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RESEARCH ARTICLE

Occurrence and removal of six pharmaceuticals and personal care products in a wastewater treatment plant employing anaerobic/anoxic/aerobic and UV processes in Shanghai, China

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Abstract The occurrence and removal of six pharmaceuticals and personal care products (PPCPs) including caffeine (CF), N, N-diethyl-meta-toluamide (DEET), carbamazepine, metoprolol, trimethoprim (TMP), and sulpiride in a municipal wastewater treatment plant (WWTP) in Shanghai, China were studied in January 2013; besides, grab samples of the influent were also taken every 6 h, to investigate the daily fluctuation of the wastewater influent. The results showed the concentrations of the investigated PPCPs ranged from 17 to 11,400 ng/L in the WWTP. A low variability of the PPCP concentrations in the wastewater influent throughout the day was observed, with the relative standard deviations less than 25 % for most samples. However, for TMP and CF, the slight daily fluctuation still reflected their consumption patterns. All the target compounds except CF and DEET, exhibited poor removal efficiencies (<40 %) by biological treatment process, probably due to the low temperature in the bioreactor, which was unfavorable for activated sludge. While for the two biodegradable PPCPs, CF, and DEET, the anaerobic and oxic tank made contributions to their removal while the anoxic tank had a negative effect to their elimination. The tertiary UV treatment removed the investigated PPCPs by 5–38 %, representing a crucial polishing step to compensate for the poor removal by the biologic treatment process in winter.

Keywords Pharmaceuticals and personal care products · Wastewater treatment plant · Daily fluctuation · Removal · UV disinfection

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Introduction

The release of pharmaceuticals and personal care products (PPCPs) has attracted much public attention (Hollender et al. 2009; Camacho-Muñoz et al. 2010; Sui et al. 2010; Salgado et al. 2012) because of their intrinsic biological activity which may cause adverse effects to aquatic and terrestrial ecosystems (Sorensen et al. 1998; Öllers et al. 2001). These compounds might be excreted by excreta and disposal of unused or expired drugs and eventually reach the wastewater treatment plants (WWTPs) (Escher et al. 2011; Nelson et al. 2011). Ineffective operations of WWTPs make their widespread appearance in the aquatic environment possible (Zhang et al. 2008; Daneshvar et al. 2012), leading to the contamination of surface water, ground water, and eventually, drinking water, where they pose a negative impact to humans (Cleuvers et al. 2004; Schnell et al. 2009). Therefore, knowledge about the occurrence, fate, and transport of PPCPs in WWTPs is of great significance.

The concentrations of PPCPs in WWTP wastewaters were routinely monitored in many countries (Castiglioni et al. 2006; Jones et al. 2007; Santos et al. 2007; Vieno et al. 2007; Jelic et al. 2011; Martín et al. 2012; Salgado et al. 2012; Duan et al. 2013). However, little attention was paid to the daily variation of PPCPs, which was crucial to evaluate their behavior in the WWTPs. Nelson et al. (2011) investigated the diurnal variability of 30 PPCPs in tertiary wastewater effluent, and indicated that trimethoprim, sulfamethoxazole, naproxen, estrone, and triclosan varied greatly during a daily cycle, with relative standard deviations (RSDs) exceeding 100 %. However, some compounds including carbamazepine, primidone, fluoxetine, and triclocarban exhibited little or no variability. Göbel et al. (2005) and Plósz et al. (2010) assessed diurnal variations in the influents using three 8-h flow-proportional composite samples obtained in one sampling day, and suggested that daily antimicrobials and antibiotics loads can correlate with the respective water flows and ammonium loads.

The anaerobic/anoxic/aerobic (A^2/O) process is extensively employed in WWTPs throughout the world (Jelic et al. 2011), mostly because it can produce effluents that meet the required quality standards (suitable for disposal or recycling purposes), at reasonable operating and maintenance cost. However, concerning the removal of PPCPs, quite variable removal efficiencies were observed in the previous studies due to chemical and biological properties of individual PPCP as well as wastewater characteristics and operational conditions. For instance, Castiglioni et al. (2006) observed low or no removal for salbutamol, furosemide, and bezafibrate, whereas Kasprzyk-Hordern et al. (2009) noted much higher removal of these compounds (>70 %). Seasonal variation of the removal performance by A^2/O was also observed. Castiglioni et al. (2006) reported a removal of 10 % for atenolol during the winter months and much better elimination in summer (55 %) due to different microbial activities. However, these studies simply focused on the PPCPs in raw influent and final effluent, as well as their overall removal efficiencies. In order to comprehensively evaluate the fate, distribution, and mass balance of PPCPs, Nie et al. (2012) and Duan et al. (2013) investigated the occurrence and release of five acidic pharmaceuticals and seven endocrine-disrupting chemicals in different units of municipal WWTPs employing A^2/O process, respectively.

Ultraviolet (UV) radiation and UV combined with hydrogen peroxide have been extensively studied as a tertiary treatment for the PPCPs removal from wastewaters. Most of the studies were carried out in lab-scale reactors rather than in full-scale treatment systems. Pereira et al. (2007a, 2007b) monitored the degradation of the selected pharmaceutical active compounds using a UV system in a batch reactor, and proved that the UV system was efficient in degrading some of the targeted compounds (such as ketoprofen and ciprofloxacin) at 100 mJ/cm^2. However, when the UV photolysis was implemented in full-scale WWTPs, more factors, including fluence rate distribution, hydraulics, reactor design, and electrical energy, might influence its performances. Recently, an investigation on the removal of 79 PPCPs by UV radiation used for disinfection in a full-scale WWTP in Portugal has been reported and revealed that UV radiation played an important role in reducing the concentrations of some target compounds (Salgado et al. 2012).

Thus, in this study, we conducted a detailed investigation on six PPCPs belonging to different groups (anticonvulsant, stimulant, antibiotics, insect repellent, antipsychotic, and antihypertensive) in a full-scale WWTP employing A^2/O-UV process in Shanghai, China, to gain an insight into their occurrence and removal along the different units taking into account the raw influent, primary treatment, secondary treatment (anaerobic, anoxic, aerobic tank, respectively), and tertiary treatment process. Special emphasis was laid on the daily fluctuations of PPCPs in the WWTP influent, which was seldom reported in China, to the best of the authors' knowledge.

Materials and methods

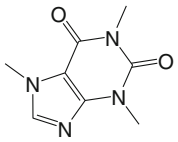
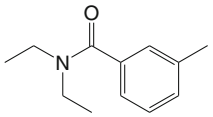
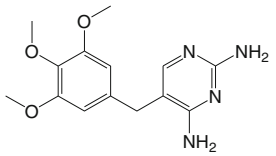
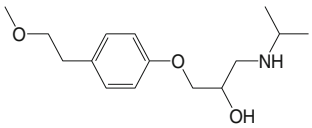
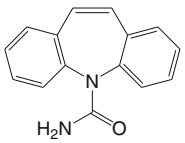
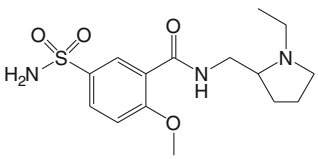
Chemicals and standards

PPCP standards (Table 1) as well as the internal standards (IS), DEET-^{7}D and Phenacetin-^{13}C, were purchased from Dr. Ehrenstorfen (Augsburg, Germany). High-performance liquid chromatography (HPLC)-grade formic acid and methanol were purchased from Fisher Chemical Company (Beijing, China). Sodium hydroxide (NaOH), ammonium acetate and hydrochloric acid (HCl) were of analytical grade and obtained from Merck (Darmstadt, Germany). Ultrapure water was obtained with Nanopure ultrapure water system from Barnstead/Thermolyne (Dubuque, IA). Stock solutions of individual compound were prepared in methanol. Working solutions were prepared by diluting the stock standard solutions and stored at 4 °C in the dark.

Sample collection

The investigated WWTP is located by the Huangpu River, the most important river across Shanghai City. The WWTP, serving 250,000 population equivalents, was designed for a capacity of 50,000 m^3/day and fed with mainly domestic wastewater. As shown in Fig. 1, the WWTP employed a physicochemical primary treatment process (screen and primary clarifier) coupled with biological treatment process (anaerobic tank, anoxic tank, oxic tank, and secondary clarifier). After settling in the secondary clarifier, part of the activated sludge was returned to the anaerobic tank (return sludge ratio: 100 %), and the rest of the sludge was conveyed to be

Table 1 Therapeutic classes, chemical structures, physicochemical properties and corresponding IS for selected PPCPs

Compounds	Therapeutic class	Chemical structure	log K_{ow} [1]	pK_a [1]	Corresponding IS
caffeine (CF)	Stimulant		-0.07	10.4	Phenacentin-^{13}C
N, N-diethyl -meta-tolua mide (DEET)	Insect repellent		2.18	< 2.0	DEET-^{7}D
trimethopri m (TP)	Antibiotic		0.91	7.1	Phenacentin-^{13}C
metoprolol (MTP)	Anti-hypertensive		1.88	9.7	Phenacentin-^{13}C
carbamazepi ne (CBZ)	Anticonvulsant		2.25-2.45	13.9	Phenacentin-^{13}C
sulpiride (SP)	Antipsychotic		1.10	9.1, 10.0	Phenacentin-^{13}C

[1] From Sui et al., 2010

dehydrated. The sludge retention time (SRT) was 20 days and hydraulic retention time (HRT) was 13–15 h (the HRTs of anaerobic tank, anoxic tank, and oxic tank were 1.0, 4.0, and 8.3 h, respectively). Finally, effluent of secondary clarifier went through UV disinfection unit (UV3000Plus, Trojan). The UV disinfection unit had two channels. Each was equipped with 120 UV lamps (low pressure, wavelength of 254 nm, 30 W), operating at the UV dosage of 95 mW/cm^2,

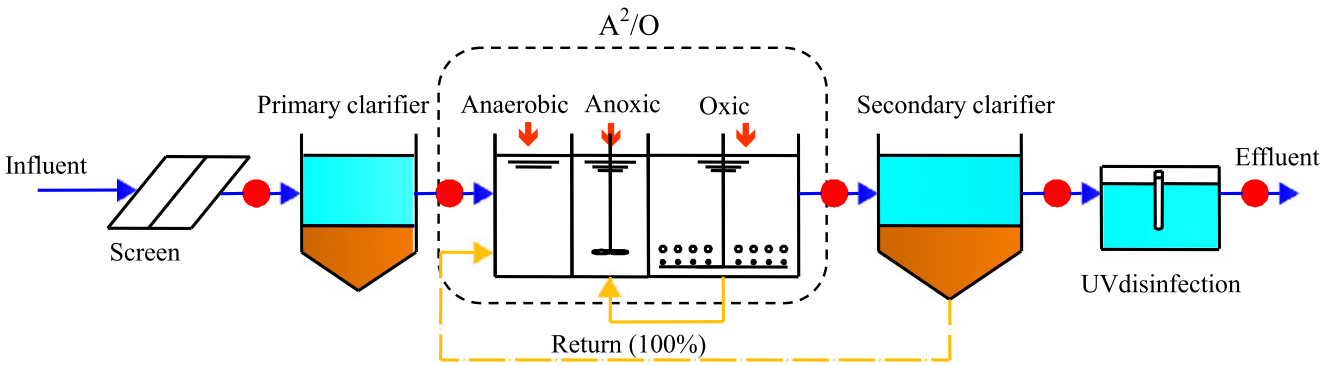


Fig. 1 Schematic diagram of the treatment processes in the WWTP and sampling sites location (*circles* and *downward arrows*)

and the total suspended solids was approximately 20 mg/L. The operation parameters of the WWTP during the sampling are presented in Table 2.

The sampling campaign was conducted in January 2013. Twenty-four-hour composite samples with the sampling interval of 6 h were taken. The sampling sites are displayed in Fig. 1. The wastewater samples were collected in amber glass bottles in duplicate and had been washed with methanol and purified water, immediately placed on ice, transported to the laboratory, and stored at 4 °C until extraction.

Sample preparation, extraction, and analysis

The method for sample preparation and extraction followed a previously developed method (Sui et al. 2009). Water samples were filtered using glass fiber filters (Whatman). Then, filtered water samples (100 mL for influent and primary clarifier and 400 mL for the others) were spiked with 200-μL internal standards and adjusted to pH=7 with 1 mol/L HCl and NaOH solutions. Following this, solid phase extraction (SPE) was performed using a 12-fold vacuum extraction manifold device (Supelco, USA). The Oasis HLB (Waters) cartridges (200 mg, 6 ml for influent and effluent of primary treatment; 500 mg, 6 ml for others) were conditioned with 5-mL methanol and 3× 5-mL ultrapure water. Then, samples were loaded onto conditioned SPE cartridges at a flow rate of 3–5 mL/min. After the enrichment step, the cartridges were washed with 5-mL methanol/water (v/v=1:19) and dried for 30 min under full vacuum. Finally, the analytes were eluted with 5-mL methanol and collected in 10-mL glass tubes. The solvent was evaporated to dryness under gentle N_2 flow, and redissolved in 0.4 mL methanol/water (v/v=1:4).

High-performance liquid chromatography (HPLC, Ultimate3000, Dionex, USA) followed by electrospray ionization and tandem mass spectrometry (ESI-MS/MS, API3200, AB Sciex, USA) was applied to quantify the target PPCPs. The PPCPs were analyzed in positive electrospray ionization (ESI+) and multiple reaction monitoring mode. The analytical method was slightly modified from Chen et al. (2012). Separation was performed on a ZORBAX Eclipse XDB C18 column (3.5 μm, 2.1×150 mm), using ultrapure water (solvent A) with 0.1 % formic acid and methanol (solvent B) as the mobile phase. The elution gradient program was as follows: from 15 to 50 % solvent B in 2 min, then to 100 % in 6 min, hold for 8 min, and back to the initial conditions in 14 min. The flow rate was 0.30 mL/min, and the injection volume was set at 10 μL. Quantification was performed following the internal standard calibration approach.

Biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), NH_3-N, total nitrogen (TN), and total phosphorus (TP) of collected samples were measured using standard methods (APHA et al. 1998).

Table 2 Wastewater characterization parameters for influent and effluent of the investigated WWTP during sampling campaign

Parameters	Influent	Effluent
Average flow (m^3/day)	49,094	
Equipment intact (%)	97	
BOD_5 (mg/L)	123.9	8.9
SS (mg/L)	121.1	12.2
COD_{cr} (mg/L)	171.1	25.2
NH_3-N (mg/L)	22.0	1.1
TN	38.4	12.1
TP	3.55	0.52
Sludge (t)	644.32	

Method validation

During sampling, field blanks (500-mL ultrapure water in amber glass bottles) were taken to site, exposed to the environment at the sampling sites. For each set of samples analyzed, a procedure blank and a recovery test sample were analyzed identically to wastewater samples. All the procedure and field blanks were below the limit of quantification (LOQ). All the samples were extracted and analyzed in duplicate, and the analytical results were reported as the average of two values.

The relative recovery (RR%) was calculated by spiking a known concentration of the 12 standard target analytes, according to Eq. (1) (Tixier et al., 2003):

$$RR(\%) = \frac{C_{ss} - C_{os}}{C_s} \times 100 \quad (1)$$

where C_{ss} and C_{os} are measured concentrations in the spiked and correspondingly unspiked water samples, respectively; C_s is the known spiking concentration.

The relative recoveries were proved to be 72–115, 81–128, and 82–122 % in the effluent, influent, and ultrapure water for most compounds, respectively. While for caffeine (CF), the recoveries in the influent samples were not satisfactory due to its high background concentration in the influent. The LOQ, set at S/N ratios ≥10, was 0.2–2.1 ng/L. Detailed information about the LOQ and RR are briefly listed in Table 3.

Results and discussion

Concentrations of PPCPs in wastewater

Influent

The PPCP concentrations in the WWTP influent varied from 17 to 11,400 ng/L, as shown in Fig. 2. CF was most abundant

Table 3 Limit of quantification (LOQ) and relative recovery (*RR*) for selected PPCPs in the ultrapure water, wastewater effluent, and influent

Compounds	LOQ (ng/L)			*RR* (%) (*n* = 4)		
	Ultrapure water	Influent	Effluent	Ultrapure water	Influent	Effluent
TMP	0.4	2.1	0.5	104 (8)[1]	80 (3)	87 (3)
MTP	0.3	1.2	0.2	102 (10)	86 (5)	110 (2)
CBZ	0.4	2.1	0.6	122 (12)	93 (4)	89 (14)
CF	0.3	0.9	0.3	96 (5)	143 (68)	96 (6)
DEET	0.2	0.8	0.2	97 (3)	95 (15)	94 (2)
SP	0.2	0.8	0.2	97 (2)	115 (5)	128 (6)

[1] Value in the brackets refers to the deviation of the recovery

in the WWTP influent, which can be attributed to its daily consumption besides pharmaceutical use, such as uptake with beverages and foods (Ogunseitan 1996). Slightly high concentrations of TMP (257 ng/L), sulpiride (SP) (143 ng/L), and metoprolol (MTP) (122 ng/L) were found. The concentration of MTP was consistent with its increased dosage in winter, when the blood pressure is relatively higher than other seasons (Brennan et al. 1982). N, N-diethyl-meta-toluamide (DEET) (66 ng/L) and carbamazepine (CBZ) (17 ng/L) were detected in raw wastewater at low concentrations (Fig. 2). The low concentration of DEET, one of the most efficient insect repellents, was probably because it is normally used less frequently in winter (Fradin et al. 2002).

The contamination levels of investigated PPCPs were low in Shanghai, compared to other reported studies. For instance, the concentration of CBZ was at least two times lower than those reported in Spain (70–1,400 ng/L) (Jelic et al. 2011; Martín et al. 2012) and USA (34–350 ng/L) (Yu et al. 2013). TMP, commonly used in combination with sulfonamides as a potentiator (Loftin et al. 2008), was slightly less than those in the influents of WWTPs in Sweden (100–1,300 ng/L) (Lindberg et al. 2005) and Beijing (700 ng/L) (Zhou et al. 2010). The anti-hypertensive MTP in the influent was recorded to be 122 ng/L in Sweden (Bendz et al. 2005), comparable with that in the wastewater influent of Shanghai. The lower

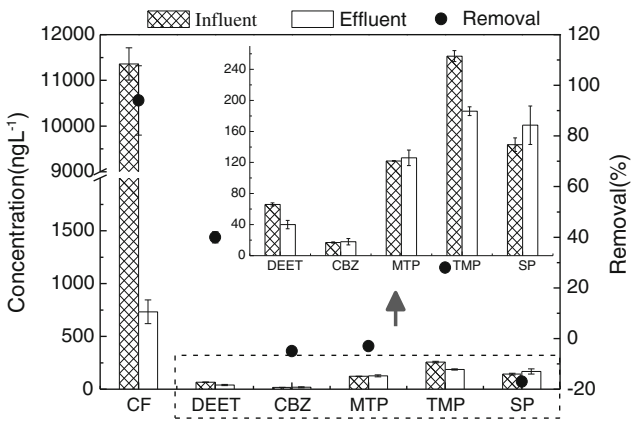


Fig. 2 Concentrations of target PPCPs in the wastewater influents and effluents as well as the removal efficiencies by the treatment process of the WWTP in Shanghai

contamination level in the WWTP of Shanghai might be ascribed to lower per capita consumption in this area, as defined by Diaz-Cruz et al. (2009) that the concentrations of PPCPs detected in the wastewater reflect their use in the society. Besides, the different types of products in pharmaceutical market in different countries and regions (Miege et al. 2009) can also be an explanation for the lower concentrations of investigated PPCPs.

To assess the daily fluctuation and dynamic behavior of selected PPCPs in the wastewater influent, grab samples were collected every 6 h and analyzed. The concentrations of PPCPs in the grab samples as well as the RSDs between grab and 24-h composite samples are presented in Fig. 3.

In general, the six PPCPs had low variability throughout a day, with the RSDs less than 25 % for most samples, which agreed with that reported in Guangzhou City of China in the dry season (Xu et al. 2006). Also, Sui et al. (2011) observed the RSDs of grab and 2-h composite samples did not exceed 30 % in the influent and 15 % in the effluent in a WWTP of Beijing. It seemed that the concentrations of PPCPs showed no sensitive daily change in many regions of China. One of the explanations for this phenomena might be the complex configuration of sewer systems connected with the WWTPs. The sewer systems receive wastewater in different regions at different times, which lead to a reduction of peak concentrations of some PPCPs. Besides, the configuration of sewer also affects the fraction of deconjugated compounds arriving at WWTPs (Suárez et al. 2008). Furthermore, the WWTPs in these regions usually have relatively large treatment capacity, which might be benefit for minimizing the fluctuation.

However, in the case of TMP and CF, the daily fluctuation still reflected their consumption patterns although it was not significant. The distribution of TMP daily load correlated well with its typical oral prescription of once a day (Göbel et al. 2005), normally in the morning. Therefore, high degree of human excretion is expected in the morning, which can explain the decreasing daily concentration. CF showed a gradually increase increasing daily profile in the daytime and the lowest load in the midnight. It was most likely caused by the consumption pattern and life habit.

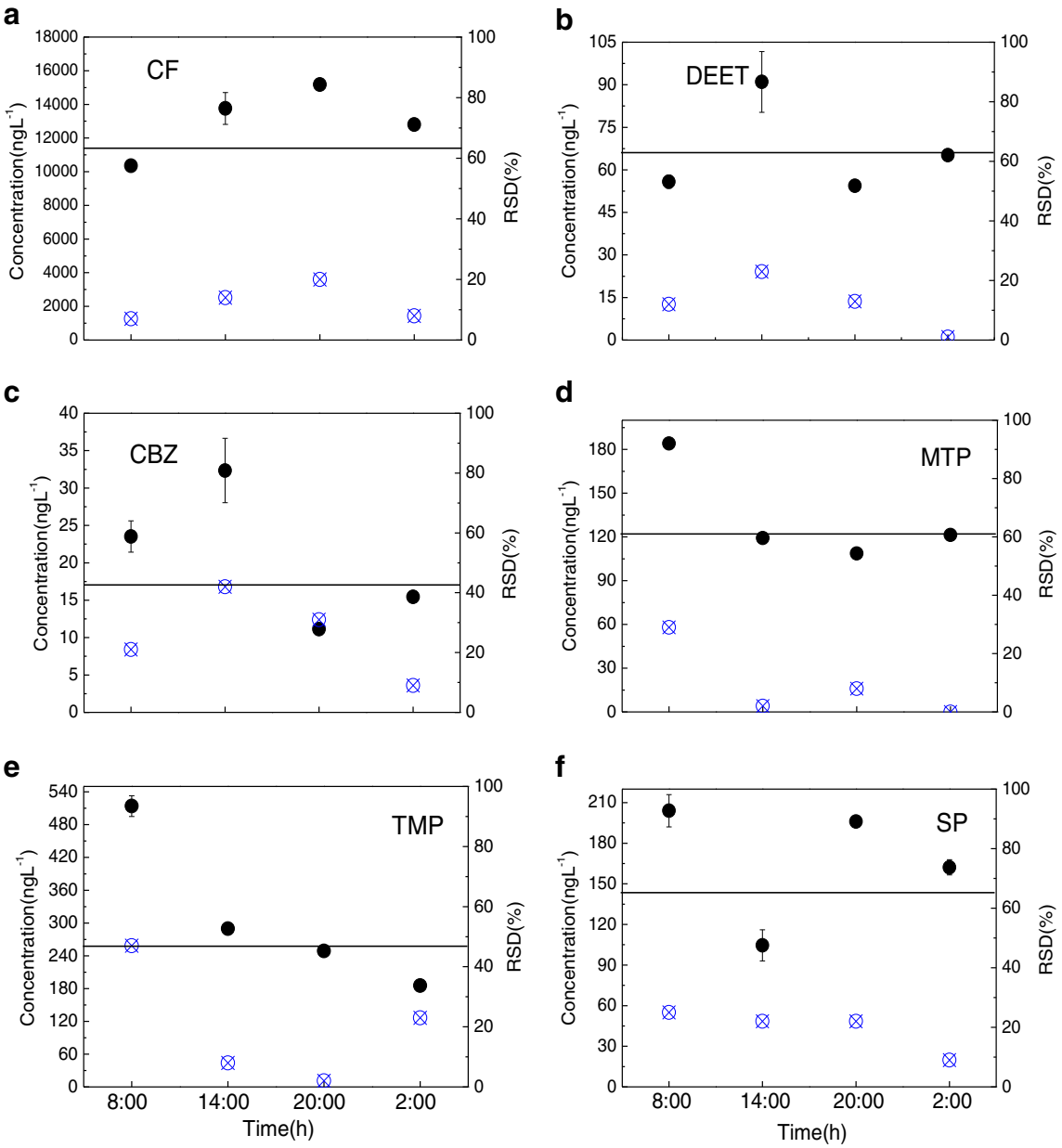


Fig. 3 Daily fluctuation of the PPCP concentrations (*circles*) and the relative standard deviation (RSD) (*crossed circles*) between grab and 24-h composite samples (*solid line*)

Effluent

It is noted that the composition profiles of the target PPCPs in the final effluents were quite similar to the influent samples. CF (733 ng/L) was dominant in the effluent, TMP (186 ng/L), SP (168 ng/L) and MTP (126 ng/L) followed. Also, DEET (40 ng/L) and CBZ (18 ng/L) were detected at low levels. Effluents of WWTPs could be the major sources for PPCPs in the surface waters (Escher et al. 2011; Nelson et al. 2011). Fortunately, concentrations of PPCPs in the WWTP effluent were similar to or lower than those reported before (Gomez et al. 2007; Santos et al. 2007; Vieno et al. 2007; Gulkowska et al. 2008; Camacho-Munoz et al. 2010; Jelic et al. 2011; Martín et al. 2012; Yu et al. 2013). For example, CBZ was found in the wastewater effluents of Spain and USA at the concentrations of 50–150 and 21 ng/L, respectively (Martín et al. 2012; Yu et al. 2013), slightly higher than that in the WWTP effluent of Shanghai. TMP were detected in five WWTPs of Hong Kong and Shenzhen, with the concentrations of 120–230 ng/L in the effluents (Gulkowska et al. 2008), consistent with the finding in our study.

Ecotoxicological risk assessment is evaluated by means of risk quotient (RQ) value, usually expressed as the ratio between the measured environmental concentration and the predicted no-effect concentration of individual compound (Santos et al. 2007). As shown in Fig. 4, the RQ values of investigated

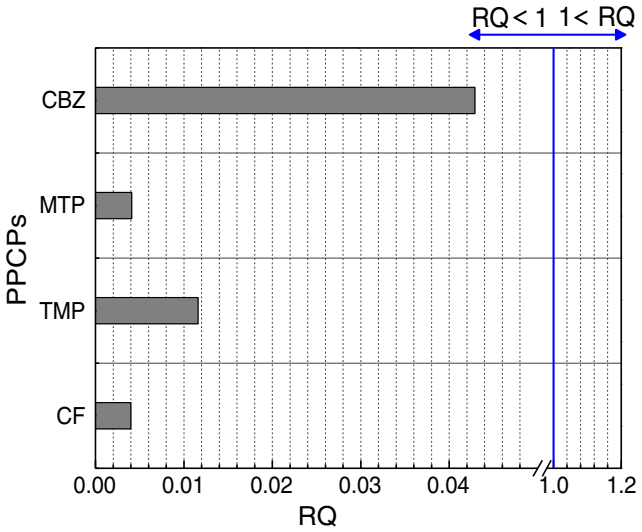


Fig. 4 Risk quotient (RQ) values of some PPCPs in the wastewater effluent

PPCPs were all below 1, varied between 0.0038 and 0.0659 in the wastewater effluent. Therefore, environmental risk, with the current use of these compounds, was unlikely.

Removal efficiency

Primary treatment

Adsorption is the main mechanism in the removal of micropollutants during primary treatment (Suárez et al. 2008). From Fig. 5, the primary clarifier showed poor removal efficiencies for most PPCPs. A reduction of less than 20 % was observed for all the six PPCPs in the primary treatment process, owing to their hydrophilic nature. The compounds studied in this study are of low octanol–water partition coefficient (K_{ow}) values (<3.0, as shown in Tab. 1), and are expected not to adsorb greatly to the particles, but to dissociate in the aqueous phase (Thomas and Foster. 2005; Salgado et al. 2012).

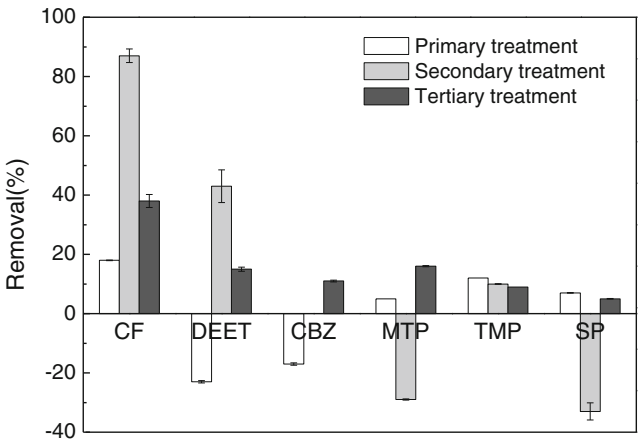


Fig. 5 Removal efficiencies of the target PPCPs in the primary, secondary and tertiary treatment processes

Secondary treatment

The removal efficiencies of investigated PPCPs by secondary treatment process ranged from −33 to 87 % (Fig. 5). CF has been proven to be readily biodegradable (>98 %) (Huerta-Fontela et al. 2008; Okuda et al. 2008; Sui et al. 2010; Xue et al. 2010), while only 87 % removal was observed in this study. Likewise, CF was eliminated by 79, 86, and 93 % during the winter months (December, January, and February, respectively) in a Beijing WWTP employing A/A/O process(Sui et al. 2011). The removal efficiency for DEET was 43 %, which was similar to or slightly less than values reported in other studies (Knepper 2004; Costanzo et al. 2007; Sui et al. 2010; Zhou et al. 2010). No significant overall removal rates during secondary treatment were observed for TMP and CBZ. The incomplete removal of these compounds during conventional treatment was reported by several studies (Göbel et al. 2005; Kasprzyk-Hordern et al. 2009; Behera et al. 2011; Jelic et al. 2011;). Göbel et al. (2005) reported that TMP was neither biodegraded nor adsorbed. Pérez et al. (2007), Behera et al. (2011), Jelic et al. (2011), and Martín et al. (2012) reported that CBZ could be hardly removed regardless of secondary treatment process applied. Therefore, CBZ is proposed as an anthropogenic marker (Clara et al. 2004; Nakada et al. 2006). Surprisingly, the concentrations of MTP and SP increased from 116 and 133 ng/L before the secondary treatment to 150 and 177 ng/L after the secondary clarifier, respectively. The case could be explained by cleavage of conjugates (glucuronides, sulfates) of target compounds (Carballa et al. 2004; Galán et al. 2012) and/or analytical deviations.

In general, the removal of most investigated PPCPs by the secondary treatment process was low and even negligible. The SRT and HRT were relatively high (20 days and 13–15 h, respectively) in the investigated WWTP, higher than the critical SRT and HRT proposed by Jones et al. (2007) and Vieno et al. (2007b). Thus, it could be excluded as the main influencing factors. However, as the sampling was conducted during winter (January), the low temperature (9.6 °C in the bioreactor), unfavorable for activated sludge, could be the cause of the inefficient removal during the biological treatment process. Clara et al. (2004) and Castiglioni et al. (2006) also found significantly low removal rates for several pharmaceuticals in winter, for example, the removal rates of atenolol, bezafibrate, and enalapril were 10, 15, and 18 % in winter and 55, 87, and 100 % in summer, respectively, in line with a temperature-dependent increase of microbial activity (average temperatures 9.7 °C in winter and 18.6 °C in summer). Through a lab-scale experiment model, Wick et al. (2009) found that there was a crucial temperature below of which the biodegradation of certain beta blockers and psycho-active drugs was completely inhibited, and suggested that lower temperature led to reduced rate constants. A batch experiment

on the removal of TMP under different temperatures by activated sludge collected from the WWTP was conducted, and the preliminary results also confirmed that the temperature had significantly negative effect on its removal from wastewater (as shown in Supporting Information).

The removal of two biodegradable PPCPs (CF and DEET) in each tank (anaerobic, anoxic, and oxic tank) during the secondary treatment process was further studied. As parts of the wastewater were recycled from the secondary clarifier to the anaerobic tank and from the oxic to the anoxic tank, it is improper to calculate the removal efficiency by concentration, due to dilution. Thus, we employ a mass load approach to assess the removal of CF and DEET (Eq.2).

$$\text{Removal}(\%) = \frac{C_{in}\cdot(Q_{in}+Q_{rec}) - C_{out}\cdot Q_{out}}{C_{in}\cdot(Q_{in}+Q_{rec})} \times 100 \qquad (2)$$

where C_{in}, C_{out}, Q_{in}, Q_{out}, and Q_{rec} are the measured compound concentration (nanogram per liter) and the flow mass of the wastewater (cubic meter per day) of inlet, outlet, and recirculation in the investigated tank, respectively.

As shown in Fig. 6, the anaerobic tank seemed to be crucial for CF and DEET removal. A 60–70 % reduction was observed for CF and DEET in the anaerobic tank. Oxic tank followed, with the removal efficiencies of 55 % (for CF) and 3 % (for DEET), respectively. On the contrary, negative removal rates were found for the two PPCPs in anoxic tank.

The rapid decrease of PPCP concentrations in the anaerobic tank could ascribe to the sorption or degradation by some types of activated sludge (Xue et al. 2010). For instance, the phosphate accumulating organisms might use PPCPs as carbon sources during the phosphorus release process (Xue et al. 2010). In oxic tank, the available condition allows the development of slow-growing bacteria, such as nitrifiers, and the retention of exocellular enzymes or soluble oxidants (Galán et al. 2012), which might be beneficial for the degradation of

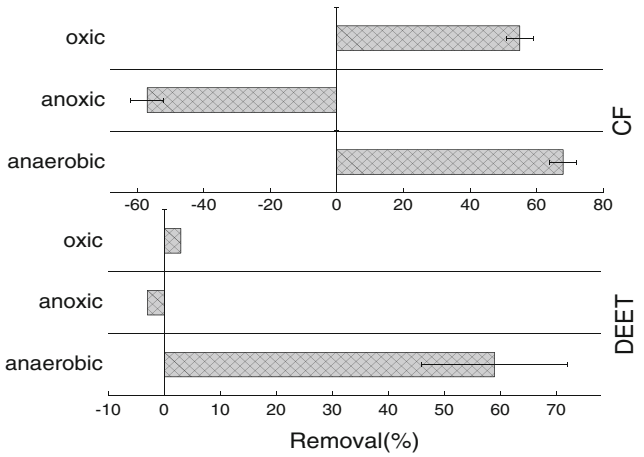


Fig. 6 Removal efficiencies of CF and DEET in each tank of A^2/O process. The *error bars* represent the maximum and minimum removal efficiencies by oxic, anoxic, and anaerobic tank

PPCPs. The negative removal during anoxic tank was consistent with our previous finding (Sui et al. 2010). We conducted a survey of CF, DEET, BF, and TMP along the A^2/O-MBR process in a WWTP of Beijing, and found the amounts of most PPCPs increased after the anoxic tank. We supposed it could be a consequence of (1) deconjugation of conjugated metabolites during the treatment process (Miao et al. 2002); and (2) a change in the adsorption behavior of compounds to particles during treatment process (Lindberg et al. 2005).

Tertiary treatment

As shown in Fig. 5, the tertiary UV treatment seemed to be positively effective in removing investigated PPCPs. Moderate reduction for CF, DEET, MTP, CBZ, and TMP by UV radiation was obtained. It was interesting that the refractory substances CBZ and MTP, which were barely removed by primary and secondary treatment processes, achieved a slightly better removal in the tertiary treatment process (CBZ=11 % and MTP=16 %). Salgado et al. (2012) also found that UV radiation had an important role in reducing some PPCPs, such as diclofenac, ibuprofen, clorazepate (25–75 %) and indapamide, enalapril, captopril, atenolol (>75 %). Some PPCPs themselves are readily subjected to photolysis (Pereira et al. 2007a, b), and others might be decomposed by UV treatment in the presence of humic acids existing in the wastewater secondary effluent. Humic acids submitted to UV irradiation are promoted to a transient and excited state, in which they may react with oxygen, forming reactive species as singlet oxygen, or react directly with other organic species, thus promoting their phototransformation (Andreozzi et al. 2003).

Conclusion

The occurrence and removal of six PPCPs (CF, DEET, CBZ, MTP, TMP, and SP) in a municipal WWTP that employed the A^2/O-UV process in Shanghai, China were studied. The concentrations ranged from 17 to 11,400 ng/L in the influent and from 18 to 733 ng/L in the effluent, respectively, which presented a lower level compared to other countries. The concentrations of PPCPs in the wastewater influent showed a low variability throughout the day, with the RSDs less than 25 % for most samples. However, for TMP and CF, the slight daily fluctuation still reflected their consumption patterns. The biological treatment process showed inefficient removal for most PPCPs, probably due to the low temperature in winter, and for the two biodegradable PPCPs, CF, and DEET, the anaerobic and oxic tank made contribution to their removal while anoxic tank had negative effect to their elimination. As a tertiary treatment, UV photolysis removed all the investigated PPCPs by 5–38 %, representing a polishing step to

compensate for the poor removal performance of PPCPs by biologic treatment process in winter.

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References

Andreozzi R, Raffaele M, Nicklas P (2003) Pharmaceuticals in STP effluents and their solar photodegradation in aquatic environment. Chemosphere 50(10):1319–1330

APHA, AWWA, WEF (1998) Standard methods for the examination of water and wastewater, 20th edn. APHA, Washington

Behera SK, Kim HW, Oh JE, Park HS (2011) Occurrence and removal of antibiotics, hormones and several other pharmaceuticals in wastewater treatment plants of the largest industrial city of Korea. Sci Total Environ 409(20):4351–4360

Bendz D, Paxéus NA, Ginn TR, Loge FJ (2005) Occurrence and fate of pharmaceutically active compounds in the environment, a case study: Höje River in Sweden. J Hazard Mater 122(3):195–204

Brennan PJ, Greenberg G, Miall WE, Thompson SG (1982) Seasonal variation in arterial blood pressure. Br Med J (Clin Res Ed) 285(6346):919–923

Camacho-Muñoz D, Martín J, Santos JLJ, Aparicio I, Alonso E (2010) Occurrence, temporal evolution and risk assessment of pharmaceutically active compounds in Doñana Park. J Hazard Mater 183(1–3): 602–608, Spain

Carballa M, Omil F, Lema JM, Llompartb M, García-Jaresb C, Rodríguezb I, Gómezc M, Ternes T (2004) Behavior of pharmaceuticals, cosmetics and hormones in a sewage treatment plant. Water Res 38(12):2918–2926

Castiglioni S, Bagnati R, Fanelli R, Pomati F, Calamari D, Zuccato E (2006) Removal of pharmaceuticals in sewage treatment plants in Italy. Environ Sci Technol 40(1):357–363

Chen YS, Cao QM, Deng SB, Huang J, Wang B, Yu G (2012) Determination of pharmaceuticals from various therapeutic classes in dewatered sludge by pressurized liquid extraction and high performance liquid chromatography and tandem mass spectrometry (HPLC-MS/MS). Intl J Environ Anal Chem 1(1):1–15

Clara M, Strenn B, Ausserleitner M, Kreuzinger N (2004) Comparison of the behaviour of selected micropollutants in a membrane bioreactor and a conventional wastewater treatment plant. Water Sci Technol 50(5):29–36

Cleuvers M (2004) Mixture toxicity of the anti-inflammatory drugs diclofenac, ibuprofen, naproxen, and acetylsalicylic acid. Ecotoxicol Environ Saf 59(3):309–315

Costanzo SD, Watkinson AJ, Murby EJ, Kolpin DW, Sandstr MW (2007) Is there a risk associated with the insect repellent DEET (N, N-diethyl-m-toluamide) commonly found in aquatic environments? Sci Total Environ 384(1–3):214–220

Daneshvar A, Aboulfadl K, Viglino L, Broséus R, Sauvé S, Madoux-Humery AS, Weyhenmeyer GA, Prévost M (2012) Evaluating pharmaceuticals and caffeine as indicators of fecal contamination in drinking water sources of the Greater Montreal region. Water Res 88(1):131–139

Diaz-Cruz MS, Garcia-Galan MJ, Guerra P, Jelic A, Postigo C, Eljarrat E, Farre M, DeAlda MJL, Petrovic M, Barcelo D (2009) Analysis of selected emerging contaminants in sewage sludge. TrAC Trends Anal Chem 28(11):1263–1275

Duan YP, Meng XZ, Wen ZH (2013) Acidic pharmaceuticals in domestic wastewater and receiving water from hyper-urbanization city of China (Shanghai): environmental release and ecological risk. Environ Sci Pollut Res 20(1):108–116

Escher BI, Baumgartner R, Koller M, Treyer K, Lienert J, Christa S, McArdell CS (2011) Environmental toxicology and risk assessment of pharmaceuticals from hospital wastewater. Water Res 45(1):75–92

Fradin MS DM, Day F (2002) Comparative efficacy of insect repellents against mosquito bites. N Engl J Med 347:13–18

Galán MJG, Díaz-Cruz MS, Barceló D (2012) Removal of sulfonamide antibiotics upon conventional activated sludge and advanced membrane bioreactor treatment. Anal Bioanal Chem 404(15):1505–1515

Göbel A, Thomsen A (2005) Occurrence and sorption behavior of sulfonamides, macrolides and trimethoprim in activated sludge treatment. Environ Sci Technol 39(11):3981–3989

Gomez MJ, Bueno MJM, Lacorte S, Fernandez-Alba AR, Aguera A (2007) Pilot survey monitoring pharmaceuticals and related compounds in a sewage treatment plant located on the Mediterranean coast. Chemosphere 66(6):993–1002

Gulkowska A, Leung HW, So MK, Taniyasu S, Yamashita N, Yeung LWY, Richardson BJ, Leic AP, Giesy JP, Lam PKS (2008) Removal of antibiotics from wastewater by sewage treatment facilities in Hong Kong and Shenzhen, China. Water Res 42(1–2):395–403

Hollender J, Zimmermann SG, Koepke S, Krauss M, McArdell CS, Ort C, Singer H, Gunten U, Siegrist H (2009) Elimination of organic micropollutants in a municipal wastewater treatment plant upgraded with a full-scale post-ozonation followed by sand filtration. Environ Sci Technol 43(20):7862–7869

Huerta-Fontela M, Galceran MT, Martin-Alonso J, Ventura F (2008) Occurrence of psychoactive stimulatory drugs in wastewaters in north-eastern Spain. Sci Total Environ 397(1–3):31–40

Jelic A, Gros M, Ginebreda A, Cespedes-Sánchez R, Ventura F, Petrovic M, Barcelo D (2011) Occurrence, partition and removal of pharmaceuticals in sewage water and sludge during wastewater treatment. Water Res 45(3):1165–1176

Jones OAH, Voulvoulis N, Lester JN (2007) The occurrence and removal of selected pharmaceutical compounds in a sewage treatment works utilising activated sludge treatment. Environ Pollut 145(3):738–744

Kasprzyk-Hordern B, Dinsdale RM, Guwy AJ (2009) The removal of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs during wastewater treatment and its impact on the quality of receiving waters. Water Res 43(2):363–380

Knepper TP (2004) Analysis and mass spectrometric characterization of the insect repellent Bayrepel and its main metabolite Bayrepel-acid. J Chromatogr A 1046(1–2):159–166

Lindberg RH, Wennberg P, Johansson MI (2005) Screening of human antibiotic substances and determination of weekly mass flows in five sewage treatment plants in Sweden. Environ Sci Technol 39(10): 3421–3429

Loftin KA, Adams CD, Meyer MT, Surampalli R (2008) Effects of ionic strength, temperature, and pH on degradation of selected antibiotics. Environ Qual 37(2):378–386

Martín J, Camacho-Muñoz D, Santos JL, Aparicio I, Alonso E (2012) Occurrence of pharmaceutical compounds in wastewater and sludge from wastewater treatment plants: removal and ecotoxicological impact of wastewater discharges and sludge disposal. J Hazard Mater 239–240:40–47

Miao XS, Koenig BG, Metcalfe CD (2002) Analysis of acidic drugs in the effluents of sewage treatment plants using liquid chromatography-electrospray ionization tandem mass spectrometry. J Chromatogr A 952(1–2):139–147

Miege C, Choubert JM, Ribeiro L, Eusebe M, Coquery M (2009) Fate of pharmaceuticals and personal care products in wastewater treatment plants-conception of a database and first results. Environ Pollut 157(5):1721–1726

Nakada N, Tanishima T, Shinohara H, Kiri K, Takada H (2006) Pharmaceutical chemicals and endocrine disrupters in municipal wastewater in Tokyo and their removal during activated sludge treatment. Water Res 40(17):3297–3303

Nelson ED, Do H, Lewis RS, Carr SA (2011) Diurnal variability of pharmaceutical, personal care product, estrogen and alkylphenol concentrations in effluent from a tertiary wastewater treatment facility. Environ Sci Technol 45(4):1228–1234

Nie Y, Qiang Z, Zhang H, Ben W (2012) Fate and seasonal variation of endocrine-disrupting chemicals in a sewage treatment plant with A/A/O process. Sep Purif Technol 84(1):9–15

Ogunseitan OA (1996) Removal of caffeine in sewage by *Pseudomonas putida*: implications for water pollution index. World J Microbiol Biotechnol 12(3):251–256

Okuda T, Kobayashi Y, Nagao R, Yamashita N, Tanaka H, Tanaka S, Fujii S, Konishi C, Houwa I (2008) Removal efficiency of 66 pharmaceuticals during wastewater treatment process in Japan. Water Sci Technol 57(1):65–71

Öllers S, Singer HP, Fässler P, Müller SR (2001) Simultaneous quantification of neutral and acidic pharmaceuticals and pesticides at the low-ng/L level in surface and waste water. J Chromatogr A 911(2):225–234

Pereira VJ, Linden KG, Weinberg HS (2007a) Evaluation of UV irradiation for photolytic and oxidative degradation of pharmaceutical compounds in water. Water Res 41(19):4413–4423

Pereira VJ, Weinberg HS, Linden KG, Singer PC (2007b) UV degradation kinetics and modeling of pharmaceutical compounds in laboratory grade and surface water via direct and indirect photolysis at 254 nm. Environ Sci Technol 41(5):1682–1688

Pérez S, Barceló D (2007) Fate and occurrence of X-ray contrast media in the environment. Anal Bioanal Chem 387(4):1235–1246

Plósz BG, Leknesb H, Liltveda H, Thomas KV (2010) Diurnal variations in the occurrence and the fate of hormones and antibiotics in activated sludge wastewater treatment in Oslo, Norway. Sci Total Environ 408(8):1915–1924

Salgado R, Marques R, Noronha JP, Eusèbe M, Coquery M (2012) Assessing the removal of pharmaceuticals and personal care products in a full-scale activated sludge plant. Environ Sci Pollut Res 19(5):1818–1827

Santos JL, Aparicio I, Alonso E (2007) Occurrence and risk assessment of pharmaceutically active compounds in wastewater treatment plants. A case study: Seville city. Environ Intl 33(4):596–601, Spain

Schnell S, Bols NC, Barata C, Porte C (2009) Single and combined toxicity of pharmaceuticals and personal care products (PPCPs) on the rainbow trout liver cell line RTL-W1. Aquat Toxicol 93(4):244–252

Sorensen BH, Nielsen SN, Lanzky PF, Ingerslev F, Lutzhotf HCH, Jorgensen SE (1998) Occurrence, fate and effects of pharmaceutical substances in the environment—a review. Chemosphere 36(2):357–393

Suárez S, Carballa M, Omil F, Lema JM (2008) How are pharmaceutical and personal care products (PPCPs) removed from urban wastewaters? Rev Environ Sci Biotechnol 7(2):125–138

Sui Q, Huang J, Deng SB, Yu G (2009) Rapid determination of pharmaceuticals from multiple therapeutic classes in wastewater by solid-phase extraction and ultra-performance liquid chromatography tandem mass spectrometry. Chin Sci Bull 54(24):4633–4643

Sui Q, Huang J, Deng SB, Yu G, Fan Q (2010) Occurrence and removal of pharmaceuticals, caffeine and DEET in wastewater treatment plants of Beijing, China. Water Res 44(2):417–426

Sui Q, Huang J, Deng SB, Chen WW, Yu G (2011) Seasonal variation in the occurrence and removal of pharmaceuticals and personal care products in different biological wastewater treatment processes. Environ Sci Technol 45(8):3341–3348

Thomas PM, Foster GD (2005) Tracking acidic pharmaceuticals, caffeine and triclosan through the wastewater treatment process. Environ Toxicol Chem 24(1):25–30

Tixier C, Singer HP, Oellers S, Muller SR (2003) Occurrence and fate of carbamazepine, clofibric acid, diclofenac, ibuprofen, ketoprofen and naproxen in surface waters. Environ Sci Technol 37(6):1061–1068

Vieno NM, Härkki H, Tuhkanen T, Kronberg L (2007) Occurrence of pharmaceuticals in river water and their elimination a pilot-scale drinking water treatment plant. Environ Sci Technol 41(14):5077–5084

Wick A, Fink G, Joss A, Siegrist H, Ternes TA (2009) Fate of beta-blockers and psycho-active drugs in conventional wastewater treatment. Water Res 43(4):1060–1074

Xu WH, Zhang G, Zou SC, Li XD, Liu YC (2006) Occurrence and seasonal changes of antibiotics in the Victoria Harbour and the Pearl River, South China. Environ Sci 27(12):2458–2462 (in Chinese)

Xue WC, Wu CY, Xiao K, Huang X, Zhou HD, Tsuno H, Tanaka H (2010) Elimination and fate of selected micro-organic pollutants in a full-scale anaerobic/anoxic/aerobic process combined with membrane bioreactor for municipal wastewater reclamation. Water Res 44(20):5999–6010

Yu Y, Wu LS, Chang AC (2013) Seasonal variation of endocrine disrupting compounds, pharmaceuticals and personal care products in wastewater treatment plants. Sci Total Environ 442:310–316

Zhang Z, Hibberd A, Zhou JL (2008) Analysis of emerging contaminants in sewage effluent and river water: comparison between spot and passive sampling. Anal Chim Acta 607(1):37–44

Zhou HD, Huang X, Wang XL, Gao MJ, Wen XH, Tsuno H, Tanaka H (2010) Behaviour of selected endocrine-disrupting chemicals in three sewage treatment plants of Beijing, China. Environ Monit Assess 161(1–4):107–121