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Occurrence and Fate of PPCPs Wastewater Treatment Plants in Korea

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Abstract. We measured 62 Pharmaceuticals and Personal Care Products (PPCPs) in the samples taken from municipal wastewater treatment plants (WWTPs) in Korea to understand their occurrence and comparison of seasonal concentrations in WWTPs. Acetaminophen, caffeine, ibuprofen, naproxen and theophylline were detected at higher concentrations than other PPCPs (more than 4 μg/L) in influent. Sulpiride, atenolol, clarithromycin, roxithromycin and sulfapyridine were detected at high concentration (517 – 223 ng/L) in final effluent. Among the disinfection process, Ozonation and UV disinfection are efficient to removal PPCPs and chlorination is ineffective in PPCPs removal.

Keywords: PPCPs, WWTPs, Occurrence

1. Introduction

PPCPs have recently raised great public attention as emerging contaminants in the aquatic environment (Herberer, 2002; Okuda, 2009). WWTPs are regarded as one of the most important source of pharmaceuticals residues in the water environment. At present, WWTPs are mainly operated to remove the classical contaminants (solid, nutrients and organic matters), not focused on the elimination of PPCPs (Nakada et al., 2007). For the reason, researches for understanding the fate of pharmaceuticals in WWTPs have been intensively performed (Clara et al., 2005). Although these researches have been mostly performed in Europe and USA (Hilton and Thomas, 2003), few researches have performed fate of pharmaceuticals in WWTPs in Korea (Choi et al., 2007, 2008; Sim et al., 2010). However, there are still limited studies dealing various PPCPs and fate in WWTPs. Therefore, in this study, the occurrence and fate of 62 PPCPs were investigated in six municipal WWTPs (Table 1).

2. Materials and Methods

2.1. Sampling and Sample pretreatment

Targeted 62 compounds were shown in Table 2. All WWTPs were conducted two times of August, November, 2011. Influent, secondary effluent, final effluent samples as grab samples. The sample bottles were first rinsed twice with the sample water before 1000 mL was collected. 1 g/L ascorbic acid was added and the bottles were stored in cooling box during their transport back to our laboratory.

Samples were filtrated through the glass fiber filter (Whatman GF/B, 1 μm pore-size). After filtration, 1 g/L EDTA-2Na was added and solid phase extraction (SPE) with Oasis HLB (Waters, 200mg, 6cc) cartridges was carried out at a flow rate of 10 mL/min. Then the cartridge was carried to Japan. The cartridge

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was dried and eluted with mainly methanol. Then, the extract was evaporated to dryness under nitrogen stream and finally redissolved in 1mL solvent.

2.2. LC-MS/MS Analysis

The PPCPs were eluted from the cartridge using methanol. The eluted solvent was evaporated to dryness by a gentle stream of nitrogen gas. The residue was dissolved in 1 mL of 0.1% formic acid–methanol mixture (85/15, v/v). For the samples, Waters ACQUITY UPLC system (Waters) equipped with ACQUITY BEH C18 column (1.7μm, 2.1mm×100mm), and Quattro micro API mass spectrometer (Waters) were used. The method using the recovery correction which was calculated from the difference between two aliquots from one sample with and without addition of target PPCPs mixture, and the internal standard method using appropriate surrogate standards (Narumiya et al., 2011) were used for the quantification for the samples, respectively.

Table 1: Information of the survey WWTPs.

WWTP	J	N	T	S	Y	K
Operation capacity(m^3/day)	1,710,000	1,000,000	1,100,000	2,000,000	48,000	25,000
Bioreactor	A_2O/CAS	CAS	CAS	CAS	B3	CAS
Disinfection	O_3/Chlorination	Chlorination	Chlorination	Chlorination	UV	UV

A_2O: anaerobic/anoxic/oxic process, CAS: conventional activated sludge, B3: bio best bacillus

Table 2: Target compounds in this study.

No.	Compound	No.	Compound	No.	Compound
1.	2-QCA	21.	Dipyridamole	41.	Oxytetracycline
2.	Acetaminophen	22.	Disopyramide	42.	Pirenzepine
3.	Antipyrine	23.	Enrofloxacin	43.	Primidone
4.	Atenolol	24.	Erythromycin	44.	Propranolol
5.	Azithromycin	25.	Ethenzamide	45.	Roxithromycin
6.	Bezafibrate	26.	Fenoprofen	46.	Salbutamol
7.	Caffeine	27.	Furosemide	47.	Sulfadimethoxine
8.	Carbamazepine	28.	Griseofulvin	48.	Sulfadimidine
9.	Chloramphenicol	29.	Ibuprofen	49.	Sulfamerazine
10.	Chlortetracycline	30.	Ifenprodil	50.	Sulfamethoxazole
11.	Ciprofloxacin	31.	Indometacin	51.	Sulfamonomethoxine
12.	Clarithromycin	32.	Isopropylantipyrine	52.	Sulfapyridine
13.	Clenbuterol	33.	Ketoprofen	53.	Sulfathiazole
14.	Clofibric acid	34.	Levofloxacin	54.	Sulpiride
15.	Crotamiton	35.	Lincomycin	55.	Tetracycline
16.	Cyclophosphamide	36.	Mefenamic acid	56.	Thiamphenicol
17.	DEET	37.	Metoprolol	57.	Tiamulin
18.	Diclazuril	38.	Nalidixic acid	58.	Triclocarban
19.	Diclofenac	39.	Naproxen	59.	Triclosan
20.	Diltiazem	40.	Norfloxacin	60.	Trimethoprim
				61.	Tylosin

3. Results & discussion

3.1. PPCPs levels in WWTPs influent and effluent

Up to 56 of 61 PPCPs were detected in each sample (Figure 1). Among the target PPCPs, acetaminophen (74.552 μg/L), caffeine (25.060 μg/L), ibuprofen (9.494 μg/L), naproxen (5.938 μg/L) and theophylline (4.195 μg/L) were detected in the highest levels in the WWTP influent. Sulpiride (0.733 μg/L), atenolol (1.974 μg/L), clarithromycin (2.160 μg/L), roxithromycin (1.117 μg/L), sulfapyridine (0.921 μg/L) and other PPCPs were also detected in the influent (Figure 1). Especially, the concentrations of acetaminophen, caffeine and ibuprofen are higher than other PPCPs in this study. Compare to other studies in Korea, concentrations of acetaminophen, caffeine and ibuprofen are higher than 5times over (Sim et al, 2010; Choi et al 2008).

The levels of PPCPs in the final effluent were lower than those in the influent. The levels of all target PPCPs in the effluent below 1 μg/L and sulpiride (0.517 μg/L) had the highest levels among them. Atenolol (0.362 μg/L), clarithromycin (0.352 μg/L), roxithromycin (0.223 μg/L), sulfapyridine (0.223 μg/L) and other PPCPs were detected in the effluent. Especially, acetaminophen (0.023 μg/L), caffeine (0.062 μg/L), theophylline (0.023 μg/L), ibuprofen (0.015 μg/L) and naproxen (0.120 μg/L), which are dominant in the influent, showed relatively lower concentrations, indicating high decrease rates of these compounds in the WWTPs.

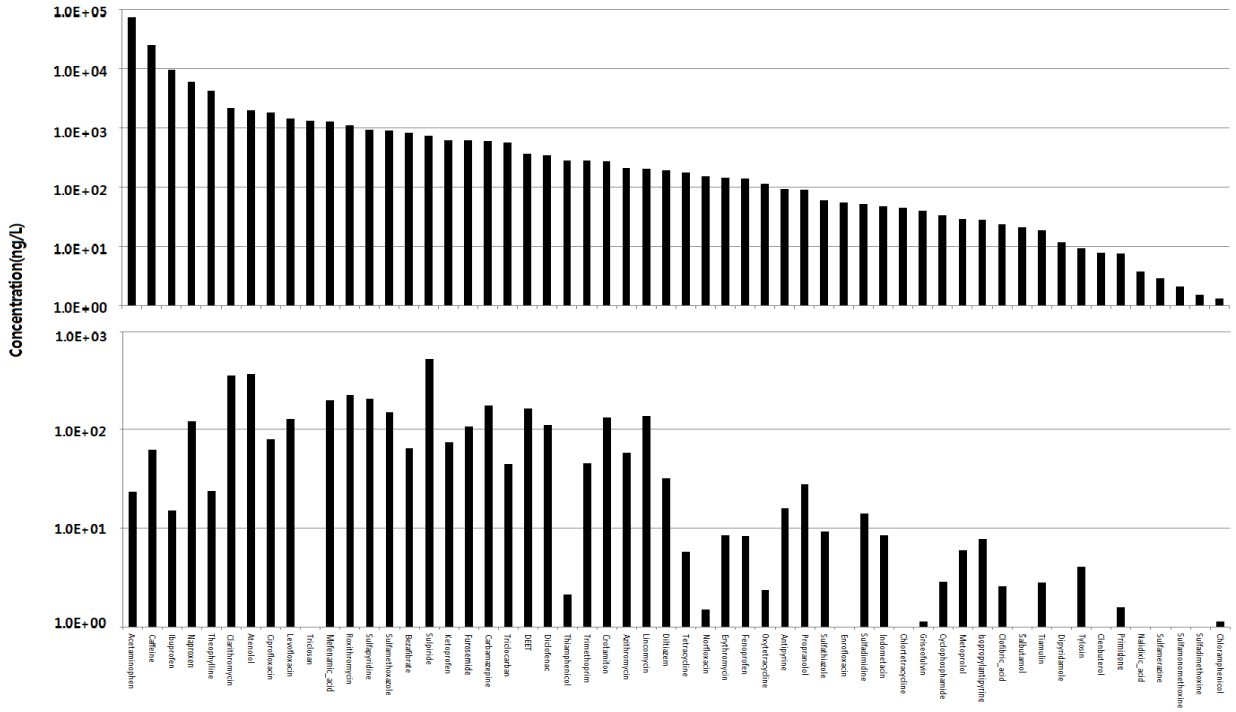
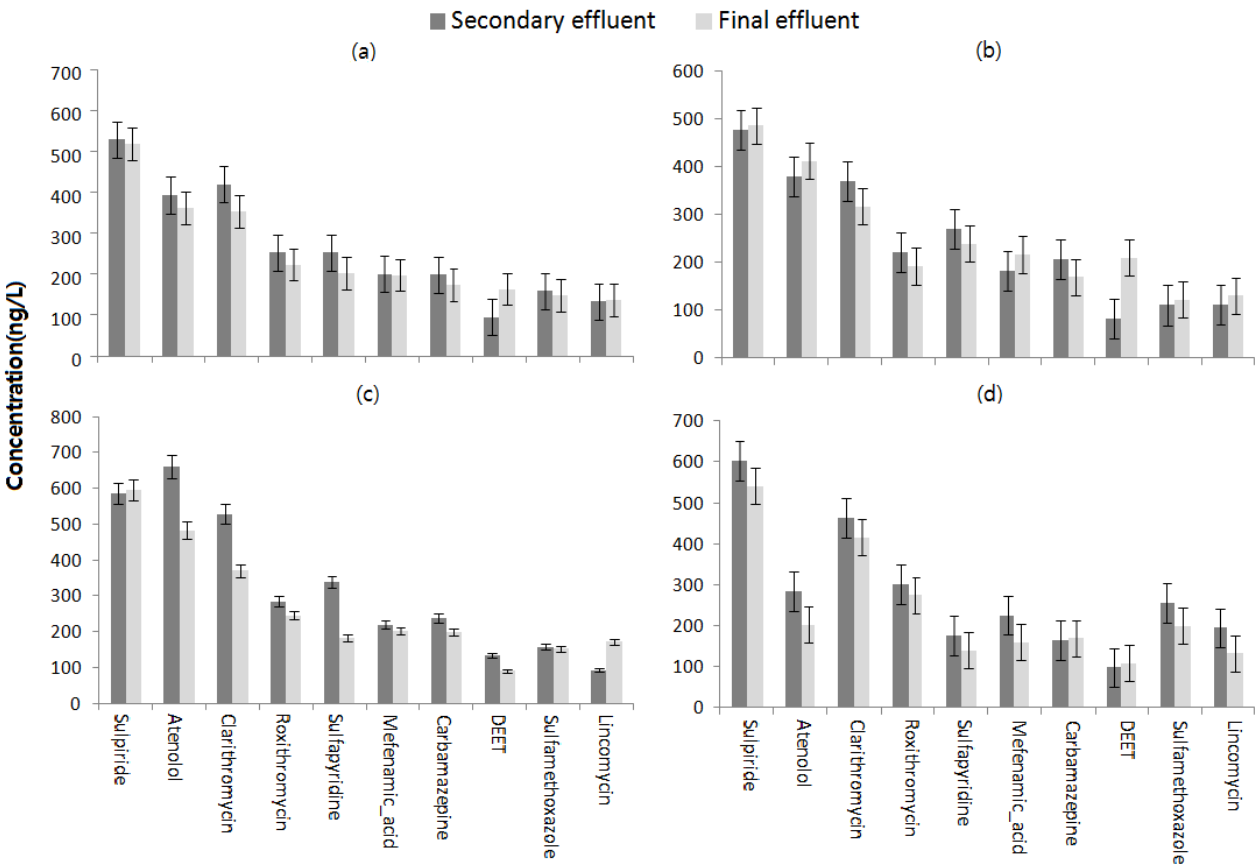


Fig. 1: The average levels of PPCPs detected in WWTPs influent and final effluent.

3.2. Effect of disinfection process in PPCPs removal

Top 10 detected PPCPs in final effluent were compared in the reduction by disinfection processes (Figure 2). Almost PPCPs reduced for disinfection process. But some substances (DEET) indicate the higher levels in final effluent than secondary effluent. In chlorination process, mostly PPCPs did not reduce. Atenolol, clarithromycin and sulfapyridine indicate their high removal efficiency of 30% over in ozonation process. In UV process, atenolol, sulfapyridine, mefenamic acid, sulfamethoxazole and lincomycin remove by 20% over. Especially, sulpiride and lincomycin indicate their higher removal efficiency than other disinfection process.



(a) Average, (b) Chlorination, (c) Ozonation, (d) UV disinfection

Fig. 2: The concentrations of PPCPs between WWTPs secondary effluent and final effluent by disinfection process.

4. Conclusions

56 out of 61 PPCPs were detected in this study. Acetaminophen, caffeine, ibuprofen, naproxen and theophylline detected high concentrations in influent. However, these compounds indicate high removal efficiency of 97%. Sulpiride, atenolol, clarithromycin, roxithromycin and sulfapyridine detected high levels in secondary and final effluent. Sulpiride, atenolol, clarithromycin, roxithromycin and sulfapyridine shows lower removal efficiency in WWPTs. Small amount of PPCPs are removed in Disinfection process. Several PPCPs reduce in Ozonation and UV disinfection, but almost PPCPs not eliminate in chlorination. Therefore, ozonation and UV disinfection is more effective process for PPCPs remove.

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