THE CONCENTRATION AND CONGENER PROFILING OF PCDDs/PCDFs IN SOIL SAMPLES FROM BUSAN CITY, SOUTH KOREA

Tae uk Jeong[1], Jae Eun Jeong[2], Kwang Soo Kim[2], Jae Hun Bin[2], Hong Sik Cheigh[2]
[1]BIHE, and Division of Applied Life Science, Gyeongsang National University, South Korea
[2]Busan Institution of Health & Environment(BIHE), South Korea

Introduction

Polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofurans(PCDDs/PCDFs) are well known as persistent organic pollutants(POPs). Soil is the main reservoir of PCDDs/PCDFs emitted from various sources such as incinerators, factories, automobils and so on. PCDDs/PCDFs released in the atmosphere from the different emission sources return to the soil, plants or organisms by dry or wet deposition process and finally accumulate to human beings through food chains. So many researchers have investigated the soil contamination of PCDDs/PCDFs in their contries[1,2].

The aim of this research was to identify the toxic equivalents and evaluate the contamination caused by PCDDs/PCDFs in different soil samples in Busan city, South Korea. And the concentration and congener profiling of PCDDs/PCDFs in different soil samples were compared.

Materials & Methods

Sampling :

The monitoring of PCDDs/PCDFs in soil samples was undertaken at different sites throughout Busan city, South Korea. 17 soil samples were collected in May 2005, classified as factory area(FA, 7 sites), traffic related area(TA, 2 sites), metal mine area(MA, 2 sites), waste landfill area(LA, 4 sites) and waste incineration area(IA, 2 sites) in Busan city, South Korea.

Every soil sample was the surface soil(about 5 cm of sampling depth) and collected by 5 point mixture method. And the collected soil samples were air dried, sieved(2 mm mesh) and mixed.

Extraction & Cleanup :

Soil samples were extracted by soxhlet extraction with toluene for 24 hours.

To cleanup sample extracts, multi-silica column, alumina column and carbon column were used according to the JIS method(JIS K 0311, 1999)[3] and ISO method(ISO 18073, 2004)[4]. Silica gel was activated by heating in dry oven at 180℃ for 2 hours after washing with dichloromethane. Multi-silica column was packed from bottom to top with : 2% KOH-silica gel, 44% H_2SO_4-silica gel, 22% H_2SO_4-silica gel and 10% $AgNO_3$-silica gel. PCDFs/PCDDs were eluted by 150mL hexane. Basic alumina was activated by heating in muffle furnace at 600℃ for 24 hours. The first fraction of alumina column was 100 mL hexane solution containing dichloromethane(2% vol.). This fraction was discarded. After then, the second fraction with 150 mL hexane solution containing dichloromethane(50% vol.) was received. Carbon column was made of 18%(w/w) mixture of carbopak C and celite 545AW and activated at 130℃ for 6 hours. Interfering compounds were eluted by hexane 3 mL, dichloromethane : cyclohexane (1:1, v/v) 2 mL and dichloromethane : methanol : toluene(15:4:1, v/v/v) 2 mL. And these fractions were discarded. After inverting column, PCDFs/PCDDs were eluted by toluene 50 mL.

Instrument analysis :

HRGC/HRMS measurement was carried out over 10,000 resolution at 10% valley by Autospec ultima (Micromass Ltd, UK) interfaced with an HP 6890 series plus gas chromatograph(Agilent, USA) equipped with SP-2331 column(Supelco ; 60m length×0.25mm ID×0.2um thick) using a positive electron ionization mode and operating in the selected ion monitoring mode. US-EPA method 1613(1994)[5] and ISO method 18073 (2004) were followed in other general procedures of instrument analysis.

Results & Discussion

The toxic equivalent values and congener profiling of PCDDs/PCDFs in soil samples according to the land use were shown in Fig. 1 and Table 1. There were considerable variations in the concentration and congener profiling according to the different localities.

The average toxic equivalent of waste incinerator area(IA) was highest(98.78 pg I-TEQ/g) among monitoring areas, but was slightly lower than in England(2003, 12-554 ng I-TEQ/kg with average 108 ng I-TEQ/kg)[6]. The average values of PCDDs/PCDFs in the FA, TA, LA and MA were 44.55, 3.77, 2.36 and 1.72 pg I-TEQ/g, respectively. The distribution of TEQ values tends to be much higher in IA and FA than in TA, LA and MA.

In the case of IA, PCDFs(75.72 pg I-TEQ/g)were identified more than PCDDs(23.06 pg I-TEQ/g) by 3.28. And the contributions of 2,3,4,7,8-PeCDF and 2,3,4,6,7,8-HxCDF were higher than the other congeners.

On the contray, in the case of FA, the level of PCDDs was ranged from 0.32 to 132.24 pg I-TEQ/g, with a average value of 30.81 pg I-TEQ/g and higher than that of PCDFs(ranged from 0.53-35.80, average 13.74 pg I-TEQ/g). OCDD(22.27 pg I-TEQ/g) was much higher than any other toxic congener.

On the other hand, the levels of TA, LA and MA were significantly lower than that of above two areas(IA and FA). The contribution of PCDFs was higher than that of PCDDs in these three areas(TA, LA and MA). The level of 2,3,4,7,8-PeCDF was highest among 17 congeners in TA, accounting for 0.15-2.60 pg I-TEQ/g and average 1.38 pg I-TEQ/g and followed by those of 2,3,4,6,7,8-HxCDF, 1,2,3,4,7,8-HxCDF and 1,2,3,7,8-PeCDD. The contributions of 2,3,4,7,8-PeCDF in LA and MA were 34.3 and 22.7 %, respectively and highest out of 17 congeners.

Consequently, the high levels of PCDDs/PCDFs in waste incinerator area(IA) and factory area(FA) have been affected by stack gas from waste incinerator and factories[7]. So it was concluded that the PCDDs/PCDFs levels in IA(3.33-194.23, average 98.78 pg I-TEQ/g) and FA(0.85-156.45, average 44.55 pg I-TEQ/g) caused a gradual contamination of the soil by dry or wet deposition, with dioxin levels increasing over time.

Acknowledgements

Financial support by Busan Institutuin of Health & Environment(BIHE) is gratefullt acknowledged.

Reference

1. Zuo-sheng. C., Wei L., Chang-qing L., Ping H., Geng-yun L., Zheng Z. *Organohalogen Comp* 2003 ; 62.
2. Eljarrat E., Caixach J., Rivera J. *Chemosphere* 2001 ; 44 : 1383.
3. JIS method K 0311, 1999, Japanese Industrial Standard.
4. ISO method 18073, 2004, International Standard Organization.
5. US-EPA method 1613, 1994, US Environmental Protection Agency.
6. Catherine V., Tanja P. M., Vivienne A., David R., Ian S., Bernd S., Olaf O. *Organohalogen Comp* 2003 ; 62.
7. Domingo J., Granero S., Schuhmacher M., *Chemosphere* 2001 ; 43 : 517-524.

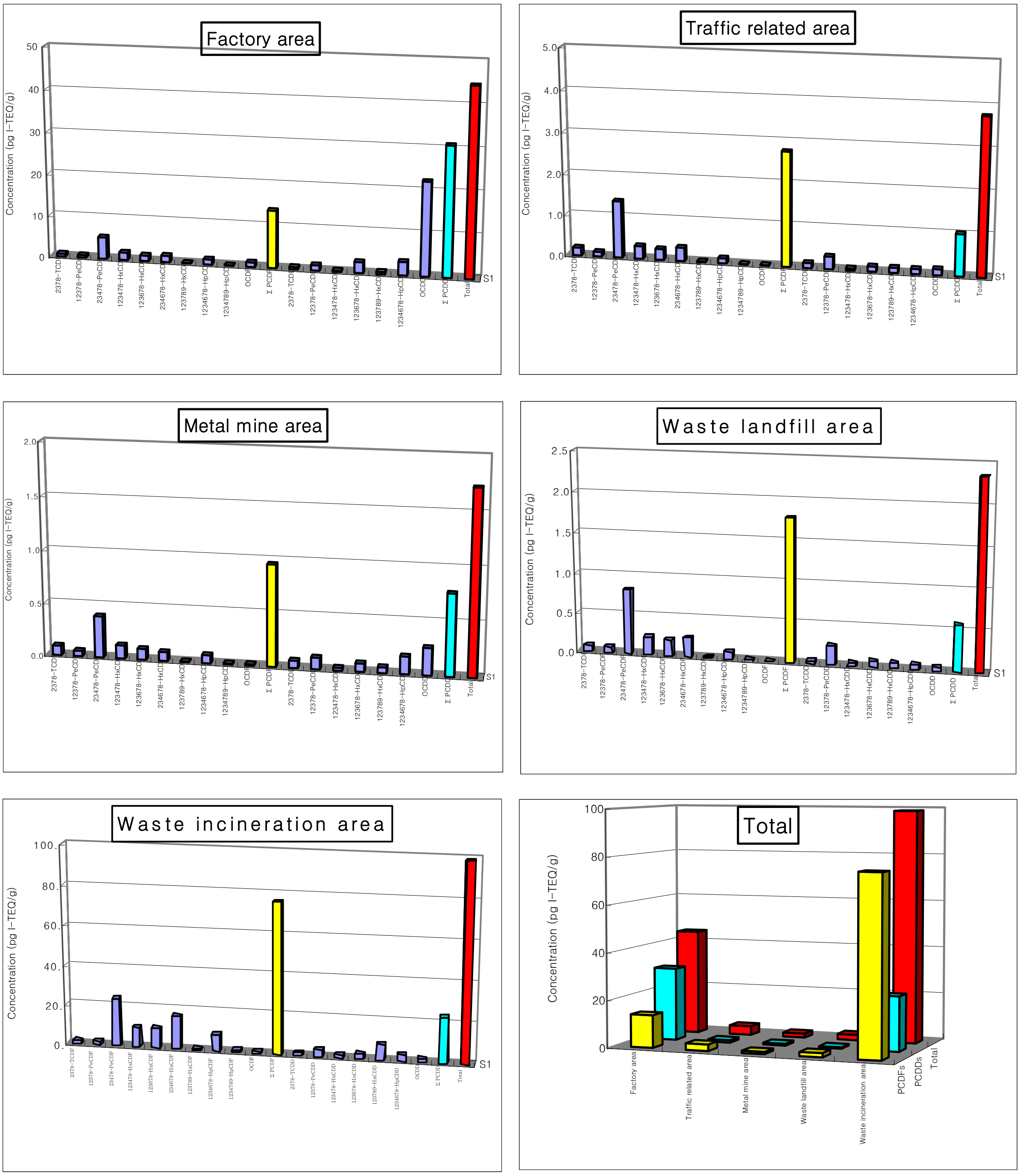

Fig. 1. PCDDs/PCDFs congener profiles in the different soil samples.

Table 1. Average I-TEQ values of PCDDs/PCDFs in soil samples according to the land use.

No.	Chemicals	Concentration (pg I-TEQ/g)				
		factory area (FA)	Traffic related area (TA)	Metal mine area (MA)	Waste landfill area (LA)	Waste Incinerationr Area (IA)
1	2378-TCDF	0.05 ~ 2.61 (0.68)	0.05 ~ 0.33 (0.19)	0.04 ~ 0.14 (0.09)	0.04 ~ 0.20 (0.08)	0.16 ~ 3.20 (1.68)
2	12378-PeCDF	0.02 ~ 2.05 (0.60)	0.01 ~ 0.22 (0.11)	0.03 ~ 0.08 (0.05)	0.00 ~ 0.20 (0.07)	0.19 ~ 3.43 (1.81)
3	23478-PeCDF	0.00 ~ 15.78 (5.20)	0.15 ~ 2.60 (1.38)	0.23 ~ 0.56 (0.39)	0.00 ~ 2.37 (0.81)	1.23 ~ 46.89 (24.06)
4	123478-HxCDF	0.08 ~ 5.01 (1.78)	0.05 ~ 0.58 (0.31)	0.04 ~ 0.21 (0.13)	0.05 ~ 0.62 (0.23)	0.29 ~ 19.61 (9.95)
5	123678-HxCDF	0.11 ~ 3.79 (1.33)	0.03 ~ 0.50 (0.26)	0.04 ~ 0.16 (0.10)	0.00 ~ 0.60 (0.20)	0.27 ~ 19.76 (10.01)
6	234678-HxCDF	0.09 ~ 4.28 (1.57)	0.00 ~ 0.66 (0.33)	0.05 ~ 0.12 (0.08)	0.03 ~ 0.75 (0.25)	0.24 ~ 33.38 (16.81)
7	123789-HxCDF	0.00 ~ 0.49 (0.14)	0.00 ~ 0.04 (0.02)	0.00 ~ 0.01 (0.01)	0.00 ~ 0.05 (0.02)	0.00 ~ 1.44 (0.72)
8	1234678-HpCDF	0.04 ~ 4.22 (1.25)	0.01 ~ 0.23 (0.12)	0.02 ~ 0.14 (0.08)	0.02 ~ 0.23 (0.09)	0.11 ~ 16.75 (8.43)
9	1234789-HpCDF	0.00 ~ 0.51 (0.12)	0.00 ~ 0.03 (0.01)	0.00 ~ 0.02 (0.01)	0.00 ~ 0.03 (0.01)	0.00 ~ 2.23 (1.11)
10	OCDF	0.00 ~ 6.92 (1.09)	0.00 ~ 0.03 (0.02)	0.00 ~ 0.03 (0.01)	0.00 ~ 0.01 (0.01)	0.00 ~ 2.25 (1.12)
	Σ PCDF	0.53 ~ 35.80 (13.74)	0.30 ~ 5.21 (2.76)	0.45 ~ 1.46 (0.96)	0.14 ~ 5.06 (1.78)	2.50 ~ 148.94 (75.72)
11	2378-TCDD	0.00 ~ 1.58 (0.56)	0.00 ~ 0.25 (0.12)	0.00 ~ 0.14 (0.07)	0.00 ~ 0.16 (0.04)	0.00 ~ 3.25 (1.63)
12	12378-PeCDD	0.00 ~ 3.42 (1.28)	0.00 ~ 0.62 (0.31)	0.06 ~ 0.16 (0.11)	0.11 ~ 0.48 (0.24)	0.34 ~ 7.14 (3.74)
13	123478-HxCDD	0.00 ~ 0.81 (0.30)	0.00 ~ 0.10 (0.05)	0.01 ~ 0.04 (0.03)	0.00 ~ 0.10 (0.04)	0.06 ~ 3.26 (1.66)
14	123678-HxCDD	0.05 ~ 15.59 (2.62)	0.00 ~ 0.26 (0.13)	0.04 ~ 0.12 (0.08)	0.00 ~ 0.19 (0.08)	0.13 ~ 5.35 (2.74)
15	123789-HxCDD	0.04 ~ 1.47 (0.57)	0.00 ~ 0.25 (0.13)	0.03 ~ 0.08 (0.05)	0.00 ~ 0.17 (0.07)	0.12 ~ 15.08 (7.96)
16	1234678-HpCDD	0.04 ~ 16.60 (3.21)	0.02 ~ 0.23 (0.13)	0.03 ~ 0.31 (0.17)	0.02 ~ 0.12 (0.06)	0.10 ~ 6.78 (3.44)
17	OCDD	0.03 ~ 124.43 (22.27)	0.01 ~ 0.28 (0.15)	0.03 ~ 0.49 (0.26)	0.02 ~ 0.06 (0.04)	0.08 ~ 3.70 (1.89)
	Σ PCDD	0.32 ~ 132.24 (30.81)	0.03 ~ 1.99 (1.01)	0.19 ~ 1.34 (0.77)	0.18 ~ 1.27 (0.58)	0.83 ~ 45.30 (23.06)
	Total	**0.85 ~ 156.45 (44.55)**	**0.34 ~ 7.20 (3.77)**	**0.64 ~ 2.81 (1.72)**	**0.33 ~ 6.33 (2.36)**	**3.33 ~ 194.23 (98.78)**