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Seasonal and spatial variations of PPCP occurrence, removal and mass loading in three wastewater treatment plants located in different urbanization areas in Xiamen, China

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ABSTRACT

The occurrence and fate of 48 pharmaceuticals and personal care products (PPCPs) in three wastewater treatment plants (WWTPs) located in different urbanization areas in Xiamen, China was investigated over one year. Results showed that PPCPs were widely detected, but the major PPCPs in the influent, effluent, and sludge were different. Spatial and seasonal variations of PPCP levels in the influent and sludge were observed. The removal efficiencies for most PPCPs were similar among the three WWTPs, although they employed different biological treatment processes. Furthermore, the mass loadings per inhabitant of most pharmaceuticals had a positive correlation with the urbanization levels, indicating that most pharmaceutical usage was higher in the urban core compared to the suburban zones. The total mass loadings of all the 48 PPCPs in the effluent and waste sludge showed close proportions, which suggested the importance of proper waste sludge disposal to prevent a large quantity of PPCPs from entering the environment.

1. Introduction

Pharmaceuticals and personal care products (PPCPs) are a class of emerging contaminants, which have been widely detected in the surface water and sediments (Kolpin et al., 2002; Lapworth et al., 2012; Lv et al., 2014). Great concerns have been raised because PPCPs are biologically active and could pose adverse effects to the ecological safety and human health (Fent et al., 2006). Previous studies indicated that the effluent from municipal wastewater treatment plants (WWTPs) was one of the major pathways for PPCP to enter the receiving water (e.g., Rosi-Marshall and Royer, 2012). Studies have investigated PPCP occurrence in the influent and effluent (Hughes et al., 2013; Ratola et al., 2012), and results showed that the concentrations of PPCPs in the wastewater ranged from pg/L to mg/L level (Ratola et al., 2012). The removal efficiencies of PPCPs in WWTPs varied in relation to the chemical properties of the individual PPCP and also the operation conditions, technology used, and microbial community composition of the activated sludge (Monteiro and Boxall, 2010). Therefore, there is a great need to further evaluate the removal efficiencies in different treatment processes.

The evaluation of PPCP removal has been conducted in the conventional activated sludge processes, which suggested PPCPs could be adsorbed onto the sludge, biodegraded by the microbes, or chemically eliminated, and subsequently removed from the aquatic phase (Suarez et al., 2008). PPCPs adsorbed onto the activated sludge might also be introduced to the environment through the sludge application (Daughton and Ternes, 1999). However, due to the limited analytical methods and the complicated matrix, fewer studies focused on the PPCPs in the sludge, and especially the available studies were based on short-term monitoring (Zuloaga et al., 2012). Thus, more information of PPCPs in WWTPs and especially in sludge over an extended period of time is still necessary. In addition, the analysis of PPCPs in the sludge could help to understand the removal pathway during the activated sludge processes, whether through biological degradation/transformation or adsorption onto the sludge.

China is undergoing a rapid economic growth, and many Chinese cities are undergoing rapid urbanization. The percentage of

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China's urban population was 17% in 1978, increased to 50% in 2010, and is predicted to be 59% by 2020 (Ren et al., 2011). The water pollution has become a serious problem due to the rapid urbanization process (Ren et al., 2014). So far, only one study investigated the PPCP contamination levels in the WWTPs with urbanization, which was based on only one sampling and focused on limited PPCPs in the wastewater (Chen et al., 2012). The PPCP concentrations in the wastewater not only depend on PPCP consumption, but also the wastewater source and the daily water consumption. The understanding of the influent PPCP mass loadings normalized to the population served could indicate to a certain degree the usage and use pattern of PPCPs in the service area (Zhou et al., 2013). In this study, 48 PPCPs were selected and investigated mainly based on their high detection frequencies and high concentrations reported in the previous studies (Lv et al., 2014; Sun et al., 2014a). The occurrence of PPCPs in three WWTPs, which are located in areas with different levels of urbanization, were investigated over one year. Special emphasis was placed on the PPCP levels in the sludge. Spatial and seasonal variations of PPCP occurrence in the influent, effluent and sludge were analyzed. In addition, the removal rates of PPCPs were compared among different biological treatment processes. In the end, the focus of this paper is to fill the knowledge gap of the relationship between PPCP contamination in WWTPs and urbanization levels.

2. Material and methods

2.1. Chemicals

48 target compounds and 7 isotope standards were purchased from Sigma–Aldrich (USA), Fluka (USA), Dr. Ehrenstorfer GmbH (Germany), AccuStandard (USA) or Cambridge Isotope Laboratories (USA). More details are given in Table S1 of the Supplemental Information (SI). Methanol and acetone (HPLC grade) were provided by Tedia (USA). The reagent water was prepared with a Milli-Q water purification system (Millipore, USA). Stock solutions of individual PPCPs were prepared in methanol and stored in −20 °C in the dark.

2.2. Sample collection

Xiamen is a major city in the southeast of China (117°53′–118°25′ E and 24°25′–24°54′ N), with a subtropical monsoon climate. Xiamen is undergoing a rapid urbanization. The population has increased from approximately 1 million in 1972 to more than 3.8 million in 2014. In this study, 3 WWTPs (W1-3) were investigated. W1 is located in the urban core, and the wastewater is all domestic wastewater. W2 and W3 are located in the suburban zones. The domestic wastewater is predominant in W2 with some industrial wastewater, while the industrial wastewater contributed to more than 50% in W3. W1-3 serves around 1.0, 0.35, and 0.30 million inhabitants, respectively. The location and service areas of each WWTP, and the land usage type were provided in Fig. S1 in SI. W1 contains the primary sedimentation, biological aerated filters (BAF), and UV disinfection. W2 contains the primary sedimentation, Orbal oxidation ditches, secondary sedimentation, and UV disinfection. W3 contains the primary sedimentation, anaerobic/anoxic/oxic (A^2/O), secondary sedimentation, and chemical disinfection. Schematic diagrams of the treatment processes in the three WWTPs are shown in Fig. S2 in SI.

Grab samples of wastewater and sludge were collected on February 20th, May 8th, August 11th, and November 12th 2014 from W1–3. The wastewater parameters, including pH, temperature, ammonia/nitrate concentrations, suspended solids, and dissolved oxygen (DO), and the sludge parameters, including carbon, nitrogen, sulfur contents, and zinc concentration, are list in SI Table S2.

2.3. Sample analysis

Wastewater samples were prepared by the solid phase extraction (SPE) and analyzed by liquid chromatography triple quadrupole mass spectrometry (LC-QqQ MS) using multiple reaction monitoring (MRM) mode (Sun et al., 2014a). Details of the wastewater preparation and instrument parameters are provided in SI.

Sludge samples were determined by the matrix solid phase dispersion (MSPD) technique coupled with LC-QqQ-MS (article in preparation). In short, 0.1 g of freeze-dried sludge was placed in an agate mortar with 0.4 g of the previously cleaned C18 sorbent. The materials were well mixed using an agate pestle to obtain a homogeneous material for the MSPD column. After blending, the sample was packed and carefully compressed into an empty column containing a polyethylene frit at the bottom and top. The packed column was attached to the SPE extraction system. The analytes were extracted using 12 mL methanol, 6 mL methanol/acetone (1/1, v/v), and 10 mL acetonitrile/5% oxalic acid (8/2, v/v). Elute was evaporated to dryness using a gentle N_2 at 40 °C, then dissolved in 1.0 mL acetonitrile/water (1/1, v/v), and filtered through a 0.45 μm filter. The samples were analyzed by LC-QqQ-MS in MRM mode.

2.4. Quality assurance and quality control (QA/QC)

QA/QC was conducted to ensure the identification and quantification of the PPCPs. Identification of PPCPs was performed by LC-MS/MS with MRM, using the 2 highest characteristic precursor ion/product ion transition pairs (SI Table SI-1). The ratios of product transitions were calculated to ensure correct identification. The method detection limits (MDLs) were in the range of 0.02–1 ng/L for wastewater and 0.02–2 μg/kg for sludge (SI Table S1). An instrumental blank, procedural blank, sample duplicate, blank spike, and matrix spike, was applied for each batch. Details are provided in SI.

2.5. Data analysis

The removal efficiency of each PPCP in the WWTP was calculated using the following equation:

$$R(\%) = \frac{\left(C_{Influent} - C_{Effluent}\right) \times V}{C_{Influent} \times V} \times 100$$

where $C_{Influent}$ and $C_{Effluent}$ is the concentration of the individual PPCP in the influent and effluent for each sampling (ng/L), V is the capacity of each WWTP (m^3/d). Friedman test was conducted by PAST v 2.17 to compare the seasonal and spatial variations of PPCP concentrations in different sampling sites and sampling seasons. Spearman's rank correlation analysis was conducted by PAST v 2.17 to evaluate the correlation between PPCP concentrations in the sludge and carbon content, heavy metals or other parameters. Principal coordinate analysis (PCoA) was conducted by SPSS to analyze the distribution behavior of PPCPs in the wastewater and sludge.

3. Results and discussion

3.1. Occurrence of PPCPs in WWTPs

The concentration range, mean concentration, median concentration, and detection frequency of each PPCP are shown in Table 1.

Table 1
The concentration range, average concentration, median concentration, and the detection frequencies of each PPCP in the influent, effluent, and sludge (n = 12).

Name	Influent (ng/L)				Effluent (ng/L)				Sludge (μg/kg)			
	Range	Mean	Median	Freq (%)	Range	Mean	Median	Freq (%)	Range	Mean	Median	Freq (%)
Acetaminophen	105–3480	1900	1640	100	BLD-11.1	0.90	BLD	8.3	BLD-180	15	BLD	8.3
Ibuprofen	34.8–406	300	320	100	BLD-99.4	50	43.2	92	BLD-30.4	6.2	BLD	25
Ketoprofen	BLD-158	77	70.6	75	BLD-183	71	57.2	42	BLD	BLD	BLD	0
Fenoprofen	BLD-46.2	9.4	BLD	33	BLD-23.4	3.6	BLD	17	BLD	BLD	BLD	0
Diclofenac acid	14.8–71.8	49	49.4	100	17.7–69.2	40	39.4	100	BLD-14.0	7.0	6.80	75
Antipyrine	BLD	BLD	BLD	0	BLD	BLD	BLD	0	BLD	BLD	BLD	0
Indomethacine	BLD-26.4	11	9.00	92	BLD-61.4	26.7	20.8	92	BLD-8.00	0.90	BLD	17
Mefenamic acid	BLD-17.8	10	9.10	92	BLD-13.7	7.3	7.50	83	BLD-14.7	3.2	BLD	42
Codeine	BLD	BLD	BLD	0	BLD	BLD	BLD	0	BLD	BLD	BLD	0
Ethenzamide	BLD-4.30	1.4	0.900	58	BLD-2.00	0.2	BLD	8.3	BLD-5.50	0.50	BLD	8.3
Naproxen	BLD-30.6	13	9.00	92	BLD-13.8	4.5	BLD	42	BLD	BLD	BLD	0
Crotamiton	BLD-5.70	2.5	1.70	92	BLD-7.80	3.5	2.10	83	BLD	BLD	BLD	0
Sulfamethoxazole	BLD-95.2	25	17.5	75	BLD-22.4	9.1	5.00	83	BLD-2.90	0.20	BLD	8.3
Enrofloxacin	BLD	BLD	BLD	0	BLD	BLD	BLD	0	7.60–26.8	17	15.3	100
Ofloxacin	23.6–786	200	132	100	13.3–702	150	94.4	100	1480–4020	2300	2020	100
Danofloxacin	BLD	BLD	BLD	0	BLD	BLD	BLD	0	BLD-13.2	BLD	BLD	8.3
Sarafloxacin	BLD-1.20	0.10	BLD	8.3	BLD-1.30	0.20	BLD	16	BLD-14.4	1.8	BLD	17
Oxytetracycline	8.60–230	91	69.2	92	BLD-51.4	20	16.5	75	208–3790	1100	775	100
Tetracycline	BLD-189	48	35.2	75	BLD-37.6	14	13.4	67	49.8–466	180	127	100
Caffeine	35.8–4580	2300	2020	100	2.50–414	62	8.20	100	BLD-278	34	8.30	83
Bisphenol A	55.6–5850	1300	737	100	BLD-123	34	BLD	50	BLD-1830	320	BLD	50
Propyl paraben	16.2–762	310	280	100	0.800–6.20	2.6	2.20	100	BLD-6.00	3.0	3.50	75
Methyl paraben	21.0–446	240	238	100	BLD-18.0	2.6	3.80	92	8.20–48.1	23	20.4	100
Benzyl paraben	BLD-1.30	0.40	BLD	67	BLD	BLD	BLD	0	BLD	BLD	BLD	0
Triclosan	1.30–211	56	53.3	100	25.9–111	59	56.4	100	354–608	470	440	100
Triclocarban	4.70–76.2	32	33.8	100	27.6–109	65	60.6	100	1130–2180	1700	1580	100
Metoprolol	BLD-248.0	59	32.8	75	BLD-280	120	130	92	BLD-226	19	BLD	17
Propranolol	BLD-9.56	1.2	BLD	25	BLD-15.0	2.0	BLD	50	BLD-29.6	3.1	BLD	33
Atenolol	BLD	BLD	BLD	0	BLD-3.80	0.30	BLD	25	BLD	BLD	BLD	0
Sotalol	BLD	BLD	BLD	0	BLD	BLD	BLD	0	BLD	BLD	BLD	0
Aspartame	BLD-187	41	17.9	58	BLD	BLD	BLD	0	BLD-80.0	21	BLD	42
Benzophenone-3	BLD-23.8	8.6	8.70	83	BLD-8.70	2.6	0.800	75	BLD-27.5	6.9	BLD	50
Acetophenone	BLD-91.8	16	BLD	67	BLD-121	17	BLD	33	BLD-16.8	1.4	BLD	8.3
3-(4′-methyl)benzylidene-bornan-2-one	BLD	BLD	BLD	0	BLD	BLD	BLD	0	BLD	BLD	BLD	0
Losartan	BLD-6.90	3.5	3.10	83	BLD-7.60	2.2	BLD	50	BLD-11.4	2.1	BLD	25
Loratadine	BLD	BLD	BLD	0	BLD	BLD	BLD	0	BLD	BLD	BLD	0
Fluoxetine	BLD	BLD	BLD	0	BLD	BLD	BLD	0	BLD	BLD	BLD	0
Carbamazepine	BLD-15.1	3.9	1.10	75	BLD-19.5	6.4	4.70	83	BLD-1.80	0.10	BLD	8.3
Diazepam	BLD	BLD	BLD	0	BLD	BLD	BLD	0	BLD	BLD	BLD	0
Miconazole	BLD	BLD	BLD	0	BLD	BLD	BLD	0	88.3–215	120	117	100
Glibenclamide	BLD-4.50	1.4	BLD	50	BLD-7.50	1.9	BLD	50	BLD	BLD	BLD	0
Cyclophosphamide	BLD-69.8	13	BLD	50	BLD-110	14	BLD	42	BLD	BLD	BLD	0
Thiabendazole	BLD	BLD	BLD	0	BLD	BLD	BLD	0	BLD	BLD	BLD	0
Clofibric acid	BLD-6.40	1.4	BLD	33	BLD-3.50	0.8	BLD	33	BLD	BLD	BLD	0
Gemfibrozil	0.700–26.6	7.2	2.54	100	BLD-2.10	1.0	1.20	75	BLD	BLD	BLD	0
Clenbuterol	BLD	BLD	BLD	0	BLD	BLD	BLD	0	BLD	BLD	BLD	0
Pirenzepine	BLD	BLD	BLD	0	BLD	BLD	BLD	0	BLD	BLD	BLD	0
Sildenafil	BLD	BLD	BLD	0	BLD-7.40	3.2	3.60	67	BLD-27.1	4.5	BLD	33

BLD: below the method detection level.

Among the 48 target PPCPs, 33, 33, and 28 PPCPs were detected at least once out of 12 samples in the influent, effluent, and sludge, respectively. Generally, the major classes in the influent, effluent, and sludge were different (Fig. S2).

In the influent, 12 PPCPs were detected in all of the samples, and 27 compounds were detected in at least half of the samples (Fig. 1a). Concerning therapeutic groups, the stimulant and the non-steroidal anti-inflammatory drugs (NSAIDs) were the most ubiquitous compounds, in terms of both individual concentrations and the detection frequencies. The highest value was observed for caffeine, followed by acetaminophen, with the average concentrations in the influent of 2300 and 1900 ng/L, respectively. Lower but still considerable levels were found for ibuprofen, ketoprofen and diclofenac, with the average concentrations of 300, 77, and 49 ng/L, respectively. The average concentration of the plasticizer (bisphenol A) was 1300 ng/L. Other groups with the considerably high levels were the preservatives (propyl parabens and methyl parabens), antibiotics (ofloxacin, oxytetracycline, tetracycline, and sulfamethoxazole), antimicrobial agents (triclosan and triclocarban), β-blockers (metoprolol), and artificial sweetener (aspartame). The average concentrations of the above PPCPs were in the range of 25–310 ng/L. The PPCP levels in the influent in these three WWTPs were comparable with the previous work in the other areas in China and all over the world (Liu and Wong, 2013; Ratola et al., 2012). However, there are differences in specific cases. The antibiotics were lower than most previous investigations, for examples, one or two order of magnitude lower than the levels in Beijing (Gao et al., 2012) and Pearl River Delta (Xu et al., 2007) in China, New York (Batt et al., 2007) and New Mexico (Brown et al., 2006) in US. It might be attributed to the low per capita consumption, the lack of the livestock and poultry raising in Xiamen city, or the dilution by the antibiotic-free industry wastewater.

In the effluent, 22 compounds were detected in at least half of the samples (Fig. 1b). Ofloxacin and metoprolol were the predominant PPCPs in the effluent, with the average concentrations more than 100 ng/L, followed by caffeine, with the average concentration

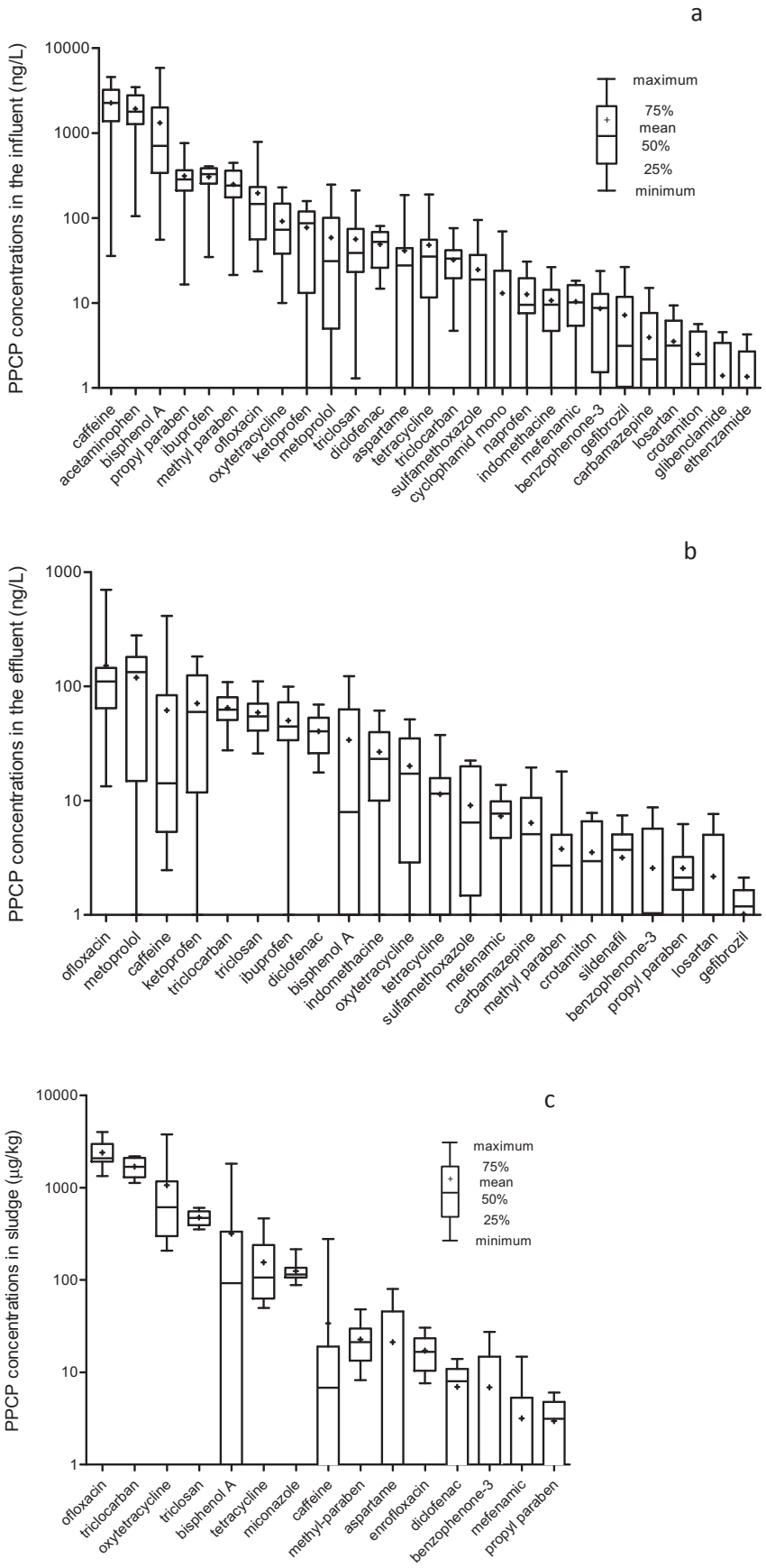

Fig. 1. PPCP concentrations in (a) influent, (b) effluent, and (c) sludge.

of 62 ng/L. The antimicrobial agents, triclosan and triclocarban, were detected in all the effluent samples, with average concentrations of 59 and 65 ng/L, respectively. Although NSAIDs showed high levels and detection frequencies in the influent, the concentrations in the effluent decreased sharply. For example, acetaminophen was below the MDL, and the average concentration of ibuprofen was 50 ng/L in the effluent. However, effluent concentrations of ketoprofen and diclofenac were under similar amount as to those found in the influent. PPCPs in the effluent could be discharged into the surrounding seawater in Xiamen coastal area.

In the sludge, 15 PPCPs were detected in at least 6 sludge samples (Fig. 1c). Ofloxacin showed highest concentrations among all PPCPs with mean concentration of 2300 μg/kg, followed by triclocarban and oxytetracycline at mean concentration of 1700 and 1100 μg/kg, respectively. The concentrations of triclosan, bisphenol A, tetracycline, and miconazole were more than 100 μg/kg. The high concentrations of the quinolone (ofloxacin) and tetracycline (oxytetracycline and tetracycline) antibiotics, and the antimicrobial agents (triclosan and triclocarban) in the sludge were also observed in the previous studies, for which the adsorption to the sludge was the principal process for their removal from the wastewater (Chen et al., 2013; Ying et al., 2007). The high concentration of bisphenol A in the sludge might be related to the high concentration in the influent and the limited removal efficiency (Sun et al., 2014a). Generally, the concentrations of PPCPs in the sludge in Xiamen were in the same order of magnitude, but slightly lower compared to the outcomes of national sewage sludge survey in US (McClellan and Halden, 2010), and survey in Beijing (Gao et al., 2012) and Guangzhou (Yu et al., 2011) in China. The detected PPCP concentrations in the sludge implied that for those samples with high levels of suspended solids or for the hydrophobic PPCP compounds (Guerra et al., 2014), it's suggested to consider the suspended solids for the PPCP determination.

3.2. Seasonal variation

Friedman test was conducted to investigate the seasonal variation. In the influent, 27 PPCPs with the detection frequency at least 50% were selected and analyzed (Fig. 2a). Significant lower PPCP concentrations were observed in August compared to the February, May, and December, with p value of 0.006, 0.001, and 0.0003. It's in accordance with the previous results (Sui et al., 2011; Sun et al., 2014a; Yu et al., 2013). The higher consumption of the antibiotics, NSAIDs, and antilipidemics in the cold seasons (Davey et al., 2008; Ockene et al., 2004) might accordingly cause the increase of PPCP levels in the influent. Previous studies showed the lower PPCP levels in the wet or hot season, indicating the dilution by the precipitation or the water consumption (Ternes, 1998). However, as shown in SI Table S3, no significant difference of the daily processing capacity was observed among the sampling seasons in all WWTPs ($p > 0.05$), excluding the concentration reduction due to the dilution in the present study. In addition, higher levels of benzophenone-3 were observed in August and November, which might be due to the high consumption of the UV filters in the hot seasons. However, there was no significant difference of PPCP concentrations between February, May, and November in this study ($p > 0.05$).

In the effluent, higher PPCP levels were in February compared to August ($p = 0.04$) (Fig. 2b). The higher PPCP levels in the cold seasons were in accordance with the previous studies. The high concentrations in the influent, and lower biological removal efficiencies due to the low temperature, might cause the high PPCP concentrations in the effluent in February (Sui et al., 2011).

In the sludge sample, 15 PPCPs with the detection frequency at least 50% were selected and analyzed (Fig. 2c). Significant lower PPCP concentrations were observed in August compared to the February, May, and December, with p value of 0.0001, 0.0001, and 0.002. The lower concentrations in the sludge in August might be due to the lower levels in the influent. In addition, the wastewater temperatures were 18, 20, 30, 25 °C, for February 20th, May 8th, August 11th, and December 12th, respectively. The higher temperature in August probably increased the biological activity via the enzymatically catalyzed reaction and the diffusion of substrate to the cells (Grady, 2011). Previous study also showed higher antibiotics in the sludge in winter, which caused by the higher consumption of antibiotics and lower dilution of the rain and water usage (Gao et al., 2012). However, no significant difference ($p > 0.05$) of PPCP concentrations was observed between February, May, and December in this study.

3.3. Spatial variation

Spatial variation of PPCPs was observed in the influent. Significantly higher PPCP concentrations were shown in W1 and W2 compared to W3 ($p < 0.001$), no significant difference was shown between W1 and W2 ($p = 0.65$). Specifically, the concentrations of the NSAID groups were significantly higher in W1 and W2 compared to W3, with the p value of 0.007 and 0.002, respectively. The spatial difference was probably because of the different wastewater source. The source of W1 and W2 are mainly domestic wastewater, while industrial wastewater contributes to more than 50% in W3. Since most PPCPs were discharged to domestic water after human usage, it might cause the higher PPCP levels in W1 and W2. However, bisphenol A levels showed an opposite trend, higher concentrations were observed in W3 (Fig. 3a). Bisphenol A is a monomer and found in epoxy resins, commonly used in can lining, hard polycarbonate plastic, and a number of products such as adhesives, building materials, and powder paints. The higher level in the influent in W3 suggested the industrial source of bisphenol A. Similar result was obtained in previous study, in which the paper production, chemical industry, and metal/wood manufacture were the major bisphenol A contributor to the influent of the WWTPs (Furhacker et al., 2000). In addition, in the effluent, significant higher PPCP levels were in W1 compared to W3 ($p = 0.01$) (Fig. 3b). The PPCP concentrations in the effluents could be related with the concentrations in the influent, and the removal efficiencies in different treatment processes.

In the sludge, higher PPCP levels were found in W2 compared to W1 ($p = 0.01$) and W3 ($p = 0.04$) (Fig. 3c). Specifically, significant higher antibiotics (including ofloxacin, oxytetracycline, tetracycline, and enrofloxacin) were observed in W2 compared to W1 ($p = 0.001$) and W3 ($p = 0.002$). Lower concentrations of other pharmaceuticals (including caffeine, aspartame, sildenafil, and miconazole) were observed in W3 compared to W2 ($p = 0.04$). It was probably due to the lower concentrations in the influent in W3, in which industrial wastewater contributed for more than 50%.

3.4. Correlation between the PPCP levels in sludge and the other parameters

Spearman's correlation analysis showed the total PPCP levels in the sludge was positively correlated to the carbon content ($p = 0.05$). Specifically, there were strong correlations between the concentrations of ofloxacin, triclocarban, diclofenac, bisphenol A and the carbon content in the sludge, with the p value of 0.048, 0.018, 0.034, and 0.012, respectively (Table S4). It might be due to the adsorption of PPCPs on the organic matters in the sludge (Carballa et al., 2008). Xu et al. reported the positive correlation of the PPCPs with the organic matter contents in the soils, indicating the adsorption on the organic matters (Xu et al., 2009). In addition,

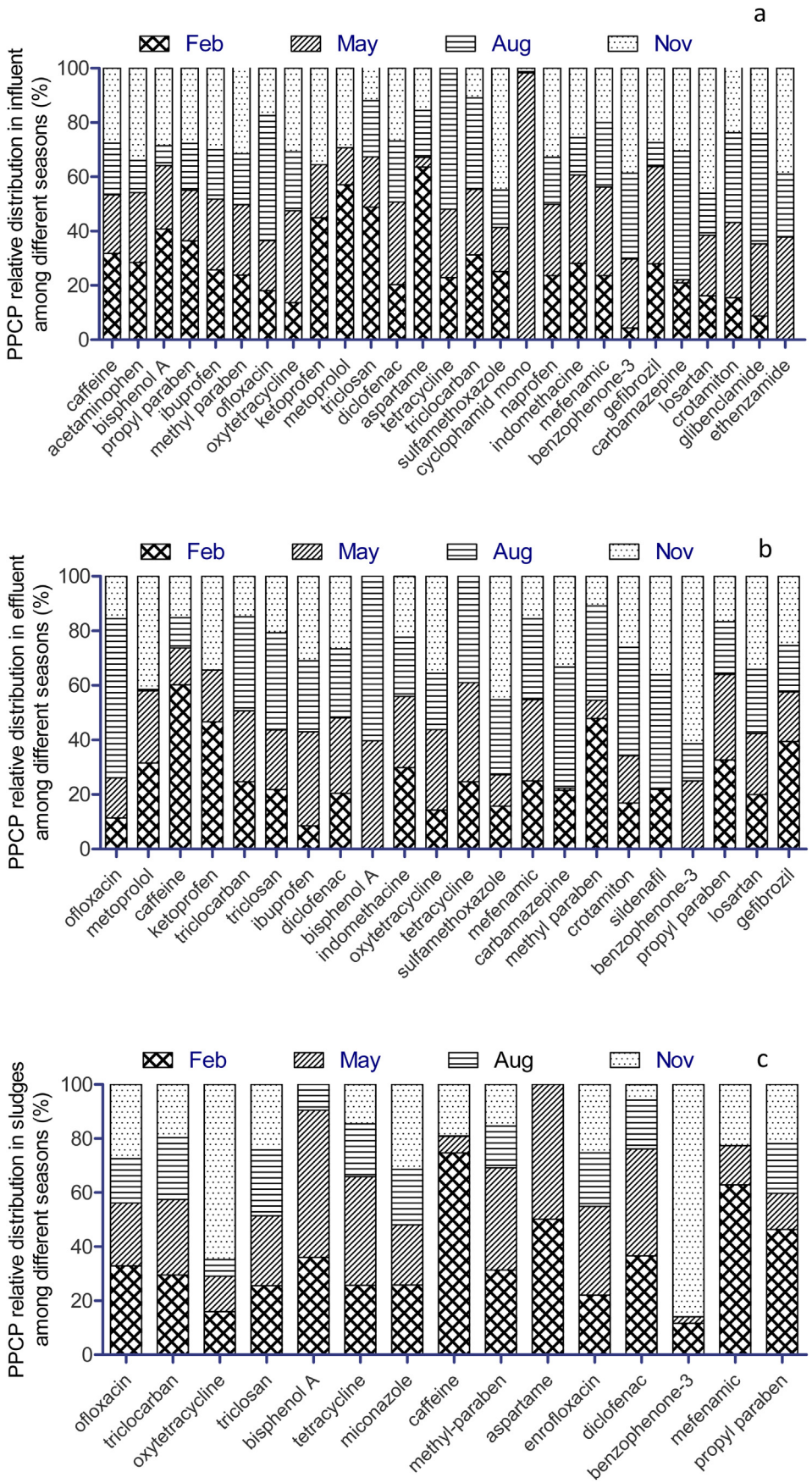

Fig. 2. Seasonal variations of the relative distribution percentages of PPCPs in (a) influents, (b) effluent, and (c) sludges.

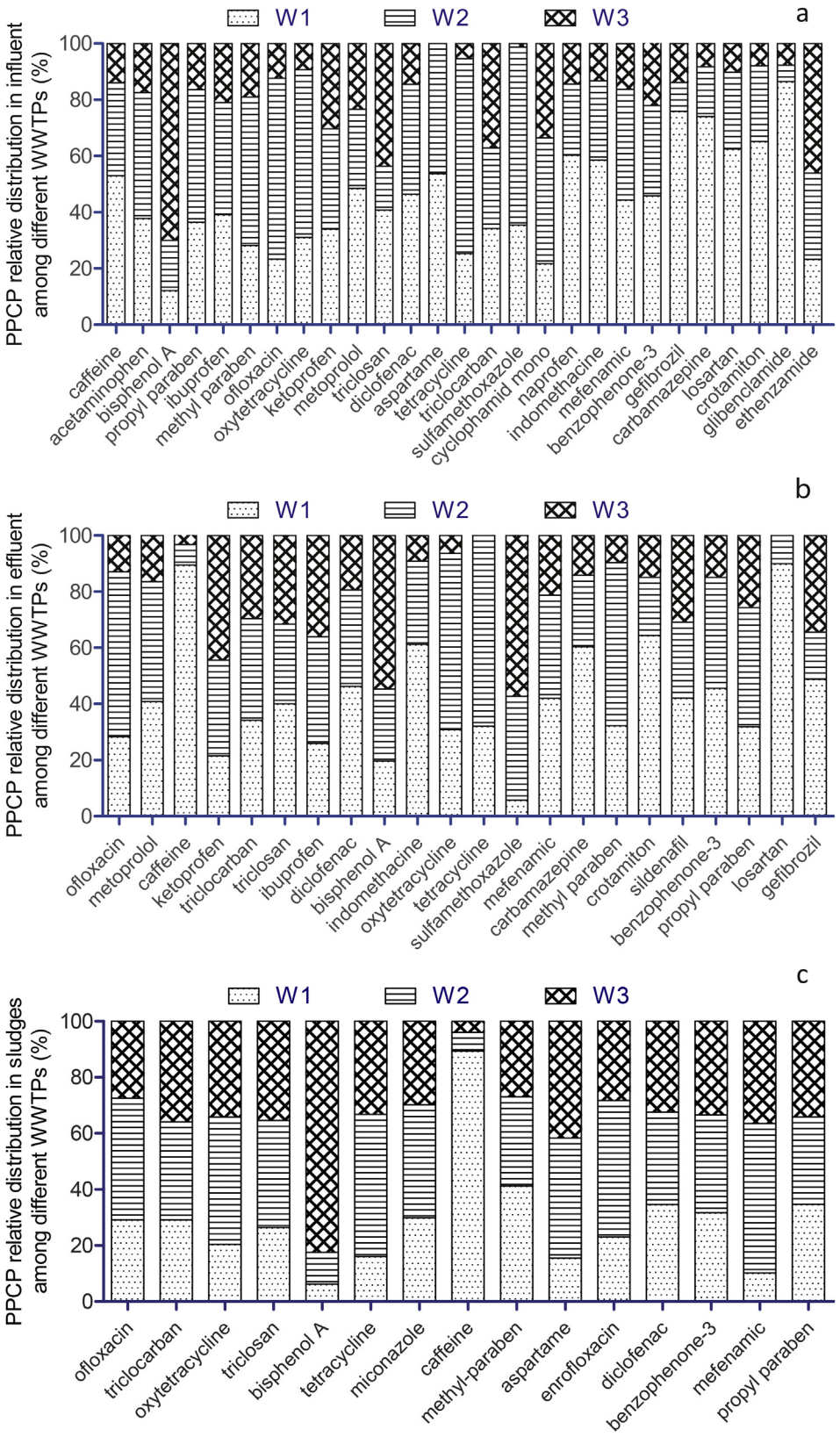

Fig. 3. Spatial variations of the relative distribution percentages of PPCPs in (a) influents, (b) effluent, and (c) sludges.

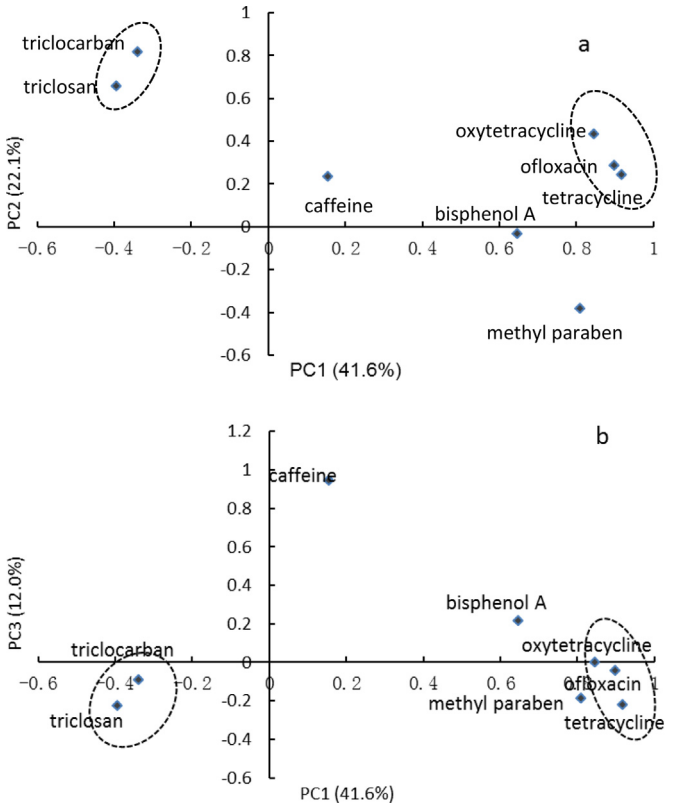

Fig. 4. Principle component analysis of PPCP distribution in the influent and sludge samples.

there was a positive correlation between the bisphenol A level and zinc concentration. Zinc is an industrial material, widely used in the galvanizing, zinc base alloy, and brass and bronze production. The positive relation between bisphenol A and zinc confirmed the industrial source of bisphenol A.

PCoA was conducted based on the relative ratio of PPCP concentrations in the influent and sludge. Eight PPCPs, with 100% detection frequencies in both influent and sludge samples, were analyzed. Fig. 4 shows the two antimicrobial agents, and three tetracycline and quinolone antibiotics were clustered, respectively. The logKow value of triclosan and triclocarban is 4.76 and 4.90, respectively. The high lgKow and low water solubility suggested they have a tendency to partition onto the sludge or soil (Ying et al., 2007). In contrast, despite their high water solubility and low logKow, ofloxacin, oxytetracycline, and tetracycline were also reported mainly partitioning onto the suspended solids and sludge (Watkinson et al., 2007). The ionic interactions and the metal-complexing properties are the major mechanism for the adsorption (Watkinson et al., 2007).

3.5. Removal efficiencies

Fig. 5 shows the PPCP removal efficiencies from the wastewater in different WWTPs. PPCPs with low detection frequencies were excluded in this section because it was difficult to run statistically analysis.

High removal efficiencies were observed for acetaminophen, caffeine, methyl paraben, and propyl paraben, with the mean values more than 97%, followed by bisphenol A and ibuprofen, with the mean removal efficiencies of 90% and 84%. Consistently high removal efficiencies of these PPCPs were observed in the previous studies (Liu and Wong, 2013; Sun et al., 2014a; Yu et al., 2011). Previous studies showed the removal of PPCPs in the WWTPs was generally the result of both the adsorption and biodegradation (Qiang et al., 2013). The high removal efficiencies from the wastewater and low levels in the sludge indicated these PPCPs were liable to degrade during the biological treatment. However, the concentrations of bisphenol A, methyl paraben, propyl paraben in the sludge indicated the adsorption onto the sludge also contributing for their removal from the wastewater. The mean removal efficiencies of naproxen, losartan, gemfibrozil, sulfamethoxazole, oxytetracycline were above 50%, indicating the WWTPs could

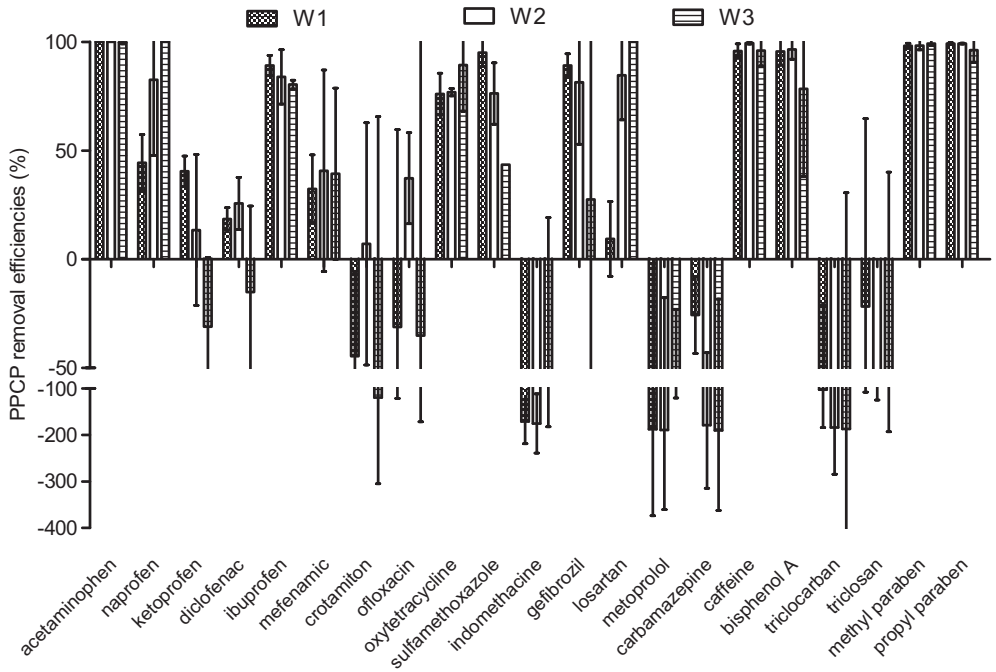

Fig. 5. PPCP removal efficiencies in three WWTPs.

partially removal these PPCPs from wastewater. Naproxen, losartan, gemfibrozil, sulfamethoxazole were under biological degradation or transformation, while the removal of oxytetracycline was mainly via the adsorption onto the sludge due to the high oxytetracycline levels in the sludge. In contrast, low removal rates of ketoprofen, diclofenac, mefenamic, crotamiton, ofloxacin, indomethacine, metoprolol, carbamazepine, triclocarban, and triclosan were observed regardless of the biological treatment processes utilized, indicating these PPCPs were persistent and hardly removed during the wastewater treatment processes. In some cases, negative removal rates were obtained. The possible reason for the poor removal during the wastewater treatment processes might be due to the lack of the PPCP degrading bacteria in the microbial community of the activated sludge. In addition, the grab sampling uncertainty might add some variations of PPCP levels and accordingly affect the evaluation of the removal rates (Ort et al., 2010). Furthermore, the conjugate PPCPs which were not detected in the influent could be transformed and released as the original compound due to the biological processes (Blair et al., 2015).

The removal rates of PPCPs varied in relation to the chemical properties of the individual PPCPs, the biological treatment technology in the WWTPs, and so on (Monteiro and Boxall, 2010). One way ANOVA was conducted to test the difference of removal efficiencies among three WWTPs. In general, no significant difference was observed for the most target PPCPs with $p > 0.05$. Similar results were also observed in the PPCP removal in eight WWTPs in Greece (Kosma et al., 2014). Although different biological and disinfection treatment processes are applied in the three WWTPs (Fig. S2), similar removal efficiencies were achieved, which probably due to the combination removal mechanism of biological degradation/transformation, adsorption onto the particles and sludge, and the chemical removal during the disinfection (Luo et al., 2014). For individual PPCP, higher removal rates of naproxen and losartan were achieved in the W2 and W3 compared to W1 ($p < 0.05$). However, the removal efficiencies of ketoprofen were high in W1 compared to the other two WWTPs ($p < 0.05$).

Recently, researchers have been attempting to use PPCPs as the sewage markers due to their wastewater origin and low natural background levels (Lv et al., 2014; Nakada et al., 2008). Results from the present study suggested that acetaminophen, caffeine, methyl paraben, propyl paraben, bisphenol A, and ibuprofen could be used as the liable markers since they were readily biodegraded in the WWTPs, while ketoprofen, diclofenac, mefenamic, crotamiton, ofloxacin, indomethacine, metoprolol, carbamazepine, triclocarban, and triclosan could be used as the conservative markers since they were persistent in the WWTPs. Similar sewage markers have been reported except for triclosan (Glassmeyer et al., 2005; Lv et al., 2014; Nakada et al., 2008). High removal efficiencies of triclosan were observed in the WWTP in Japan, and triclosan was suggested to be the liable markers accordingly (Nakada et al., 2008). Therefore, the understanding of the PPCP removal efficiencies in the upstream or surrounding WWTPs before selecting specific PPCPs as sewage markers is important.

3.6. Mass loading of PPCPs in WWTPs and urbanization levels

The daily mass loading of PPCPs was calculated by the following equation:

$$M_{Influent} = k \times C_{Influent} \times V_{Influent}$$

$$M_{Effluent} = k \times C_{Effluent} \times V_{Effluent}$$

$$M_{Sludge} = k \times C_{Sludge} \times W_{Sludge} \times \left(1 - MC_{Sludge}\right)$$

where $C_{Influent}$ and $C_{Effluent}$ is the concentration of the total PPCPs in the effluent for each sampling (ng/L), $V_{Influent}$ and $V_{Effluent}$ is the capacity of each WWTP (m^3/d), C_{Sludge} is the concentration of PPCPs in the sludge (ng/g, dw), W_{Sludge} is the weight of the sludge produced daily in each WWTP (t/d), MC_{Sludge} is the moisture content of the dewatered sludge, and k is the unit conversion factor.

The discarded or excreted PPCPs mainly go into the WWTPs. The mass loading of PPCPs per inhabitant in the influent could be calculated to show the input into the WWTP and to indicate to a certain degree the usage and use pattern in the service area (Zhou et al., 2013). In this study, W1-3 are located in areas with different urbanization levels. W1 is located in the urban core (old urban areas where the population density is higher than 127 persons per ha in 2012), while W2 and W3 are located in the suburban zones (old urban areas and new urban transitional zones, where the population density is higher than 23 persons per ha in 2012) (Fig. S1). The urbanization level, which refers to the ratio of urban population to the total population, was 100% for W1 serving area in 2014, and 70.9% for W2 and W3. The average disposable income for people living around W1 was 44084 RMB/yr in 2014, while that was 37608 RMB/yr around W2 and W3 (Xiamen Statistical Bureau, 2014). As shown in Table 2, the mass loadings per inhabitant for the total PPCPs in the influent are 2100, 1000, and 1000 μg/d/inhabitant for W1, W2, and W3, respectively. Higher mass loadings per inhabitant were observed in the urban core compared to the suburban zones. Especially for the NSAIDs, stimulant, other pharmaceuticals, and other personal care products, linear positive correlation was observed between these PPCP levels with the urban ratios with R^2 higher than 0.87. The mass loadings per inhabitant of the above groups in the urban core were 1.5–5.3 times higher than the suburban zones. However, the mass loadings per inhabitant of the antibiotics, antimicrobial agents, and bisphenol A were similar. The results indicated that most pharmaceutical usage was higher in the urban core compared to the suburban zones. It might be because the higher disposable incomes and the more awareness of personal health and hygiene for the people living in the urban core compared to the suburban zones (Sun et al., 2014b; Xiamen Statistical Bureau, 2014). In addition, higher mass loadings per inhabitant for the effluent and sludge were also found in the urban core compared to the suburban zones with $p < 0.001$ under Freidman's test. Results suggested that we should pay more attention to the WWTPs in the urban core for the PPCP contamination, due to the larger emission from these WWTPs to the receiving environment.

WWTP is one of the major sources for releasing PPCPs via final effluent and sewage sludge. The total mass loadings of PPCPs via the effluent and sludge of WWTPs were 513, 75.5, and 87.8 g/d in W1–3. W1 serves half of the population in the urban core in Xiamen City, and W2 and 3 serve nearly half of the population in the suburban zones, with the rest areas having almost the same urbanization rates and the rest people having almost the same disposable income in the urban core or suburban zones. Assuming the total mass loading of PPCPs per inhabitant was similar in the urban core or suburban zones in Xiamen, which has a population of 3.81 million, the estimated mass loading of the 48 target PPCPs via WWTP would be 1500 g/d. The effluent and waste sludge shared close proportions. NSAIDs, stimulant, and other pharmaceuticals reached the coastal receiving waterbody mainly from the discharge of effluent, while the antibiotics and personal care products were likely released via the disposal of waste sludge (Table 2). Therefore, the results emphasize the importance of proper disposal of waste

Table 2
Average mass loadings of the detected PPCPs among the four sampling seasons.

	Mass loadings									Mass loadings per inhabitant								
	Influent (g/d)			Final effluent (g/d)			Excess sludge (g/d)			Influent (μg/d/inhabitant)			Final effluent (μg/d/inhabitant)			Excess sludge (μg/d/inhabitant)		
	W1	W2	W3	W1	W2	W3	W1	W2	W3	W1	W2	W3	W1	W2	W3	W1	W2	W3
Total PPCPs	2116	376	316	250	41.7	37.1	263	33.8	50.7	2100	1000	1000	250	120	124	270	97	170
NSAIDs	722	158	76.1	58.1	9.80	11.1	0.400	0.400	0.100	720	420	250	58	28	37	0.40	1.1	0.33
Antibiotics	76.2	30.8	6.20	44.2	15.3	5.04	146	21.5	26.4	76	88	21	44	44	16.8	150	61	88
Antimicrobials	27.3	3.04	5.70	37.9	5.60	6.80	95.9	10.5	17.4	27	8.7	19	38	16	23	96	30	58
Stimulant	960	105	53.6	43.8	0.600	0.400	4.80	0.0300	0.0300	960	300	180	44	1.7	1.3	4.8	0.086	0.10
Bisphenol A	126	34.2	146	5.90	1.20	3.70	3.00	0.400	5.40	130	98	490	5.9	3.4	12	3.0	1.1	18
Other pharmaceuticals	53.8	6.20	3.80	52.4	8.20	6.10	4.70	0.100	0.300	54	18	13	52	23.4	20	4.7	0.29	1.0
Other personal care products	151	39.1	24.6	7.40	0.900	4.00	8.08	0.855	1.10	150	110	82	7.4	2.6	13	8.1	2.4	3.7

sludge to prevent a large quantity of PPCPs from being released into the environment.

4. Conclusions

In this study, the occurrence of 48 PPCPs in the influent, effluent, and sludge was investigated in three WWTPs located in different urbanization areas in Xiamen, China over one year. There were 33, 33, and 28 PPCPs detected at least once from three WWTPs in four sampling seasons in the influent, effluent, and sludge, respectively. Generally, the major components in the influent, effluent, and sludge were different. In the influent, the stimulant and NSAIDs were the most ubiquitous compounds, in terms of both individual concentrations and the detection frequencies. In the effluent, the antibiotics, β-blockers, and antimicrobial agents were predominant. The quinolone and tetracycline antibiotics and the antimicrobial agents were with high levels in the sludge. These results suggested that WWTPs could partly remove PPCPs from the wastewater mainly via the degradation in the treatment processes and adsorption onto the sludge. The removal efficiencies for most PPCPs were similar in the three WWTPs yet with completely different biological treatment processes.

Seasonal variations of PPCP levels were observed, and lower PPCP levels were detected in August compared to the other sampling seasons. In addition, spatial variations of PPCP levels in the influent and sludge were also observed, which might be due to the wastewater source from different urbanized areas. The mass loading per inhabitant showed that most pharmaceutical usage was higher in the urban core compared to the suburban zones, suggesting the high consumption of PPCPs for the people living in the urban core. In addition, the mass loadings for the effluent and sludge were higher in the urban core, indicating that we should pay more attention in the urban core for the PPCP contamination, due to the high population density and more PPCP consumption. The effluent and waste sludge could share close proportions for the potential PPCP releasing to the receiving environment. However, the results emphasize the importance of proper disposal of waste sludge to prevent a large quantity of PPCPs from being released into the environment.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2015.10.003.

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