicating low risk from these PhACs to three aquatic organisms. However, the MET and PRA with RQ values approaching to 0.1 should need further attention.

The RQ values derived for the single compounds are relatively low, but the coexistence of various PhACs and food chain effects are known to have additive effects in aquatic environment (Backhaus et al., 2000; Quinn et al., 2009). Consequently, further research to assess the environmental risk should be conducted considering additive effects and a wider range of organisms.

4 Conclusions

In this study, the occurrence, removal, and environmental risk of 10 antihypertensive drugs and lipid regulators were investigated at three operating WWTPs in south China in August and November. The results supplement the database on PhACs occurrence and environmental risks in south China and provide an important reference data set describing the behavior and fate of PhACs in WWTPs. The following conclusions were obtained:

1) Five PhACs were detected in the influents of the three WWTPs at concentrations ranging from 5.79 to 594.09 ng/L. The concentrations of all of the PhACs studied were higher in November than in August. The average daily

Table 2 Removal efficiencies (%) of PhACs detected in various treatment unit of three WWTPs

			NIP	ATE	MET	VAL	PRA
August	WWTPA	Primary	17.4	20.0	22.4	6.2	3.6
		Secondary	43.5	31.0	–30.0	47.4	39.3
		Disinfection	13.0	49.0	2.8	12.3	9.8
		Total	73.9	100.0	–4.7	65.9	52.7
	WWTPB-1	Primary	14.1	–	16.4	16.4	8.9
		Secondary	23.3	–	–17.5	69.6	21.1
		Disinfection	51.9	–	0	4.4	0.6
		Total	89.3	–	–1.1	90.4	30.6
	WWTPB-2	Primary	–	–	10.2	3.4	0.9
		Secondary	–	–	–24.2	48.1	29.8
		Disinfection	–	–	0.1	6.0	13.7
		Total	–	–	–13.8	57.5	44.4
	WWTPB-3	Primary	20.9	–	11.3	8.5	16.8
		Secondary	37.3	–	–28.3	69.3	39.5
		Disinfection	17.9	–	0.1	3.0	6.7
		Total	76.1	–	–16.9	89.1	46.9
	WWTPC	Primary	12.0	–	4.8	4.3	3.7
		Secondary	8.5	–	–86.3	45.1	32.8
		Disinfection	79.5	–	28.2	5.7	9.6
		Total	100.0	–	–53.3	55.1	46.2
November	WWTPA	Primary	9.3	13.9	0.3	8.9	8.4
		Secondary	28.6	23.4	–47.3	26.1	37.9
		Disinfection	4.4	7.8	–21.8	9.6	13.3
		Total	42.2	45.3	–68.8	44.7	59.6
	WWTPB-1	Primary	10.2	–	1.6	14.7	26.0
		Secondary	10.7	–	–62.4	42.1	2.3
		Disinfection	15.1	–	0.5	14.0	15.5
		Total	36.0	–	–60.3	70.8	43.8
	WWTPB-2	Primary	–	–	–1.3	14.5	46.7
		Secondary	–	–	–59.0	20.6	40.2
		Disinfection	–	–	0.6	8.2	5.4
		Total	–	–	–59.8	43.3	92.3
	WWTPB-3	Primary	11.0	–	3.6	4.5	25.5
		Secondary	40.6	–	–9.1	84.3	26.8
		Disinfection	8.4	–	4.3	2.2	5.8
		Total	60.1	–	–1.1	91.1	58.1
	WWTPC	Primary	10.9	–	12.3	22.6	21.1
		Secondary	49.0	–	–206.8	42.1	33.4
		Disinfection	4.0	–	15.4	3.7	5.0
		Total	64.0	–	–179.1	68.4	59.5

Note: – not available

mass loadings of all of the PhACs were calculated to be 289.52 to 430.46 μg/d for each person in the catchment area.

2) The removal efficiencies of PhACs varied from "negative removal" to almost complete removal. The removal occurs mainly in the biological treatment stage;

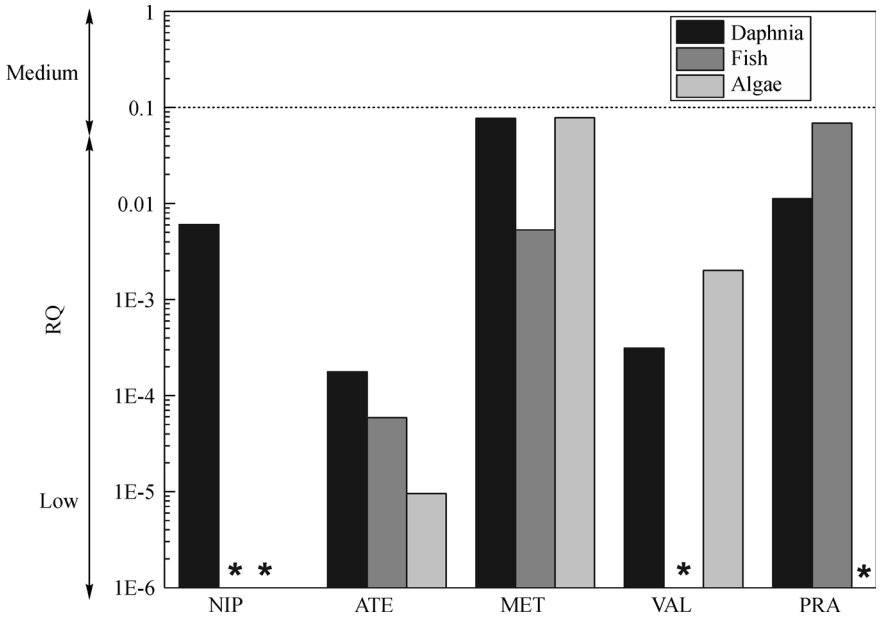

Fig. 5 Estimated RQs of the PhACs in effluents of WWTPs for acute toxicity of daphnia, fish, and algae
Note: * indicates data unavailable

removal in primary treatment and disinfection were minimal. The Unitank process combined with secondary clarifier in WWTPC showed the most consistent removal efficiencies for all of the PhACs studied, though MET increased during this process. The removal efficiencies in August were significantly higher than those in November.

3) The RQs of the single PhACs were less than 0.1, indicating a low environmental risk to aquatic ecosystems. However, the additive effects of various PhACs deserve further study to assess the potential risk in the near future.

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