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# Survey of PCDDs and PCDFs in Air and Soil Around Various Incinerators in Korea, 2003–2007

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**Abstract** To investigate the levels of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) pollution in soils and air around incinerators, a total of 574 soil and 48 air samples were collected around 22 incineration facilities in Korea from 2003 to 2007. The concentrations of PCDD/Fs in the flue gases and air ranged from 0.01 to 21.50 ng I-TEQ $Sm^{-3}$ and 0.0002 to 9.95 pg I-TEQ $Sm^{-3}$, respectively whereas concentrations in soils ranged from n.d. to 153.23 pg I-TEQ $g^{-1}$ dw. The average value was 8.14 pg I-TEQ $g^{-1}$ dw in soil samples.

**Keywords** PCDD/Fs · Incinerator · Soil · Air

Persistent organic pollutants (POPs) are highly toxic chemicals that remain in the environment for long times, bioaccumulate and cause environmental contamination through water and air. In order to address this problem, the Stockholm Convention was enacted in 2005 and ratified by Korea in 2007. Currently, among the 12 POPs, Korea is focusing attention on unintentional POPs. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are created during incineration or heat processing in certain industries (Schuhmacher et al. 1997). Once released into the environment, they spread into other media through air, and accumulate in media containing organic matter due to their semi-volatile and hydrophobic properties (Adriaens et al. 1995).

Since the investigation of PCDD/Fs in Korea in 1997, a public concern about toxic materials is growing. In 2003, a study reported that PCDD/Fs in the soil near an incineration facility located in Pyeongtaek, Korea, contained high concentrations. The report demanded a full investigation into the influence of these materials, which has led this project.

In order to estimate contamination levels and identify the sources of PCDD/Fs, PCDD/Fs levels were investigated in flue gases, airs and soils around incinerators. In addition the PCDD/Fs congener profiles and the relationship between the distance from the incinerators and the concentration of PCDD/Fs in soil were assessed.

## Materials and Methods

Samples of incineration gas were collected from the 22 facilities during summer and winter using stack sampler (n = 38). However, samples could not be taken from three of the facilities because they were under maintenance at the time. A total of 48 ambient air samples were collected over a 24 h period using a high volume air sampler equipped with a glass fiber filter and polyurethane foam. The air sampling sites were selected through the US EPA ISCLT 3 model, considering the weather data accumulated over the

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previous 3 years. A total 574 soil samples were collected at the sites 250, 500, 1,000 and 2,000 m from the facilities, according to the prevailing wind direction, and opposite as well as 2-vertical directions against the prevailing wind direction. However, sampling of three facilities was carried out using systematic/grid sampling method because they were located within 2.5 km of each other.

The cleanup procedure was performed according to the EPA 1613 method and Korean analytical method for endocrine disruptor chemicals. More than 16 h of Soxhlet extraction with distilled toluene was carried out for solid phase sample extraction. For emission gas, liquid phase samples (Diethylene glycol, rinse solution and others) were collected by liquid–liquid extraction. The extracts were treated with sulfuric acid, multilayer silicagel column ($Na_2SO_4$ 1 g + 10% $AgNO_3$/silica 1 g + silica 1 g + 44% $H_2SO_4$/Silica 12 g + silica 1 g + $Na_2SO_4$ 1 g), and alumina column (8 g). A $^{13}C$-labeled recovery standard was then added to the final concentrated solution for HRGC/HRMS analysis. This study used two columns to make a clear distinction: 17 2,3,7,8-substituted congeners; DB-5(MS) column (60 m, 0.25 mm ID, 0.25 μm) was used for the hepta- and octa-CDD/Fs, and a SP-2331 column (60 m, 0.25 mm ID, 0.2 μm) column was used for the tetra-, penta-, and hexa-CDD/Fs. The average recovery rate of the standard solution ranged from 60% to 110%. All concentrations below the quantitation limit were considered to be zero. The limit of quantitation for tetra-chlorinated compounds is 1 pg/g dw.

Multivariate analysis was carried out using the STATISTICA 2000 for Windows® release 5.0 software. In order to understand the relationships between the source PCDD/Fs and soil PCDD/Fs, a comparison of the 2,3,7,8-congener profile was carried out and the soil samples were categorized into four groups according to the PCDD/Fs congener profile through cluster analysis.

## Results and Discussion

Table 1 shows the concentration of PCDD/Fs in flue gases, ambient air and soil. In the flue gas samples, the PCDD/Fs concentrations ranged from 0.01 to 21.50 ng I-TEQ $Sm^{-3}$, and the mean and median value was 3.12 and 1.55 ng I-TEQ $Sm^{-3}$, respectively. This variation of concentration was explained by the types of combustion materials because all the facilities have similar treatment equipment. The concentration of PCDD/Fs in the flue gas samples were similar or lower than the levels reported in other studies (Kim et al. 2005; Yu et al. 2006). In general, the

**Table 1** Concentration of the PCDD/F congeners in various samples collected around incinerators in Korea

| Congener | Flue gases (n = 38) (ng $Sm^{-3}$) | | | | Ambient airs (n = 48) (pg $Sm^{-3}$) | | | | Soils (n = 574) (pg $g^{-1}$ dry matter) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Minimum | Maximum | Mean | Median | Minimum | Maximum | Mean | Median | Minimum | Maximum | Mean | Median |
| 2,3,7,8-TCDF | 0.00 | 11.39 | 0.99 | 0.29 | 0.00 | 1.76 | 0.14 | 0.06 | 0.00 | 124.37 | 2.80 | 0.00 |
| 1,2,3,7,8-PeCDF | 0.02 | 15.78 | 1.66 | 0.70 | 0.00 | 5.62 | 0.25 | 0.07 | 0.00 | 62.58 | 3.70 | 1.12 |
| 2,3,4,7,8-PeCDF | 0.00 | 19.67 | 2.48 | 1.09 | 0.00 | 6.24 | 0.34 | 0.10 | 0.00 | 103.37 | 5.38 | 1.54 |
| 1,2,3,4,7,8-HxCDF | 0.00 | 17.63 | 2.39 | 1.13 | 0.00 | 5.06 | 0.27 | 0.09 | 0.00 | 79.92 | 5.43 | 0.00 |
| 1,2,3,6,7,8-HxCDF | 0.00 | 19.96 | 3.36 | 1.91 | 0.00 | 7.83 | 0.43 | 0.14 | 0.00 | 156.87 | 7.30 | 2.15 |
| 2,3,4,6,7,8-HxCDF | 0.00 | 14.88 | 3.83 | 1.93 | 0.00 | 13.24 | 0.59 | 0.15 | 0.00 | 117.80 | 7.17 | 0.00 |
| 1,2,3,7,8,9-HxCDF | 0.00 | 1.83 | 0.29 | 0.17 | 0.00 | 0.99 | 0.06 | 0.00 | 0.00 | 167.08 | 2.22 | 0.00 |
| 1,2,3,4,6,7,8-HpCDF | 0.00 | 72.17 | 13.59 | 6.40 | 0.02 | 41.23 | 1.87 | 0.60 | 0.00 | 494.48 | 40.72 | 10.06 |
| 1,2,3,4,7,8,9-HpCDF | 0.00 | 7.07 | 1.71 | 1.07 | 0.00 | 4.41 | 0.24 | 0.08 | 0.00 | 93.68 | 5.43 | 0.00 |
| OCDF | 0.00 | 57.27 | 8.60 | 4.04 | 0.00 | 22.66 | 1.17 | 0.42 | 0.00 | 982.01 | 61.38 | 14.00 |
| 2,3,7,8-TCDD | 0.00 | 1.49 | 0.11 | 0.02 | 0.00 | 0.35 | 0.02 | 0.00 | 0.00 | 8.19 | 0.14 | 0.00 |
| 1,2,3,7,8-PeCDD | 0.00 | 4.89 | 0.46 | 0.12 | 0.00 | 2.28 | 0.09 | 0.03 | 0.00 | 21.76 | 0.97 | 0.00 |
| 1,2,3,4,7,8-HxCDD | 0.00 | 1.93 | 0.38 | 0.17 | 0.00 | 2.04 | 0.08 | 0.03 | 0.00 | 19.80 | 0.86 | 0.00 |
| 1,2,3,6,7,8-HxCDD | 0.00 | 4.64 | 0.79 | 0.44 | 0.00 | 6.76 | 0.21 | 0.05 | 0.00 | 50.93 | 2.38 | 0.00 |
| 1,2,3,7,8,9-HxCDD | 0.00 | 2.11 | 0.45 | 0.25 | 0.00 | 4.63 | 0.15 | 0.03 | 0.00 | 44.07 | 1.76 | 0.00 |
| 1,2,3,4,6,7,8-HpCDD | 0.00 | 24.69 | 4.39 | 2.55 | 0.00 | 34.06 | 1.15 | 0.24 | 0.00 | 604.53 | 31.40 | 10.92 |
| OCDD | 0.00 | 49.66 | 8.11 | 5.00 | 0.00 | 40.31 | 1.58 | 0.50 | 0.00 | 9,380.04 | 298.92 | 67.15 |
| PCDFs | 0.07 | 177.90 | 38.90 | 22.00 | 0.02 | 108.69 | 5.33 | 1.74 | 0.00 | 1,789.54 | 149.62 | 38.18 |
| PCDDs | 0.00 | 84.08 | 14.68 | 9.96 | 0.00 | 90.42 | 3.29 | 0.83 | 0.00 | 10,021.31 | 339.38 | 83.03 |
| PCDFs + PCDDs | 0.07 | 261.98 | 53.58 | 31.02 | 0.02 | 199.11 | 8.62 | 2.59 | 0.00 | 10,488.36 | 482.16 | 143.44 |
| I-TEQ | 0.01 | 21.50 | 3.12 | 1.55 | 0.00 | 9.95 | 0.47 | 0.13 | 0.00 | 153.23 | 8.14 | 1.97 |

concentration of PCDFs was higher than that of the PCDDs in the incinerator emission gas samples. Kim et al. (2001) reported that the PCDF:PCDD emission ratios from incinerators were 78:22 and 84:16 and Yu et al. (2006) also reported PCDF:PCDD ratios of 60–84:16–40 in emission gases various metallurgy industries. In this study, the PCDF:PCDD ratio was 71:29, which is similar to the data from other reports, and these ratios are considered to be characteristic of incineration gas.

The ambient air collected at the maximum concentration deposition points, the concentration of PCDD/Fs ranged from 0 to 9.95 pg I-TEQ $Sm^{-3}$ with a mean and median value of 0.47 and 0.13 pg I-TEQ $Sm^{-3}$, respectively. These results are comparable to other research results. Cheng et al. (2003) reported that the concentration of PCDD/Fs ranged from 0.06 to 0.13 pg I-TEQ $m^{-3}$ at four points within a 2.5 km radius from the incinerator. Caserini et al. (2004) also reported that the concentration of PCDD/Fs around three incineration facilities in Italy ranged from 0.01 to 0.34 pg I-TEQ $m^{-3}$. According to the data obtained by the National Institute of Environmental Research (NIER) from 1999 to 2006, the concentration of PCDD/Fs ranged from 0 to 4.45 pg I-TEQ $Sm^{-3}$, with an average and median value of 0.34 and 0.14 pg I-TEQ $Sm^{-3}$, respectively. The average and median PCDF:PCDD ratios in ambient air collected near the incinerators were both 70:30, which is similar to the emission ratios from incineration gas.

The concentrations of PCDD/Fs in the soil ranged from 0 to 153.23 pg I-TEQ $g^{-1}$ dw with a mean and median value of 8.14 and 1.97 pg I-TEQ $g^{-1}$ dw, respectively in this study. Table 2 summarizes the concentration of PCDD/Fs in soils around incinerators. These results indicate a higher value than the levels reported in other studies. This can be explained by the fact that this study focused on the high risk incineration facilities in Korea. Therefore, the PCDD/Fs concentration in Korean soil samples might be within range of this study.

The potential effects of the incinerator can be estimated by comparing the concentration of PCDD/Fs in soil at certain distances from the incinerator. Table 3 shows that the PCDD/Fs concentration decreased with increasing distance. The median value at 250, 500, 1,000 and 2,000 m was 6.20, 1.85, 1.29, and 0.83 pg I-TEQ $g^{-1}$, respectively. In addition, the highest values were found within a 250 m radius. This is evidence of the effects of the facilities on the soil. In the soil samples, the concentration of PCDD was higher than PCDF, the average and median PCDF:PCDD ratio was 30:70 and 26:74, respectively, which is in contrast to that in the air and flue gas. As shown in Table 1, OCDD was predominant among the PCDD/F congeners. This result can be explained by the remaining influence of PCP herbicide.

Multi regression analysis was carried out to determine the relationships between the concentration of PCDD/Fs in soil and the factors of the incinerator, such as the operation period, stack height, combustion volume and concentration of flue gas. No clear relationships were found within the 95% confidence interval. In addition, there was no relationship between the concentration of PCDD/Fs in ambient air and that of flue gas. These results can be explained by other combustion sources and/or degradation of PCDD/Fs within the soil.

Figure 1 shows the contribution of 17 PCDD/F congeners against I-TEQ concentration in flue gas, ambient air, and soil. This makes the contribution more independent of the concentration levels. In addition, congeners that mainly contribute to the I-TEQ of combustion-origin samples are different from those from agrochemical-influenced samples (Lohmann et al. 1999; Capuano et al. 2005). 2,3,4,7,8-PeCDF was the largest contributor to the I-TEQ in the soil samples followed by OCDD, 1,2,3,4,6,7,8-HpCDF and 1,2,3,4,6,7,8-HpCDD. Among the these congeners, 1,2,3,4,6,7,8-HpCDF is a major toxic congener (2,3,7,8-chlorine-substituted) of PCP herbicides (Masunaga et al. 2001). In addition, the OCDD-dominated profile is a

**Table 2** PCDD/Fs concentrations (pg I-TEQ $g^{-1}$) in the soil samples collected near incinerators in previous studies

| Place | Number of samples | Concentration | Reference |
|---|---|---|---|
| Po Valley, Italy | 3 | 0.7–1.5 | Caserini et al. (2004) |
| Veneto, Italy | 3 | 1.1–1.4 | Caserini et al. (2004) |
| Adige Valley, Italy | 3 | 0.08–1.2 | Caserini et al. (2004) |
| Reggio Emilia, Italy | 18 | 1.9–63.0 | Capuano et al. (2005) |
| Hsinchu, Taiwan | 8 | 0.52–5.02 | Cheng et al. (2003) |
| Barcelona, Spain | 24 | 1.22–34.28 | Domingo et al. (2000) |
| Newcastle, UK | 86 | 6–1,911 (32)[b] | Catherine et al. (2006) |
| Buchon, Korea | 10 | 1.25–74.98 | Oh et al. (2006) |
| Nationwide, Korea[a] | 190 | 0.0–80.93 (0.03)[b] | NIER (1999–2005) |
| Nationwide, Korea | 574 | 0.00–153.23 (1.97)[b] | This study |

[a] Means not soil samples collected near incinerator

[b] Mean median value

**Table 3** PCDD/Fs concentrations (pg I-TEQ $g^{-1}$ dry matter) in soil samples collected at different distances from the incinerators in this study

| Approximate distance (m) | Minimum | Maximum | Mean | Median | Standard deviation |
|---|---|---|---|---|---|
| 250 | 0.00 | 153.23 | 16.00 | 6.20 | 24.56 |
| 500 | 0.00 | 95.55 | 8.11 | 1.85 | 15.64 |
| 1,000 | 0.00 | 94.30 | 4.88 | 1.29 | 11.31 |
| 2,000 | 0.00 | 37.24 | 2.78 | 0.83 | 5.33 |

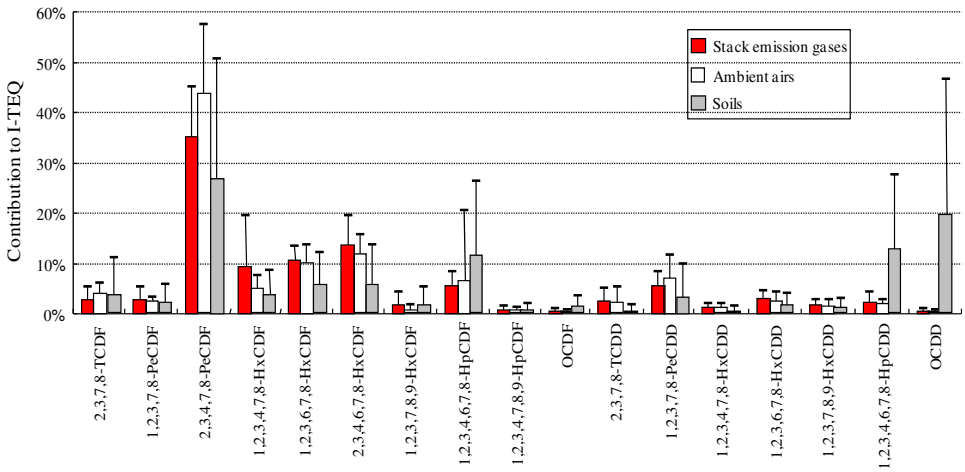


**Fig. 1** Contribution of 2,3,7,8-chlorine substituted congeners to the I-TEQ in stack emission gas, ambient air, and soil samples. Each *box* and *vertical bar* represent the mean and SD, respectively

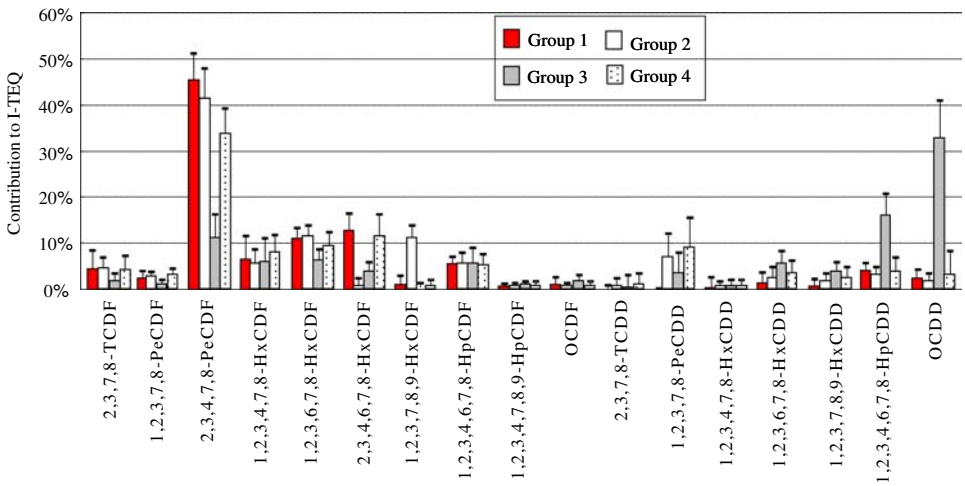


**Fig. 2** Contribution of 2,3,7,8-chlorine substituted congeners to the I-TEQ in each soil-group by cluster analysis. Each *box* and *vertical bar* represent the mean and SD, respectively

typical one that is often found in compost, sewage sludge or PCP samples (Zook and Rappe 1994). On the other hand, 2,3,4,7,8-PeCDF was predominant in flue gas samples, followed by 2,3,4,6,7,8-HxCDF and 1,2,3,6,7,8-HxCDF. Therefore, these congeners were considered to originate from combustion. This pattern was observed in ambient air and flue gases, which suggests that air is directly affected by incineration. In addition, the 2,3,4,7,8-PeCDF was assumed to be the origin of the incineration process (Zook and Rappe 1994; Capuano et al. 2005), and was found to make the largest contribution to the flue gases and soil samples in this study.

Figure 2 shows the PCDD/Fs congener profile of the 4 groups categorized by cluster analysis in soil samples. The profile of Group 1 is similar to the combined profile of flue gas and air (see Fig. 1), and may be influenced by unknown sources due to the small the contribution from 1,2,3,7,8-PeCDD – specific congener of incineration. Seventy-two samples (27%) showed this congener pattern. The profile of Group 2 was typical of incineration facilities, and 52 samples belonged to Group 2. The difference between Groups 1 and 2 in terms of the congener was 2,3,4,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF and 1,2,3,7,8,9-PeCDD. 11% of the 267 samples showed an OCDD-dominated pattern,

which indicates the influence of PCP. Most samples (43%) are included in Group 4, and this group showed a similar congener pattern to Group 1 except for 1,2,3,7,8-PeCDD. These samples showed similar patterns to the air samples, which were taken around the incineration facilities, and also had the typical characteristics of flue gas. This highlights the multiple influences of incinerators and air. Overall, the soil samples around an incinerator were influenced by both the combustion products and PCP.

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