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Occurrence and removal of contaminants of emerging concern in water reclamation facilities in Korea

Soohyung Park, Wontae Lee*

Department of Environmental Engineering, Kumoh National Institute of Technology, Gumi, Korea, Tel. +82 54 478 7636; Fax: +82 54 478 7859; email: wtlee@kumoh.ac.kr (W. Lee), Tel. +82 54 478 7643; email: pigjaebum@hanmail.net (S. Park)

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ABSTRACT

In this study, we investigated the occurrence and removal of contaminants of emerging concern including 10 pharmaceuticals and personal care products (PPCPs) and 3 endocrine disrupting compounds in 6 water reclamation facilities (WRFs) in Korea for better understanding of the fate of those contaminants through the water reuse system. The sampling campaigns were performed six times at each WRF from influent, and after biological, coagulation and ultraviolet disinfection processes. Concentrations of the monitored compounds in WRFs (A, B and C), which were located in industrial and urban areas, were relatively higher compared with other WRFs. Concentrations of caffeine and ibuprofen in influents were relatively higher than other PPCPs. Biological processes in the WRFs removed most of the PPCPs except carbamazepine and primidone. Carbamazepine was not readily removed by coagulation and filtration processes, which were followed by biological processes in the WRFs. Continuous monitoring and management for carbamazepine and primidone may be required to reduce or eliminate the potential adverse impact of those contaminants to ecosystems and downstream utilities.

Keywords: Contaminants of emerging concern; Pharmaceuticals and personal care products; Endocrine disrupting compounds; Water reuse

1. Introduction

Over the past decades rapid industrialization in Korea has been putting an increasing strain on the water resources and water quality. Especially, the presence of contaminants of emerging concern (CECs) including pharmaceuticals and personal care products (PPCPs) and endocrine disrupting compounds (EDCs) in water has received attention due to their adverse influence on human health, aquatic lives and ecosystems [1–4]. Approximately, 12,000 PPCPs have been distributed for human consumption worldwide. PPCPs include a diverse collection of chemical substances including human and veterinary drugs used for preventing or treating human and animal diseases, as well as disinfectants or fragrances used in personal care products (e.g., lotions, body cleaning products and sunscreens) and household chemicals for improving the quality of daily life [5–7].

Although PPCPs are commonly present in water bodies at very low concentrations from a few ng/L to μg/L, these are enough to cause threats to ecosystems or organism exposed [8]. Furthermore, pharmaceuticals are known to have potential risks to the aquatic ecosystems such as endocrine disrupting and severe side effects because they originally cause specific biological effects [9,10]. For these reasons, the pharmaceutical pollution became emerging environmental problems worldwide [11]. While PPCPs are a mostly well-defined group of compounds, EDCs are an extremely diverse group of compounds that interfere with the functioning of natural hormones in animals. It is difficult to determine which chemicals should or should not be classified as endocrine disruptors. A few naturally occurring and man-made chemicals are

* Corresponding author.

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widely considered to be endocrine disruptors, including certain pharmaceuticals, pesticides, industrial chemicals, combustion by-products, phytoestrogens and hormones excreted by animals and humans [12].

PPCPs are likely to be found in any body of water influenced by raw and/or treated wastewater, including rivers, streams, lakes and impoundments, and groundwater, many of which are used as drinking water sources [13]. The increased use of PPCPs, continual release of new compounds into water bodies, and lack of efficient wastewater treatment technologies made them a challenge for water utilities; the presence of PPCPs could also endanger the water reclamation and reuse, a potential option to achieve sustainable water management [14]. Typical water reclamation facilities (WRFs) consist of biological and physicochemical treatment processes. At present, WRFs are mainly operated to remove solids, nutrients and organic matters, not focused on the elimination of CECs such as PPCPs and EDCs [15]. Effluents from wastewater treatment plants and/or WRFs are regarded as one of the most important sources of PPCP residues in the water environment. Thus, the occurrence and fate of PPCPs in WRFs have been investigated [16–18].

Growing concern over the safety of drinking water containing PPCPs and EDCs has resulted in increased research worldwide [14,19,20]. Many water utilities in developed countries are adopting advanced water treatment processes to provide a reliable supply of safe drinking water. However, little is known about the fate of transformation products formed in drinking water treatment processes such as advanced oxidation and biodegradation. Snyder et al. [22] evaluated the removal of PPCPs and EDCs in 13 full-scale water treatment facilities. Conventional coagulation, flocculation and sedimentation processes were ineffective at removing most of the target PPCPs and EDCs [21,22]. It is important to manage CECs such as PPCPs and EDCs at wastewater treatment plants and/or WRFs thus reducing the adverse impact on downstream water utilities. Therefore, we investigated the occurrence and removal of 10 PPCPs and 3 EDCs in 6 WRFs in Korea to better understand their fate through the WRFs and to provide the information on the compounds to water utilities. Additionally, this study assessed water reclamation processes including biodegradation, coagulation and ultraviolet (UV) oxidation for the removal of the CECs in WRFs.

2. Materials and methods

2.1. Chemicals and analytical methods

Among a diverse group of PPCPs and EDCs, we selected 10 PPCPs and 3 EDCs which have been widely reported to occur in aquatic systems. Physical and chemical properties of the target compounds are listed in Table 1. The compounds were chosen to represent different groups of PPCPs such as antihypertensive, antiepileptic, anticoagulant, analgesic, antibiotic and personal care products such as photo initiator, corrosion inhibitor and antiseptic. Frequently detected and reported compounds were considered in each class. These compounds were listed in the 30 most frequently detected organic wastewater contaminants reported by the USGS [27]. Atenolol, carbamazepine, gemfibrozil, ibuprofen and sulfamethoxazole were among the top 10 high priority pharmaceuticals identified in a European assessment of PPCPs [28].

All standards were of high purity grade (>99%) and were purchased mainly from Sigma-Aldrich (USA). Deionized water was produced by a Milli-Q (Millipore, Direct 8.8 L/h) unit. Stock solutions of individual chemicals were prepared in methanol, and standard mixtures were prepared by diluting the stock solution. All the solutions were stored at 4°C in the dark.

A highly sensitive analytical method was developed and validated for the determination of the PPCPs and EDCs in wastewater. PPCPs were separated and detected by LC-MS/MS methods based on direct injection of sample into the chromatograph. A 1260 High-Performance Liquid Chromatography tandem with 6410 Triple Quad Mass Spectrophotometer (MS/MS) (Agilent Technologies, USA) was used in the electrospray ionization (ESI; positive/negative)

Table 1
Properties of target compounds

Class	Compound name	Chemical formula	Usage	Molecular weight (g/mol)	logK_{ow}	pK_a
Pharmaceuticals	Atenolol	$C_{14}H_{22}N_2O_3$	Antihypertensive	266.34	0.16	9.6
	Carbamazepine	$C_{15}H_{12}N_2O$	Antiepileptic	236.27	2.45	13.9
	Gemfibrozil	$C_{15}H_{22}O_3$	Anticoagulant	250.34	4.77	4.7
	Ibuprofen	$C_{13}H_{18}O_2$	Analgesic	206.23	3.97	4.9
	Primidone	$C_{12}H_{14}N_2O_2$	Antiepileptic	218.25	0.91	11.5
	Sulfamethoxazole	$C_{10}H_{11}N_3O_3S$	Antibiotic	253.28	0.89	5.7
Personal care products	Benzophenone	$C_{13}H_{10}O$	Photo initiator [23]	182.22	3.18 [25]	–7.5
	Benzotriazole	$C_6H_5N_3$	Corrosion inhibitor [24]	119.13	1.44 [26]	8.2
	Triclocarban	$C_{13}H_9Cl_3N_2O$	Antiseptic	315.58	4.2–6	12.7
Endocrine disruptors	Estradiol	$C_{18}H_{24}O_2$	Hormone	272.38	4.01	10.46
	Ethinylestradiol	$C_{20}H_{24}O_2$	Hormone	296.4	3.67	10.33
Industrial materials	Bisphenol A	$C_{15}H_{16}O_2$	Plasticizer	228.29	3.4	9.59
	Caffeine	$C_8H_{10}N_4O_2$	Stimulant	194.19	–0.07	10.4

Note: pK_a, negative log of acidity constant(s); K_{ow}, octanol–water partition coefficient.

mode. EDCs were analyzed by GC-MS/MS methods based on direct injection of sample into the chromatograph. ESI ionization separation was carried out on an Eclipse XDB C18 analytical column AS 21 (150 × 4.5 mm, 5 μm particle size) of Dionex (AS-21, only perchlorate). Mobile phase A (15 min) consisted of methanol and water with 0.1% formic acid and 90% hydrogen peroxide. Mobile phase B (15 min) consisted of methanol and water with 0.1% formic acid and 10% methanol as mobile phase additives. The flow rate was 0.5 mL/min, and the column temperature was 30°C (Table 2).

2.2. Sampling campaign

Samples were collected from six WRFs in Gumi, South Korea: two in industrial complex, one in urban area and three in rural areas. Treatment capacities of the WRFs ranged from 750 to 330,000 m^3/d (Table 3). The WRFs mainly consisted of a primary treatment followed by biological process, coagulation/filtration and UV disinfection (Fig. 1). Raw wastewater (i.e., influent to each facility) and treated wastewater (by biological process, coagulation process and UV disinfection) were collected from each WRF in 2015, basically six times at each WRF. All samples were collected in 4 L glass bottles, immediately transferred to the laboratory in an ice bath and passed through glass fiber filters (GF/F, 0.7 μm, Whatman, USA) to remove particulate materials. The GF/F were baked for 2 h at 450°C before use. All water samples were extracted within 1 week for further analysis. Table 4 summarizes chemical characteristics of raw wastewater and treated wastewater by biological process, coagulation process and UV disinfection in the WRFs.

3. Results and discussion

3.1. Occurrence of CECs in wastewater

In raw wastewaters (influents to the WRFs), 10 of the 13 target compounds were detected from the sampling events. EDCs including estradiol, ethinylestradiol and bisphenol A were below their method reporting limits (MRL) in all samples. Table 5 summarizes monitoring results of 10 PPCPs detected in raw wastewaters and treated wastewaters by biological process, coagulation process and UV disinfection of the WRF A, B and C in industrial complex and urban areas. Table 6 presents the results of WRF D, E and F in rural area. Minimum, maximum and average concentrations were presented for atenolol, benzophenone, benzotriazole, caffeine, carbamazepine, gemfibrozil, ibuprofen, primidone, sulfamethoxazole and triclocarban. Concentrations of PPCPs in WRF A, B and C, which were located in industrial and urban areas, were higher than other WRFs in rural area. Unfortunately, we could not find a statistically meaningful trend for seasonal variations in this study.

Most of compounds were found at average concentrations on the order of hundreds of ng/L except benzotriazole, caffeine and ibuprofen (1,000–2,000 ng/L). Caffeine and ibuprofen are steroid and analgesic, and they are one of the most widely used PPCPs in Korea. Previous studies also reported that caffeine and ibuprofen have been usually found at higher concentrations in municipal wastewater. For caffeine, Yang et al. [13] reported concentration ranging 54,000–120,000 ng/L in USA; Behera et al. [14] reported 1,608–3,217 ng/L of caffeine in wastewater in Korea; Tran et al. [29] reported concentrations ranging below detection limit –16,249 in urban catchment area in Singapore; Conkle et al. [30] reported 25,567 ± 5,710 of caffeine in Louisiana, USA; Santos et al. [31] reported an average concentration of caffeine at 6,168 ng/L in influents of four wastewater treatment plants in Seville, Spain; Daneshvar et al. [32] reported 32,894 ng/L in Greater Montreal, Canada; Li et al. [33] found caffeine at 51,300–57,700 ng/L in a wastewater treatment plant in Illinois, USA. Also, detection of ibuprofen in wastewater has been reported. Ferrari et al. [2] reported concentration range of 3,900–15,000 ng/L in USA; Carballa et al. [34,35] reported concentration range of 3,697–19,000 ng/L in Galicia, Spain; Santos et al. [31] reported an average concentration of 93,925 ng/L in Seville, Spain; Lindqvist et al. [36] reported an average concentration of 13,100 ng/L in Finland; Lishman et al. [37] reported an average concentration of 8.450 ng/L in Ontario, Canada. Sulfamethoxazole concentrations varied from 18 to 555 ng/L with an average concentration of 282 ng/L. The high concentrations of sulfamethoxazole could be due to its high rate of consumption for antibiotic purposes. Carbamazepine

Table 2
Analytical conditions for PPCPs

Liquid chromatograph	Agilent 1260
Column	Eclipse XDB C18 (150 mm, 4.5 mm, 5 μm)
Mobile phase (15 min)	A: 0.1% formic acid/H_2O_2 90% B: 0.1% formic acid/MeOH 10%
Column temperature	30°C
Sample volume	40 μm
Flow rate	0.5 mL/min
MS	Agilent 6410 Triple Quadrupole LC/MS
Ionization	ESI (positive/negative)
Collision energy	Taale (N_2 gas)
Scan range	*m*/*z* 100–450
Drying gas	10 L/min at 300°C
Nebulizer gas	456 kPa
Fragmentor	100 V
Vcap	4,000 V

Table 3
Characteristics of six water reclamation facilities (WRFs) surveyed

WRFs	Treatment capacity (m^3/d)	Wastewater flow (m^3/d)
A	50,000	Industrial: 35,000/ Urban: 15,000
B	330,000	Industrial: 137,000/ Urban: 173,000
C	60,000	Urban: 60,000
D	9,000	Rural: 9,000
E	750	Rural: 750
F	8,000	Rural: 8,000

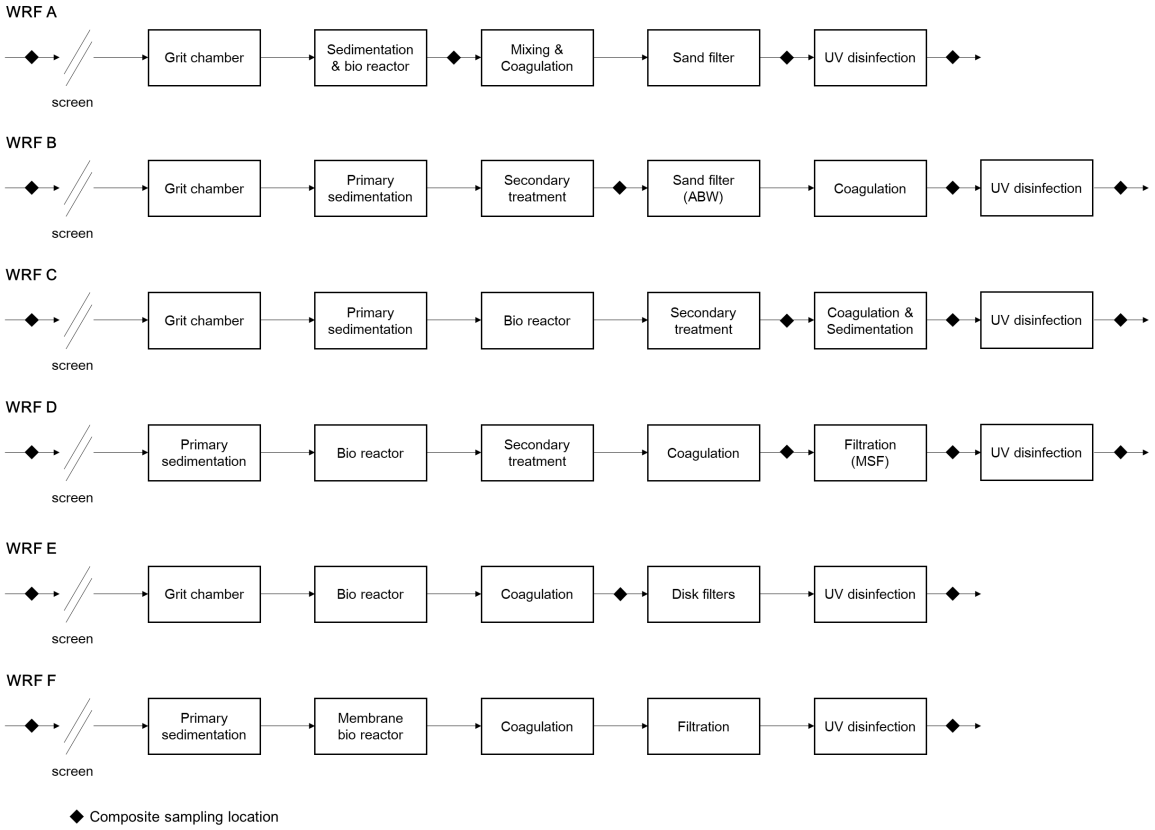

Fig. 1. Process flow diagrams of the six water reclamation facilities surveyed.

Table 4
General water quality parameters of raw wastewater (influent), biological process, coagulation process and UV disinfection effluents

WRFs		DOC (mg/L)	SS (mg/L)	UV
A	Influent	25.5	140	0.246
	Biological process	8.9	2.6	0.100
	Coagulation process	5.3	6	0.086
	UV disinfection	5.1	1.9	0.082
B	Influent	22.5	97.3	0.219
	Biological process	7.6	3.8	0.119
	Coagulation process	7.4	2.3	0.115
	UV disinfection	7.1	4.2	0.112
C	Influent	49.4	134	0.280
	Biological process	5.6	7	0.118
	Coagulation process	5.6	3.4	0.116
	UV disinfection	5.8	2.6	0.097
D	Influent	77.1	278	0.388
	Biological process	24.2	230	0.243
	Coagulation process	9.4	81.7	0.225
	UV disinfection	5	5.7	0.081
E	Influent	55.1	95	0.349
	UV disinfection	4.5	7.1	0.070
F	Influent	30.5	32	0.378
	Coagulation process	5.5	0.1	0.118
	UV disinfection	5.2	1.4	0.104

Table 5
Concentrations of PPCPs in influent, biological process, coagulation process and UV disinfection effluents of WRFs (A, B and C) in industrial complex and urban area

Compounds	Influent			Biological process			Coagulation process			UV disinfection		
	Minimum (ng/L)	Maximum (ng/L)	Average (ng/L)	Minimum (ng/L)	Maximum (ng/L)	Average (ng/L)	Minimum (ng/L)	Maximum (ng/L)	Average (ng/L)	Minimum (ng/L)	Maximum (ng/L)	Average (ng/L)
Atenolol	219	885	496	55	344	195	45	373	172	42	355	161
Benzophenone	220	1,618	752	210	1,241	583	83	1,006	372	58	636	288
Benzotriazole	62	2,306	873	50	2,177	692	17	2,196	625	4	838	220
Caffeine	873	2,372	1,429	99	457	221	44	249	162	33	230	114
Carbamazepine	42	140	93	39	104	76	38	98	73	34	92	68
Gemfibrozil	58	405	225	25	226	113	25	184	91	27	174	88
Ibuprofen	525	1,840	1,075	76	428	189	35	294	129	25	294	109
Primidone	32	192	97	31	171	90	31	162	87	34	164	86
Sulfamethoxazole	18	396	174	23	220	97	24	193	92	16	116	64
Triclocarban	31	598	306	10	312	147	11	288	121	6	254	97

Table 6
Concentrations of PPCPs in influent, biological process, coagulation process and UV disinfection effluents of WRFs (D, E and F) in rural area

Compounds	Influent			Biological process			Coagulation process			UV disinfection		
	Minimum (ng/L)	Maximum (ng/L)	Average (ng/L)	Minimum (ng/L)	Maximum (ng/L)	Average (ng/L)	Minimum (ng/L)	Maximum (ng/L)	Average (ng/L)	Minimum (ng/L)	Maximum (ng/L)	Average (ng/L)
Atenolol	67	1,022	333	48	450	150	21	418	138	15	391	110
Benzophenone	84	1,074	397	51	724	327	44	668	250	24	589	195
Benzotriazole	52	959	455	51	784	324	25	577	250	9	320	121
Caffeine	206	1,083	446	44	231	92	23	204	60	0	257	45
Carbamazepine	29	127	84	26	89	66	25	95	66	19	114	68
Gemfibrozil	81	351	153	38	144	75	30	114	58	17	122	52
Ibuprofen	302	2,307	776	84	389	182	49	210	112	31	184	92
Primidone	24	92	56	34	89	59	28	80	52	30	80	53
Sulfamethoxazole	109	555	357	53	277	172	51	259	158	34	385	133
Triclocarban	67	455	157	50	255	111	36	197	85	27	134	66

and primidone (both antiepileptic) were measured at concentrations below 200 ng/L in raw wastewater. The concentrations of these compounds were lower than other compounds in this study, while they are similar to previous studies [2,6,7,38–44].

3.2. Removal of CECs by treatment processes

Fig. 2 presents the removal efficiencies of PPCPs while passing through the conventional wastewater treatment processes, mainly by biological treatment, in the WRFs. Ten PPCPs were detected in the effluent of biological processes of the WRFs; EDCs such as estradiol, ethinylestradiol and bisphenol A were below their MRL in all samples. During the biological process, the average removal efficiencies of the PPCPs ranged from 4.8% to 86.8%. Caffeine and ibuprofen were effectively removed, with the average removal rates of 84.7% and 80%, respectively. The removal rates of caffeine and ibuprofen in our study were similar to those observed by other researchers. Caffeine was generally reported to be readily biodegradable [18,45–47]. Also, ibuprofen (analgesic drug) exhibited high removal rate (~80%) as previously reported by other researches [2,15,16]. Removal rate of carbamazepine was 16% on average because carbamazepine could be resistant to biodegradation [15,16]. In the meantime, concentrations of the compounds were even higher in the effluent than the influent. This was possibly due to the hydrolysis of conjugates originating from the parent compounds during the conventional biological treatment process [48–50]. Primidone (antiepileptic drug) showed the lowest removal rate among the detected PPCPs ranging 4.8%–8.6%.

Fig. 3 presents the removal efficiencies of PPCPs by coagulation process. Coagulation did not effectively remove most of the PPCPs, and especially carbamazepine and primidone were hard to remove. Removal rate of ibuprofen by coagulation was relatively higher than other compounds yet less than 50% in average. Anionic compounds such as sulfamethoxazole are not readily removed by coagulation [51]. Referring to related studies, two chemical-specific factors could influence the removal performance of coagulation, that is, the octanol–water partition coefficient (K_{ow}) and the weak acid hydrolysis coefficient (pK_a) [52–54]. Higher values of both pK_a and K_{ow} were associated with higher PPCP removal efficiencies, which evidenced a cooperative effect of these two properties on the combined coagulation and sedimentation processes in removing PPCPs. During treatment, a contaminant's higher pK_a value would contribute to the exchange of the compounds into ionic states where they could be easily adsorbed onto particles and the flocs formed by coagulation via electrostatic interactions [55]. Higher K_{ow} contributed less to the removal efficiency of combined coagulation and sedimentation in agreement with previous study in which K_{ow} was a limited and unstable predictor for the removal of some PPCPs such as polar compounds [56].

Fig. 4 presents the removal efficiencies of PPCPs by UV disinfection in the form of a series of box plots. Removal rates of the compounds by UV disinfection ranged from 0% to 90.7%. However, UV disinfection did not effectively remove most of the PPCPs except for benzotriazole. Benzotriazole was effectively removed by UV with the average removal rate of 60%. Benzotriazole is an anticorrosion agent that is widely applied in various industrial processes and in household products, and it has been detected in surface water and groundwater due to its high mobility and low biodegradability. Under monochromatic irradiation at 253.7 nm (i.e., low-pressure lamp), benzotriazole can be readily removed due to the advantageous combination of large molar absorption coefficients and quantum yield at 253.7 nm. Benzotriazole was found to undergo rapid transformation to form several photoproducts. The half-lives for the photolysis of benzotriazole ranged from 2.8 to 14.3 h in various aqueous solutions containing metal ions and dissolved organic matter [57]. Other compounds exhibited minimal absorption and/or low quantum yield at 253.7 nm, which indicated their poor removal by the low-pressure UV lamps. Virtually no

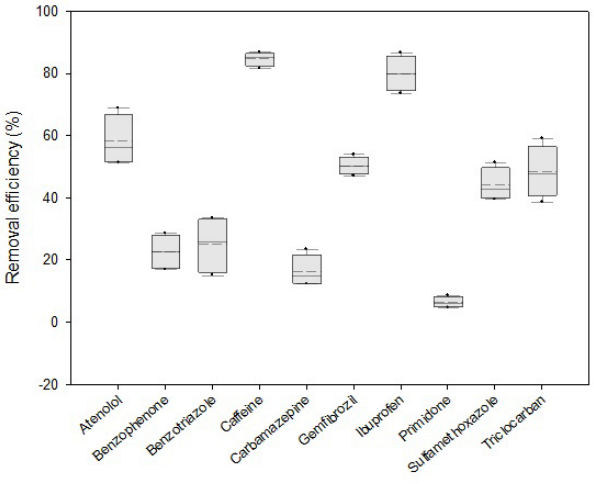

Fig. 2. Removal efficiencies of PPCPs by biological treatment at four WRFs (A, B, C and D). (Box plot: 25th percentile, median, average and 75th percentile, I: 10th and 90th percentiles.)

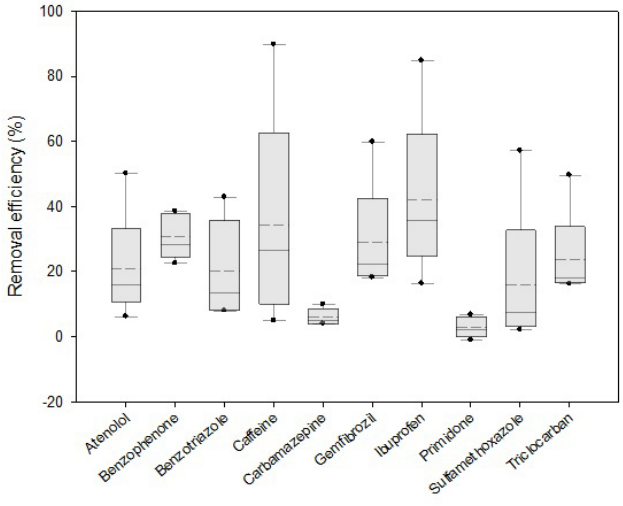

Fig. 3. Removal efficiencies of PPCPs by coagulation treatment at five WRFs (A, B, C, D and E). (Box plot: 25th percentile, median, average and 75th percentile, I: 10th and 90th percentiles.)

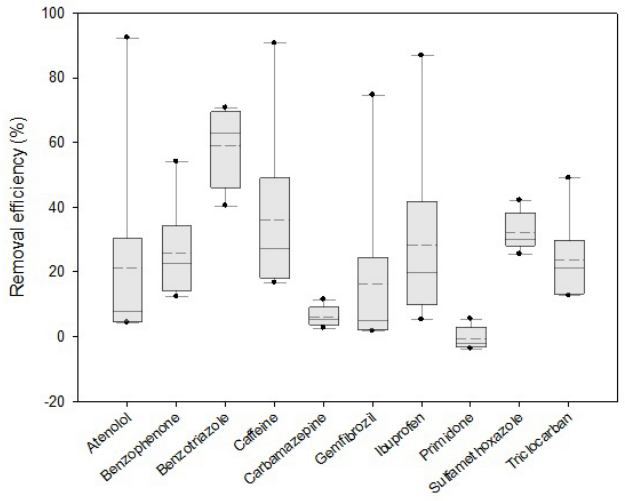

Fig. 4. Removal efficiencies of PPCPs by UV disinfection at six WRFs (A, B, C, D, E and F). (Box plot: 25th percentile, median, average and 75th percentile, ⌶: 10th and 90th percentiles.)

direct photolysis at 253.7 nm was observed for carbamazepine and primidone.

4. Conclusions

CECs including PPCPs and EDCs have raised environmental concerns among the public, scientists and regulatory groups [58,59]. The occurrence and fate of CECs through WRFs were investigated at six WRFs in Korea. The facilities included two in industrial area, one in urban area and three in rural area. The targeted PPCPs and EDCs included antihypertensive, antiepileptic, anticoagulant, analgesic, antibiotic, photoinitiator, corrosion inhibitor, antiseptic, plasticizer and stimulant. In this study, 10 PPCPs were detected in influents to the facilities whereas 3 EDCs (bisphenol-A, estradiol and ethinylestradiol) were not detected. Most of compounds were found at average concentrations on the order of hundreds of ng/L except benzotriazole, caffeine and ibuprofen (1,000–2,000 ng/L). Concentrations of PPCPs in WRFs (A, B and C), which were located in industrial and urban areas, were higher than other WRFs in rural area. Most of the CECs except carbamazepine and primidone were removed over 60% through the WRFs. Carbamazepine (21%) and primidone (7%) were not readily removed by coagulation and UV disinfection processes, which were followed by biological processes in the WRFs. Therefore, it may be more efficient to monitor and manage the two compounds at the WRFs rather than establishing effluent limits for all CECs, if needed.

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