

## Distribution Characteristics of Dioxins in Soils under Different Land Use in Busan, Korea

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In this study, distribution characteristics of dioxins in soils in Busan, Korea were investigated regarding different land use types. Soil sampling sites that distributed through the Busan city showed dioxin concentration ranging from 0.489 to 322.736 pg-TEQ g<sup>-1</sup> dry weight with a mean value of 26.257 pg-TEQ g<sup>-1</sup> dry weight. The mean dioxin concentrations of investigated soils ranged from 1.554 to 50.357 pg-TEQ g<sup>-1</sup> dry weight in consideration of each land use type. That in metal refinery sites with 50.357 pg-TEQ g<sup>-1</sup> dry weight was higher than any other sites, followed by waste incinerator sites with 44.285 pg-TEQ g<sup>-1</sup> dry weight. The majority of soil samples had the same dioxin congener profiling despite the different range of dioxin concentration. Octa-CDD was the major contributor among seventeen dioxin congeners with the range from 29.5 to 70.1% in real values. In contrast to real values, dioxin congener profiles in TEQ values were dominated by 2,3,4,7,8-PeCDF which contributed about 35.3~43.8% to the total dioxin concentrations. It was judged by these results that penta-CDF was the major contributor of soil samples in Busan city. The mean ratio of PCDFs/PCDDs in real values was about 0.71, but that in TEQ values was, in contrast to it, approximately 3.03.

**Key words:** Dioxin, Soil, Contribution rate

### Introduction

PCDDs/PCDFs (Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans; known as dioxin) are one of persistent organic pollutants (POPs) listed by Stockholm Convention on Persistent Organic Pollutants which was adopted in 2001 and entered into force in 2004.

Dioxins among various pollutants, having the highest toxicity, occur as unintentional by-products of incinerators and chemical factories. Dioxins are organic chemicals which are stable to photochemical, chemical and biological decomposition. Especially, they are not produced but are formed as by-products in the process of certain human activities, i.e. industrial processes, fossil fuel combustion or waste destruction (Guerzoni et al., 2004). In general,

dioxins emitted by incinerators exist in gaseous and particle phase according to the ambient temperature and vapor pressure of dioxin congeners (Lee et al., 2003). Dioxins are found throughout the world in the environment and they accumulate in the food chain. So it is assumed that soils and sediments are the largest reservoir media of dioxins that reflect the characteristics of various sources such as incinerators, factories, automobiles and so on. Soil is the main reservoir of dioxins emitted from various sources such as incinerators, factories, automobiles and so on (Kim et al., 2008; Eljarrat et al., 2001). Therefore, soil pollutants can be absorbed by plants and enter food chains. Furthermore, soils show high affinity for hydrophobic organic pollutants and can act as a natural sink. It is also very important to evaluate the environmental quality of soil concerning with the distribution and contamination of dioxins (Jinsong and Weiping, 2009). Therefore, many researchers have investigated dioxin contaminations in soils (Eljarrat et al., 2001; Zuo-sheng et al., 2003).

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The goal of this study was to investigate the dioxin levels and their contribution rate in soil samples differentiated by land use such as industrial sites, traffic-related sites, metal mine sites, metal refinery sites, waste open-storage sites, waste landfill sites and waste incinerator sites.

## Materials and Methods

Soil samples used in this study were collected at 40 sites through the city Busan from 2007 to 2008 (Fig. 1). Sampling sites were as follows; eleven industrial sites, four traffic-related sites, two metal mine sites, three metal refinery sites, four waste open-storage sites, three waste landfill sites and thirteen waste incinerator sites. Each soil sample which included one center point and four cardinals points was mixed equally, and then air dried, sieved (2 mm mesh), and homogenized. All soil samples were from top soils in depth of about 0~15 cm. All soil sampling was carried out taking into account the need to represent average sampling point conditions and to avoid interference from possible local variations in soil characteristics according to the standard method (APHA, 2005) and guide to soil analysis (NAAS, 2000).

Dioxin analysis of soil samples was carried out according to the standard method (APHA, 2005), US EPA method 1613 (USEPA, 1994), JIS method K 0311 (Japanese Industrial Standard, 2005), and ISO method 18073 (International Standard Organization, 2004). The internal

standard ( $^{37}\text{Cl}$ -2,3,7,8-TCDD,  $2\text{ ng mL}^{-1}$ ) was spiked in air-dried and sieved soil samples followed by treating with 2N HCl and filtering. The acid-treated samples were extracted by soxhlet extraction with toluene for 24 hours right after spiking 100  $\mu\text{L}$  of labeled compound standard solution with mixture of 15 labeled dioxins congeners (Wellington EPA-1613 LCS, USA). To cleanup sample extracts, three column chromatography such as multi-layer silica column, alumina column, and carbon column were carried out according to the Korean standard method and JIS method. Silica gel was activated by washing with dichloromethane followed by heating in dryoven at  $180^\circ\text{C}$  for 2 hours. Multi-silica column was packed from bottom to top with 2% KOH-silica gel, 44%  $\text{H}_2\text{SO}_4$ -silica gel, 22%  $\text{H}_2\text{SO}_4$ -silica gel, and 10%  $\text{AgNO}_3$ -silica gel. PCDDs/PCDFs were eluted by 150 mL hexane. Basic alumina was activated by heating in muffle furnace at  $600^\circ\text{C}$  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-silica gel was used for carbon column. Interfering compounds were eluted by hexane solution containing dichloromethane (25% vol.). After this fraction was discarded, then PCDDs/PCDFs were eluted by toluene 200 mL. This eluting solution was concentrated using by vacuum evaporator and nitrogen evaporator for instrument analysis.

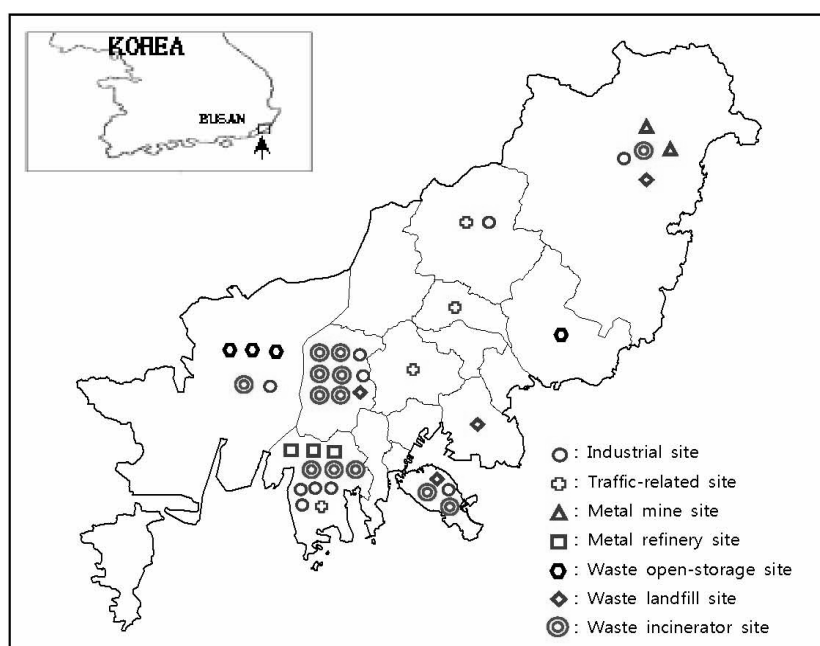
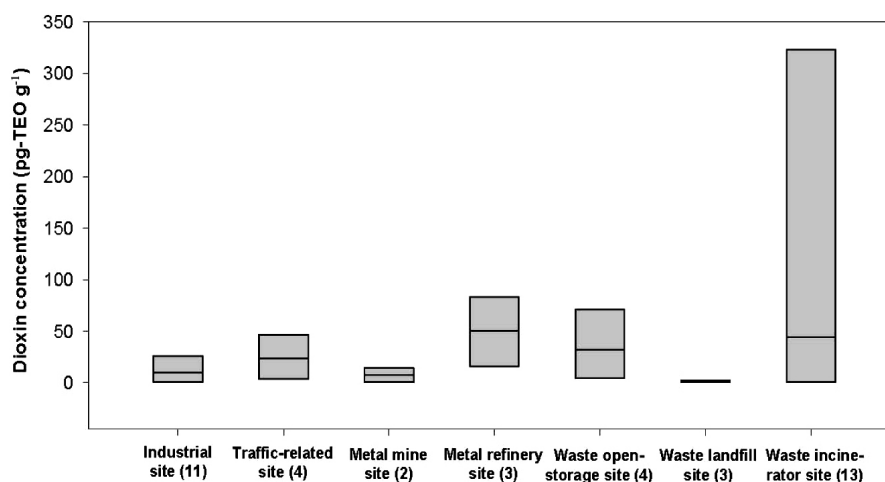


Fig. 1. Soil sampling location with regard to different land use types in Busan, Korea.

**Table 1. Conditions of gas chromatograph and mass spectrometry.**

Descriptor	GC Condition	Descriptor	Mass Condition
Instrument	HP 6890	Instrument	Autospec Ultima
Column	SP-2331 (60 m × 0.25 mm ID × 0.2 μm)	Source temp.	260°C
Carrier gas	Helium 1.0 mL/min	Electron energy	35.0 eV
Injection mode	Splitless mode	Resolution	Over 10,000 at 0% valley
Inlet temp.	260°C	Ionization mode	EI positive mode
Oven ramping	Initial temp. 100°C (5 min.) 20°C/min. → 200°C (7 min.) 5°C/min. → 260°C (36 min.) 10°C/min. → 270°C (2 min.)	Selected Ion Mode	M/M+2 or M+2/M+4
Injection volume	1 μL	Interface temp.	
		- Capillary line 1	260°C
		- Capillary line 2	260°C
		- Re-entrant	260°C
		- PFK septum	160°C



**Fig. 2. Mean concentrations of dioxins in soil samples with regard to different land use types. ( ) indicates the number of soil sampling sites.**

Instrument analysis of pretreated samples was conducted with HRGC/HRMS (Autospecultima, Micromass Ltd, UK) interfaced with an HP 6890 series plus gas chromatograph (Agilent, USA). A SP-2331 capillary column (Supelco: 60 m length × 0.25 mm ID × 0.2 μm film thick) was used for the separation of the isomer specific analysis. HRGC/HRMS measurement was carried out over 10,000 resolution at 10% valley using a positive electron ionization mode and operating in the selected ion monitoring mode. Table 1 shows the operating conditions of gas chromatograph and mass spectrometry.

The identification and quantification of dioxin congeners were performed using the isotope dilution method using relative response factors previously obtained from five standard solution (CS1~5, Wellington EPA-1613CVS, USA). The recovery of each dioxin congener was always in the range 50-120%.

## Results and Discussion

Soil samples collected from 2007 to 2008 showed dioxin concentration ranging from 0.489 to 322.739 pg-TEQ g<sup>-1</sup> dry weight with a mean concentration of 26.257 pg-TEQ g<sup>-1</sup> dry weight. Fig. 2 summarizes mean concentrations of dioxins under different land use types. We have found that the mean dioxin concentration in metal refinery sites among all investigated soil samples was the highest concentration with mean 50.357 pg-TEQ g<sup>-1</sup> dry weight. The site with the second highest level was waste incinerator site of which mean concentration was 44.285 pg-TEQ g<sup>-1</sup> dry weight. Because there were many dioxin sources in metal refinery sites and waste incinerator sites, these sites have relatively higher dioxin concentration than that in the other sites. The dioxin found in soil was generally exits by dry or wet deposition process of dioxin released in the

**Table 2.** Mean contribution rates of real values and TEQ values in dioxin congeners and homologues under different land use types.

No.	Congeners	Industrial site		Traffic-related site		Metal mine site		Metal refinery site		Waste open-storage site		Waste landfill site		Waste incinerator site	
		Real values	TEQ values	Real values	TEQ values	Real values	TEQ values	Real values	TEQ values	Real values	TEQ values	Real values	TEQ values	Real values	TEQ values
1	2378-TCDF	0.9	4.9	0.8	4.5	18.2	16.5	2.7	8.4	1.9	4.9	1.0	5.5	0.7	2.0
	Tetra-CDF	0.9	4.9	0.8	4.5	18.2	16.5	2.7	8.4	1.9	4.9	1.0	5.5	0.7	2.0
2	12378-PeCDF	1.4	3.6	1.2	3.2	8.4	3.8	2.5	4.0	2.9	3.8	1.3	3.7	2.3	3.4
3	23478-PeCDF	1.3	33.1	1.2	32.1	8.0	36.1	2.4	37.3	3.1	40.1	1.2	32.2	2.2	33.3
	Penta-CDF	2.7	36.7	2.3	35.3	16.4	39.9	4.9	41.3	6.1	43.8	2.5	35.9	4.5	36.7
4	123478-HxCDF	1.5	7.8	1.3	7.2	3.9	3.6	2.6	8.2	3.3	8.5	1.9	10.6	4.1	12.4
5	123678-HxCDF	1.3	6.7	1.2	6.4	3.8	3.5	2.1	6.5	2.8	7.2	1.3	7.1	3.5	10.4
6	234678-HxCDF	1.7	8.9	1.3	7.4	5.0	4.5	2.3	7.2	4.5	11.4	1.3	7.4	3.9	11.7
7	123789-HxCDF	0.0	0.2	0.1	0.4	0.5	0.5	0.3	0.9	0.2	0.4	0.0	0.2	0.3	0.9
	Hexa-CDF	4.6	23.6	3.9	21.4	13.2	12.0	7.2	22.8	10.8	27.6	4.5	25.4	11.9	35.5
8	1234678-HpCDF	7.4	3.8	22.8	12.6	5.3	0.5	8.5	2.7	14.0	3.6	5.5	3.1	16.3	4.9
9	1234789-HpCDF	0.6	0.3	0.5	0.3	0.8	0.1	1.1	0.4	1.6	0.4	0.8	0.4	2.6	0.8
	Hepta-CDF	8.0	4.1	23.3	12.9	6.1	0.6	9.6	3.0	15.6	4.0	6.3	3.6	18.9	5.6
10	OCDF	6.7	0.3	8.5	0.5	5.9	0.1	6.3	0.2	9.1	0.2	2.8	0.2	17.1	0.5
	Octa-CDF	6.7	0.3	8.5	0.5	5.9	0.1	6.3	0.2	9.1	0.2	2.8	0.2	17.1	0.5
	PCDF	22.8	69.6	38.7	74.6	59.8	69.0	30.7	75.7	43.5	80.6	17.2	70.5	53.0	80.4
11	2378-TCDD	0.1	5.2	0.1	3.4	2.0	18.2	0.1	3.8	0.1	3.1	0.0	1.4	0.1	1.8
	Tetra-CDD	0.1	5.2	0.1	3.4	2.0	18.2	0.1	3.8	0.1	3.1	0.0	1.4	0.1	1.8
12	12378-PeCDD	0.3	8.5	0.3	7.5	2.2	10.1	0.5	7.3	0.5	6.1	0.1	3.9	0.5	7.4
	Penta-CDD	0.3	8.5	0.3	7.5	2.2	10.1	0.5	7.3	0.5	6.1	0.1	3.9	0.5	7.4
13	123478-HxCDD	0.3	1.7	0.2	1.4	0.5	0.5	0.5	1.6	0.5	1.2	0.5	2.5	0.4	1.2
14	123678-HxCDD	0.7	3.8	0.7	3.6	0.9	0.8	1.0	3.2	1.0	2.7	1.1	6.3	0.9	2.6
15	123789-HxCDD	0.6	3.1	0.5	2.6	0.9	0.8	0.9	2.9	1.0	2.5	1.1	5.9	0.9	2.7
	Hexa-CDD	1.7	8.6	1.4	7.6	2.4	2.1	2.4	7.7	2.5	6.3	2.6	14.8	2.2	6.5
16	1234678-HpCDD	9.0	4.7	7.1	4.0	4.1	0.4	12.1	3.8	11.0	2.8	10.0	5.6	9.5	2.8
	Hepta-CDD	9.0	4.7	7.1	4.0	4.1	0.4	12.1	3.8	11.0	2.8	10.0	5.6	9.5	2.8
17	OCDD	66.0	3.4	52.5	2.9	29.5	0.3	54.2	1.7	42.5	1.1	70.1	3.9	34.8	1.0
	Octa-CDD	66.0	3.4	52.5	2.9	29.5	0.3	54.2	1.7	42.5	1.1	70.1	3.9	34.8	1.0
	PCDD	77.2	30.4	61.3	25.4	40.2	31.0	69.3	24.3	56.5	19.4	82.8	29.5	47.0	19.6
	Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

atmosphere from the various emission source (Wagrowski and Hites, 2000). It was judged that the sites with many dioxin sources such as incinerator and electric arc furnace have higher dioxin concentration. Especially, the dioxin concentration in one of waste incinerator sites was the highest concentration with 322.736 pg-TEQ g<sup>-1</sup> dry weight. But this level was the about 32% of Japanese Standard of 1,000 pg-TEQ g<sup>-1</sup>. In the case of metal mine sites and waste landfill sites, dioxin concentrations were lower level in comparison to the other sites.

Table 2 showed the mean contribution rates of real values and TEQ values in dioxin congeners and homologues according to the land use. In the case of real values, Octa-CDD in all investigated sites was the major contributor with 29.5~70.1%. In contrast to the real values, dioxin homologues profiles in TEQ values were dominated by penta-CDF which contributed about 35.3~43.8% to total dioxin concentrations. In the case of dioxin congeners, 2,3,4,7,8-penta-CDF was the most dominating congener in all sites. The ratio of PCDFs/PCDDs in real values was in the range of 0.21 to 1.49 with average 0.71, but that in TEQ values was the opposite having about 3.03 (2.22~4.14). The sites where the ratio of PCDFs/PCDDs have over 1 were only two sites which were metal mine site and waste incinerator site. The ratios in the other sites were under 1. In the case of TEQ values, that ratio was over 1 in

all investigated sites. Especially that ratio in waste open-storage sites and waste incinerator sites had over 4. It means that the concentration of PCDFs was four times higher than that of PCDDs. The majority of soil samples had the same dioxin congener profiling despite the different range of dioxin concentration. This phenomenon was quite similar to that reported for soil samples collected from eastern China and southern China (Jinsong and Weiping, 2009). A similar tendency could be observed in the results of Jin-juh Jou (Jou et al., 2007). Wagrowski and Hites (2000) suggested that the profile is classified as “source”, whilst “sink” profiles are dominated by PCDD.

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