PCDDs/Fs LEVELS AND REMOVAL EFFICIENCY IN VARIOUS TYPES OF WASTEWATER TREATMENT PLANTS

Jeong-Eun Oh[1,*], In-Seok Lee[1], Hyo-Keun Park[2], Yoon-Seok Chang[2], Chang-Won Kim[1]

1. Department of Environmental Engineering, Pusan National University, Busan, Korea
2. School of Environmental Science and Engineering, POSTECH, Pohang, Korea

Introduction

In the past years, control and management of pollutants in water treatment mostly focused on removing the conventional water regulatory compounds, such as nitrate, phosphate, etc. However, in recent decades, micropollutants including endocrine disruptors and pharmaceuticals have become a major environmental issue, especially in the aquatic environment. Among these compounds, polychlorinated dibenzo-p-dioxins and polychlorinated furans (PCDDs/Fs) are the extremely hazardous pollutants because of their acute toxicity. Numerous studies have highlighted the PCDDs/Fs formation, sources and control technologies, but they have mostly focused on incinerators, not on the water treatment plant. The US EPA has set the MCL (maximum contamination level) of 2,3,7,8-tetra chlorinated dioxin (TCDD) in drinking water at 30 fg/L and Japan has regulated PCDDs/Fs discharge in wastewater (10 pg-TEQ/L). The water treatment plant is regarded as a PCDDs/Fs emission source in the aquatic environment, so the investigation of PCDDs/Fs levels is necessary to control PCDDs/Fs in water. However, only a few studies have been performed to investigate the PCDDs/Fs levels and their removal efficiency in a water treatment plant (Kim et al, 2002; Behnisch et al, 2001). Kim et al (2002) reported that most of the dioxin congeners were sufficiently removed (87% removal efficiency) by drinking water treatment, but they also observed an increase in TeCDFs levels as a result of chlorination. The possibility of the formation of toxic PCDDs/Fs congener via dechlorination/chlorination mechanism in a water plant is reported, but there is still a lack of information to identify PCDDs/Fs formation, fates and removal mechanisms in water treatment plants.

Therefore, in this study, the PCDDs/Fs levels and their removal efficiency were investigated in various types of wastewater treatment plants. The relationship concerning the sources and PCDDs/Fs emission and the fates of PCDDs/Fs were also investigated.

Materials and Methods

Influent and effluent water samples were collected from 9 different wastewater treatment plants (WWTPs) in Korea. The wastewater treatment processes in each WWTP are shown in Table 1 and the input sources of wastewater in each WWTP are in Table 2. Collected 2L water samples were extracted with toluene and sample preparation was done according to the modified US EPA method 1613. PCDD/Fs were analyzed by high-resolution gas chromatography / high-resolution mass spectrometry (Hewlett-Packard Model 6890 series Ⅱ/ JMS 700T) with a DB-5MS column (60m, 0.25 mm i.d. 0.25 um film thickness). 17 toxic PCDDs/Fs isomers as well as homologues from tetra-CDDs/Fs and octa-CDD/F were analyzed. To evaluate similarities and differences in the PCDDs/Fs isomer distributions among the samples and investigate the relationship with wastewater treatment plants types, principal component analysis (PCA) was used. PCA was performed using software SIMCA-P 7.01 (Umetrics, Sweden).

Results and Discussion

PCDDs/Fs levels and distribution patterns in WWTP

PCDDs/Fs levels in influent water samples varied from 8.6 pg/L to 1549.6 pg/L (0.425 ~ 36.6 pg-TEQ/L) and

those of effluent water samples ranged from 0.1 pg/L to 105.0 pg/L (0.027 ~ 5.473 pg-TEQ/L). There are many studies which report the PCDDs/Fs levels in sludge samples in WWTPs (Stevens et al, 2001; Pereira and Kuch, 2005), but few studies have reported the PCDDs/Fs levels in wastewater. Even though the Ministry of Korea monitored PCDDs/Fs levels in water at 48 sites for six years from 2001~2006, most of the water samples were taken from rivers. Therefore, the comparison of PCDDs/Fs levels with other studies was not applicable, but the PCDDs/Fs levels in effluent water samples were below the Japanese PCDDs/Fs regulation in wastewater (<10 pg-TEQ/L).

The PCDDs/Fs levels in influent water samples are shown in Figure 1. The three groups are divided by their influent PCDDs/Fs concentration. Group 1, which shows the high PCDDs/Fs levels was composed of two WWCPs (SP and CS). The major wastewater input source in this group was the paper industry (86% and 62% each). It is known that the paper industry is one of major PCDDs/Fs sources due to chlorine bleaching, which is in good accordance with this result. PCA analysis was performed to investigate the relationship between PCDDs/Fs levels in influent and wastewater input sources, and a close relationship was observed between these two (Figure 2). Group 2, which shows the middle PCDDs/Fs levels, was composed mostly of WWTPs in this study (NC, GJ, DA, DS and SS). The major input source of this group was the textile industry (53~83%), except DA which was the metal industry (74%). Group 3, which had low PCDDs/Fs levels, had the food industry as its major input source. These results indicate that the paper industry discharges PCDDs/Fs at a very high level, the PCDDs/Fs discharged from chemical industry are relatively small and the levels of the food industry are very small.

The PCDDs/Fs homologue distribution patterns varied greatly according to WWCP, but PCDFs were dominant in influent water samples. However, for toxic isomers, low chlorinated furans (ex : tetra- to hexa-CDF) and high chlorinated dioxin (ex: 1,2,3,4,6,7,8-HpCDD and OCDD) were dominant in both influent and effluent water samples regardless of WWTPs types.

PCDDs/Fs Removal efficiency
Kim et al (2002) investigated the PCDDs/Fs removal efficiency in 45 drinking water treatment plants and reported that PCDDs/Fs sufficiently removed (93% for total dioxin and 87% for TEQ dioxins) by water treatment. However, the PCDDs/Fs removal efficiency in this study varied from 8% to 99% in terms of total PCDDs/Fs (Table 3). NC, GJ, DA and DS, which had a sedimentation (w/wo chemical precipitation) and a biological treatment system, showed ~ 30% removal efficiency. Unlike for the total of PCDDs/Fs, the removal efficiency of toxic TEQ isomers increased, which might be due to sampling without considering the hydraulic retention time. The other WWTPs which had a filtration system, except UG, had a good PCDDs/Fs removal efficiency (>50% and mostly over 70%) (Table 3). The influent PCDDs/Fs concentration in UG was very low, therefore, this caused relatively low removal efficiency compared to the others which had a filtration system.

Considering all of these results, it seems that the paper industry is has a higher concentration of PCDDs/Fs discharge to the water compared with the other industries. Also, the filtration system in WWTP is effective to remove PCDDs/Fs.

References

1. Kim HK, Masaki H, Matsumura T, Kamei T, Magara Y. *Water Research* 2002; 36: 4861-4869.
2. Choi KH, Kang D, Yoon J, Lee C, Jeon S, Na J. *Organohalogen Compounds* 2003; 62: 484-486.
3. Behnusch P, Fujii K, Shiozaki K, Kawakami I, Saka S. *Chmosphere* 2001; 43: 977-984.
4. Sumpter J, Johnson A. Environmental Science and Technology 2005; 39(12):4321-4332.
5. Pereira M, Kuch B. *Chemosphere* 2005; 60: 844-853.
6. Stevens J, Green N. J.L, Jones K.C, *Chemosphere* 2001; 44: 1455-1462.

Table 1. Wastewater treatment processes in 9 WWTPs in this study.

	waste water treatment processes		
WWTP	1st treatment	2nd treatment	3rd treatment
NC	gravity sedimentation	activated sludge	-
GJ	gravity sedimentation	pressure rising	-
DA	gravity sedimentation with chemical precipitation	RBC	-
DS	gravity sedimentation	activated sludge	chemical precipitation
SS	gravity sedimentation	activated sludge + RBC	chemical precipitation+sand filter
SP	gravity sedimentation	activated sludge	chemical precipitation+sand filter
YS	gravity sedimentation with chemical precipitation	activated sludge	sand filter
UG	gravity sedimentation	activated sludge	sand filter + activated carbon
CS	gravity sedimentation with chemical precipitation	activated sludge	sand filter + ozonation

Table 2. The input sources of wastewater in WWTPs

(unit ; %)

Classification	NC	GJ	DA	DS	SS	SP	YS	UG	CS
textile	24	70	-	32	26	-	-	-	-
dyeing	1	-	-	9	49	5	-	-	-
fiber	58	-	-	12	1	1	-	6	-
metal molding	4	-	74	12	8	-	21	-	3
plating	-	-	-	-	4	-	-	-	-
chemistry	4	1	26	3	1	-	16	23	4
food	1	27	-	11	5	6	52	71	21
paper	5	-	-	-	3	86	1	-	62
others	3	2	-	21	4	1	10	-	10

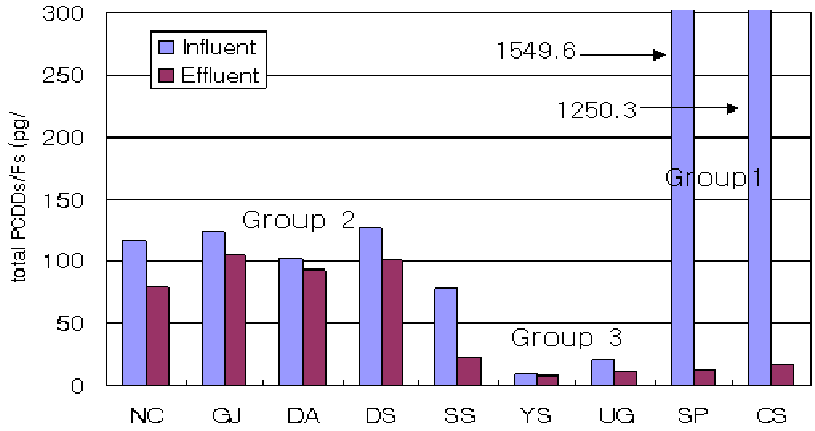

Figure 1. PCDDs/Fs levels in influent and effluent water samples

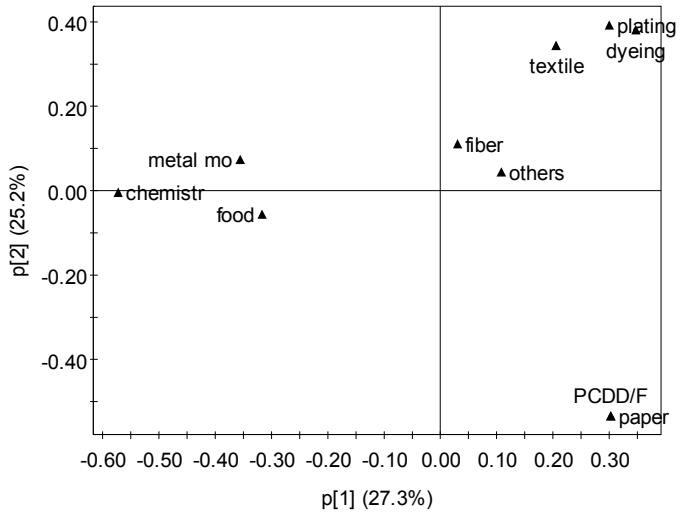

Figure 2. The relationship between PCDDs/Fs levels in influent and the input source of wastewater (PCA loading plot)

Table 3. PCDDs/Fs concentration and removal efficiency in each WWTP.

WWTPs	PCDDs/Fs (pg-TEQ/L		TEQ PCDDs/Fs	total PCDDs/Fs (pg/L)		total PCDDs/Fs
	influnet	effluent	removal efficiency	influnet	effluent	removal efficiency
NC	1.893	2.571	-35.8	115.8	80.0	30.9
GJ	3.741	5.473	-46.3	124.3	105.0	15.5
DA	3.771	2.994	20.6	102.8	93.1	9.4
DS	1.899	3.412	-79.7	126.7	101.1	20.2
SS	1.711	0.291	83.0	78.5	22.4	71.5
SP	36.58	0.045	99.9	1549.6	12.4	99.2
YS	0.048	0.027	43.8	8.3	6.4	22.3
UG	0.692	0.034	95.1	20.7	9.7	53.2
CS	25.00	0.148	99.4	1250.3	16.9	98.6