EVALUATION OF PCDDs/Fs AND COPLANAR-PCBs IN SEWAGE SLUDGE FROM WASTEWATER TREATMENT PLANTS IN KOREA

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Abstract
The concentration of PCDDs/Fs and Co-PCBs were investigated in sewage sludge discharged from WWTPs using HRGC/HRMS for the monitoring of PCDD/Fs and Co-PCBs in sewage sludge. The correlation between the levels of PCDD/Fs and Co-PCBs in sludge samples and the relation between PCDD/Fs levels in sludge samples and the removal efficiency of PCDD/Fs in WWTPs were also investigated. The PCDD/Fs levels in sludge samples ranged from 99.2pg/g to 66562.6pg/g (0.179~1242.6pg-TEQ/g), and the Co-PCBs levels ranged from 445.6pg/g to 13156.2pg/g (0.286~ 24.9pg-TEQ/g). The CS and SP WWTPs show the high PCDD/Fs levels, and the SS and CS WWTPs show the high Co-PCBs levels. It seems that the PCDD/Fs and Co-PCBs levels in sewage sludge are influenced by the input source into WWTPs. The correlation between PCDD/Fs and Co-PCBs levels in sewage sludge was investigated and a close relationship was observed. Also, a positive correlation between the removal efficiency of PCDD/Fs in WWTPs and PCDD/Fs levels in sewage sludge was found in a semi-log scale. Unlike previous studies, the PCDDs/Fs homologue distribution patterns varied greatly according to the type of WWTPs. However, NC and YS samples are characterized by OCDD/Fs and HpCDD/Fs that are similar to studies reported by other authors.

Introduction
Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/Fs) and coplanar polychlorinated biphenyls (Co-PCBs) remain intact in the environment for a long time and have intense toxicity to humans and wildlife. Also these chemicals are accumulated in the adipose of biota through food chains[1]. Because of these characteristics, a considerable number of studies have been conducted to investigate the effects of PCDDs/Fs and Co-PCBs on the environment in recent decades. Many studies have been done to investigate micro-pollutants in sludge, especially in Europe since they mainly dispose of sewage sludge on land for fertilization. PCDD/Fs and Co-PCBs enter the wastewater through wet and dry deposition, runoff into urban drains, industrial effluents and the discharge of wastewater treatment plants (WWTPs)[2]. The activated sludge treatment that is applied to WWTPs remove hydrophobic compounds like PCDD/Fs and Co-PCBs from wastewater by sorption to sludge.
The management of sewage sludge has become an important issue because of an international treaty about the disposal of sewage sludge. In particular, the London convention regulated the dumping of sewage sludge into oceans in order to preserve ocean environments. The disposal of sewage sludge using landfill and incineration also causes secondary pollution to the air and soil, respectively. Sewage sludge is applied to the land to enrich soil in the U.S. and the European Union countries because sewage sludge contains many nutrients and organics, which are useful to the growth of plants. But contaminants, such as heavy metals, pathogens and organic pollutants are also contained in sewage sludge[3], and especially persistent organic pollutants, such as PCDD/Fs and Co-PCBs, remain in soil for a long time. The European Union has regulated PCDD/Fs and PCBs (∑PCB 28, 52, 101, 118, 138, 153 and 180) in sludge for land use since 2000, and the limit values are 100ng-TEQ/kg dry mass and 0.8mg/kg dry mass, respectively[4]. However, only few studies on POPs in sludge samples have been performed in Korea, even though most of the sewage sludge has been disposed by ocean dumping in Korea.
Therefore, in this study, the concentration of PCDDs/Fs and Co-PCBs were investigated in sewage sludge discharged from WWTPs to examine the levels and distribution patterns in Korea. In addition, this study investigated the correlation between the levels of PCDD/Fs and Co-PCBs in sludge samples and the relation between PCDD/Fs levels in sludge samples and the removal efficiency of PCDD/Fs in WWTPs.

Materials and Methods
Sludge samples were collected from 6 different WWTPs in Korea. The sources of the wastewater influent in each WWTP were presented Table 1. 2.5g of dry sludge samples were extracted for 16h with 200ml of toluene

with Soxhlet and concentrated. For clean-up, the extracts were passed through a column (15mm i.d.) packed with a multilayer acid silica gel (Wako, Japan), rinsed with hexane to remove other interferences and then eluted with 260 mL of hexane. The concentrated extracts were passed through a column (8mm i.d) packed with 0.8g of silica gel impregnated activated carbon (Wako, Japan). The first fraction was eluted with 60 mL of 25% DCM/hexane to separate *mono-ortho* PCBs. Then a second fraction was eluted with 300 mL of toluene to analyze PCDD/Fs and *non-ortho* substituted PCBs. Some $^{13}C_{12}$-labeled CB-70, CB-111 and CB-138 were added to the first fraction. 1,2,3,4,6-pentaCDF and 1,2,3,4,6,8,9-heptaCDF with the above-labeled CB congeners were added to the second fractions as injection spikes.

PCDD/Fs and Co-PCBs were analyzed by a high-resolution gas chromatography coupled with a high-resolution mass spectrometric detector (Hewlett-Packard Model 6890/Auto Spec Ultima-Micromass) with DB-5MS (J&W Scientific; 60 m × 0.25 mm i.d. with 0.25 um film thickness) for hepta-to octa-CDD/Fs and Co-PCBs and SP-2331 (J&W Scientific; 60 m × 0.32 mm i.d. with 0.20 um film thickness) fused silica capillary columns for tetra- to hexa-CDD/Fs. Recovery ranges for $^{13}C_{12}$-labeled Co-PCBs and PCDD/Fs were 83～98% and 77～115%, respectively.

Table 1. The input sources of wastewater in WWTPs

Unit : %

Classification	SS	DS	NC	CS	YS	SP
Textile	**26**	**32**	**24**	-	-	-
Dying	**49**	9	1	-	-	5
Fiber	1	12	**58**	-	-	1
Metal molding	8	12	4	3	**21**	-
Plating	4	-	-	-	-	-
Chemistry	1	3	4	4	16	-
Food	5	11	1	21	**52**	6
Paper	3	-	5	**62**	1	**86**
Other	4	21	3	10	10	1

Table 2. PCDD/Fs levels in sewage sludge

Sample	∑PCDDs (pg/g)	∑PCDFs (pg/g)	∑PCDD/Fs (pg/g)	PCDD/Fs (pg-TEQ/g)	∑Co-PCBs (pg/g)	Co-PCBs (pg-TEQ/g)	PCDD/Fs in Influent[5] (pg-TEQ/L)
SS	1212.69	1718.64	2931.33	10.67	13156.21	4.14	1.70
DS	159.56	240.81	400.37	1.073	1024.54	0.84	1.89
NC	192.91	142.63	335.55	0.247	NA	NA	1.86
CS	15473.79	51088.80	66562.59	1242.6	1868.29	23.93	24.96
YS	53.51	45.67	99.18	0.179	445.57	0.29	0.42
SP	1524.69	3080.04	4604.74	94.38	NA	NA	42.13

NA : not analyzed

Results and Discussion

PCDD/Fs and Co-PCBs levels in WWTPs

The PCDDs/Fs levels in sewage sludge and influent water samples and the Co-PCBs levels in sewage sludge samples are shown in Table 2. The levels of PCDD/Fs and Co-PCBs varied according to WWTP types. The PCDD/Fs levels in sewage sludge samples were below the regulation of PCDD/Fs levels for land application in EU (<100 ng-TEQ/kg dm) except one WWTP, and PCBs levels in all sludge samples were also lower than the 0.8 mg/kg dm regulated by EU.

The concentrations of PCDD/Fs in sludge samples ranged from 99.2pg/g to 66562.6pg/g (0.179~1242.6pg-

TEQ/g), and Co-PCBs levels ranged from 445.6pg/g to 13156.2pg/g (0.286~ 24.9pg-TEQ/g). The PCDD/Fs levels in influent water samples and the removal efficiency in the same target WWTPs have been already investigated by Oh et al. (2006)[5], who reported that the PCDD/Fs levels in influent water samples varied from 8.6 pg/L to 1549.6 pg/L (0.422 ~ 42.1 pg-TEQ/L).

The CS and SP show high PCDD/Fs levels. The paper industry is the main source of wastewater in CS and SP and, generally, the paper industry is regarded as one of the primary PCDD/Fs sources because of chlorine bleaching. Therefore, it seems that this is the main reason the CS and SP had high PCDDs/Fs levels. Most WWTPs (NC, DA and DS) in this study show the low PCDD/Fs levels, which ranged from 99.2pg/g to 400.37pg/g (0.179~1.073pg-TEQ/g). SS shows a middle PCDDs/Fs level (10.67pg-TEQ/g). The input sources of these WWTPs are textile (32% in DS), dyeing (49% in SS), fiber (58% in NC) and food industries (52% in YS).

The Co-PCBs levels in sewage sludge were analyzed for samples corrected from 4 WWTPs(SS, DS, CS and YS) and ranged from 445.6pg/g to 13156.2pg/g (0.286~23.9pg-TEQ/g). The SS and CS WWTPs show relatively high Co-PCBs levels. The major input sources of SS and CS WWTPs are textile and paper industries, and chlorine bleaching is the main cause of high Co-PCBs levels like PCDD/Fs. Correlation analysis was performed to investigate the relationship between PCDD/Fs and Co-PCBs levels in sewage sludge, even though the number of samples is low. A positive relationship was observed between PCDD/Fs and Co-PCBs in sewage sludge and the coefficient of correlation was 0.99(p<0.01).

PCDD/Fs Homologue Distribution patterns in WWTPs

Figure 1 shows the PCDD/Fs homologue profiles in sewage sludge. Previous studies[4,6] reported that hepta and octa-CDD/F were dominant in sewage sludge, but, in this study, the PCDDs/Fs homologue distribution patterns varied greatly according to WWTPs types. However, NC and YS samples are characterized by OCDD/Fs and HpCDD/Fs that are similar to previous studies. Martinez et al. (2006) reported that the deposition is one of the sources of PCDD/Fs in sewage sludge[7] and the PCDD/Fs deposition is dominated by high chlorinated dioxins and furans[8]. Because NC and YS samples show the low PCDD/Fs levels and the homologue profile match with the PCDD/Fs deposition profile, it seems that PCDD/Fs in the NC and YS sludge samples were influenced by the PCDD/Fs deposition, rather than the input sources of wastewater in WWTPs.

Figure 2 shows a score plot of a principal component analysis (PCA) from a fraction of the PCDD/Fs homologue in different sludge samples. Group 1 is composed of CS, DS and SP samples, and PCDFs are dominant rather than PCDDs in this group. According to Mcdonald et al. (1998), a total TCDF is a characteristic marker for chlorine bleaching[9] and Dimmel et al. (1993) reported that lower chlorinated PCDFs are formed by the chlorination of dibenzofuran (DBF) during the chlorine bleaching process of pulp[10]. Because the major input sources in group 1 are textile (DS) and paper (CS and SP) industries, group 1 is influenced by PCDD/Fs that are formed from the chlorine bleaching process.

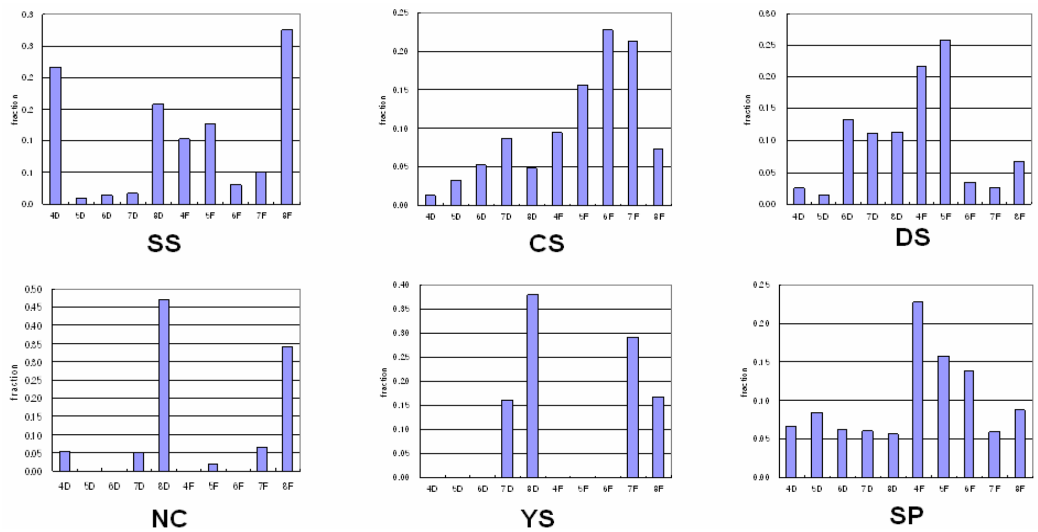

Figure 1. The fraction of PCDDs/Fs homologue in sewage sludge

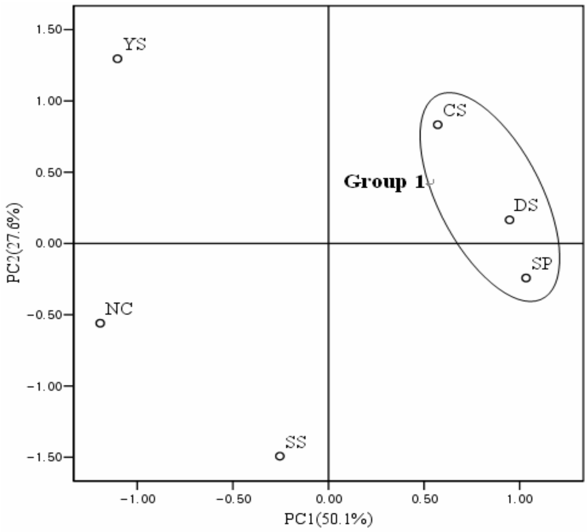

Figure 2. A score plot of PCA from a fraction of PCDDs/Fs homologue in sludge samples

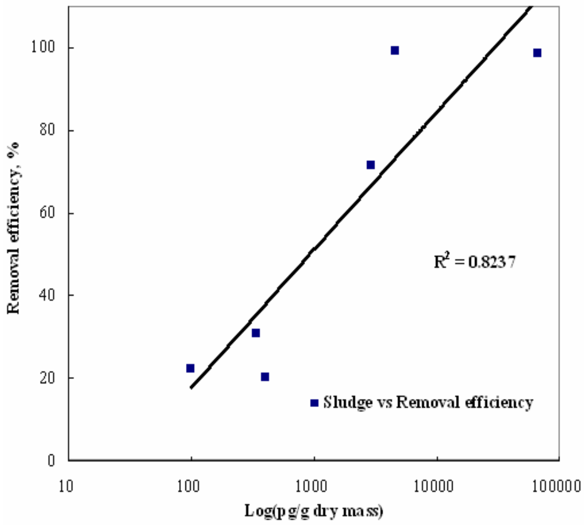

Figure 3. The relation between PCDD/Fs levels in sewage sludge and the removal efficiency of WWTPs in a semi-log scale

The relation between PCDD/Fs levels in sewage sludge and removal efficiency of WWTPs

The relationship between the removal efficiency of PCDD/Fs in WWTPs that was reported by Oh et al. (2006) and PCDD/Fs levels in sewage sludge in this study was investigated. A positive correlation, which is statistically significant, $p<0.012$, was found in a semi-log scale with a R^2 of 0.824 (Figure 3). This result indicates that PCDD/Fs in wastewater might be transferred to sludge by sorption while passing through WWTPs.

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