MULTIVARIANT STATISTICAL ANALYSIS OF DIOXIN CONGENERS IN SOIL SAMPLE FROM DIFFERENT SITES IN BUSAN, SOUTH KOREA

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Abstract

In this study, soil samples in Busan have been sampled and analysed to determine the level of dioxins, summarize the sysmatic information and provide the major trends of the data. Soil samples collected in 2008 showed concentration ranging from 0.157 to 28.772 pg-TEQ/g dry weight with an mean values of 11.929 pg-TEQ/g dry weight. In the case of real values, OCDD is the major contributor with 53.3%. In contrast to real values, dioxin congeners profiles in TEQ values were dominated by 2,3,4,7,8-PeCDF, which contributed about 36.7% to the total dioxin concentrations. The ratio of PCDFs/PCDDs in real values was about 0.45, but that in TEQ values was the opposite with approximately 2.4 of the ratio of PCDF/PCDDs. Multivariate data analysis method was adopted in this research to combine a large amount of variables into several underlying compounds, which summarize the sysmatic information and provide the major trends of the data. PCA provides a two dimentional model, which would explain the data variance. The first principal component(PC1) explains 82.4% of the total variance. The second principal component(PC2) explains 9.0% of the total variane.

Introduction

Busan metropolitan city, having approximately 3.6 million residents and 765 km^2 which is 0.8% of the whole land of the Korean peninsula, is located on the southeastern tip of the Korean peninsula called the East Sea as shown in Fig. 1. Busan is the second largest city in South Korea and have a good natural environment with mountains, rivers and sea. This city can be divided into several areas such as industrial area, commercial area, resident area, green area and so on. So there are various pollutants according to the pollutant sources. Especially, dioxins among various pollutants, having high toxicity, occur as unintentional by-products of incinerator and chemical factories. Dioxins are organic chemicals which are stable to photochemical, chemical and biological decomposition. So dioxins are, among others, persistent organic pollutants listed in the Stockholm Convention[1,2)]. Soil is the main reservoir of dioxins emitted from various sources such as incinerators, factories, automobils and so on. Due to the physicochemical properties of dioxins, such as their high affinity to organic carbon, most dioxins deposited in soils are localized in the top soil layer from 0 to 15 cm [3)]. Soil pollutants can pass to vegetation and enter food chains. Furthermore, the soil has high affinity for hydrophobic organic pollutants and can act as a natural sink. Therefore, it is very important to evaluate the environmental quality of soil concerning with the distribution and contamination of dioxins[4)]. In this paper we present dioxin levels and their contribution in different soil samples taken from Busan in South Korea. And we applied PCA(Principal Component Analysis) to estimate possible similarities and discrepancies in the dioxin congeners profiles of all data.

Fig. 1. Location of Busan in South Korea

Materials & Methods

The soil samples that used in this studies were collected at 30 sites through the city in from March to May 2008. The sampling sites were as follows ; two traffic-related sites, 7 industrial sites, 2 metal mine sites, 3 metal refinery sites, 3 scrape iron heaping sites, 12 waste-related sites and 2 other sites. The each sample included 1 center point and 4 cardinals points was mixed equally, air dried, sieved(2 mm mesh) and homogenized. Every collected soil sample was topsoil in depth of about 0~15 cm from the surface. All samplings were 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 Korean standard method and guide to soil analysis. Dioxin analysis of soil samples were carried out according to the Korean standard method, EPA-1613, JIS method K 0311 and ISO method 18073. About 30 g of air dried and sieved sample added the internal standard for sampling(^{37}Cl-2,3,7,8-TCDD, 2 ng/mL) was treated with 2N-HCl and filtered. Acid-treated samples were spiked with 10 uL of mixtures of 15 labeled dioxins congeners(Wellington EPA-1613 LCS, USA) and then, extracted by soxhlet extraction with toluene for 24 hours. To cleanup sample extracts, three column chromatographies such as multi layer silica column, alumina column and carbon column were carried out according to the Korean standard method and JIS method. Instrument analysis of pretreated samples was conducted with HRGC/HRMS(Autospec ultima, Micromass Ltd, UK) interfaced with an HP 6890 series plus gas chromatograph(Agilent, USA). A SP-2331 capillary column(Supelco ; 60m length × 0.25mm ID × 0.2um 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 isotop 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%.

Table 1. The conditions of gas chromatograph and mass spectrometry.

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

Results & Discussion

Soil samples collected in 2008 showed concentration ranging from 0.157 to 28.772 pg-TEQ/g dry weight with an average values of 11.929 pg-TEQ/g dry weight. Fig. 2 summarizes the mean levels of dioxins according to the pollutant sources. We have found that the dioxin level in metal refinery site was the highest of all investigated soil samples followed by other sites, waste-related sites, scrape iron heaping sites, traffic-related sites, industrial sites and metal mine sites. Table 2 showed the mean concentration and contribution rate of dioxins of all investigated soil samples. In the case of real values, OCDD is the major contributor with 53.3%, followed by 1,2,3,4,6,7,8-HpCDD with 12.1%. In contrast to real values, dioxin congeners profiles in TEQ values were dominated by 2,3,4,7,8-PeCDF, which contributed about 36.7% to the total dioxin concentrations. The ratio of PCDFs/PCDDs in real values was about 0.45, but that in TEQ values was the opposite having about 2.4 of the ratio of PCDF/PCDDs. This phenomenon was quite similar to that reported for soil samples collected from eastern China[4)] and southern China[5)]. And a similar tendencies could be observed in the results of Jin-juh Jou[6)]. Wagrowski and Hites[7)] suggested that, when PCDFs are predominant, the profile is classified as "source", whilst "sink" profiles are dominated by PCDD. Multivariate data analysis method was adopted in this research to combine a large amount of variables into several underlying compounds, which summarize the sysmatic information and provide the major trends of the data[8)]. PCA provides a two dimentional model, which would explain the data variance. We applied PCA to estimate possible similarities and discrepancies in the dioxin congener profiles of all data. Scatter plot of the factor loading with two principal component is shown in Fig. 3. The first principal component(PC1) explains 82.4% of the total variance. The second principal component(PC2) explains 9.0% of the total variane. The total variance from two principal components accounts for 91.4%. Since the variance accounts for 91.4%, it almost account for all the variance observed among the different dioxin congener profiles. Group 1 contains the majority of soil samples except for 2 metal mine samples. A similar behavior could be observed for most soil samples of Busan. The contribution rate of PCDFs is about twice as high as that of PCDDs in group 1. And the contribution rate of PCDFs is about ten as high as that of PCDDs in group 2. The concentration profile for group 1 and 2 showed 2,3,4,7,8-PeCDF and 1,2,3,4,7,8-HxCDF is a major contribution more than 30% of the total, respectively.

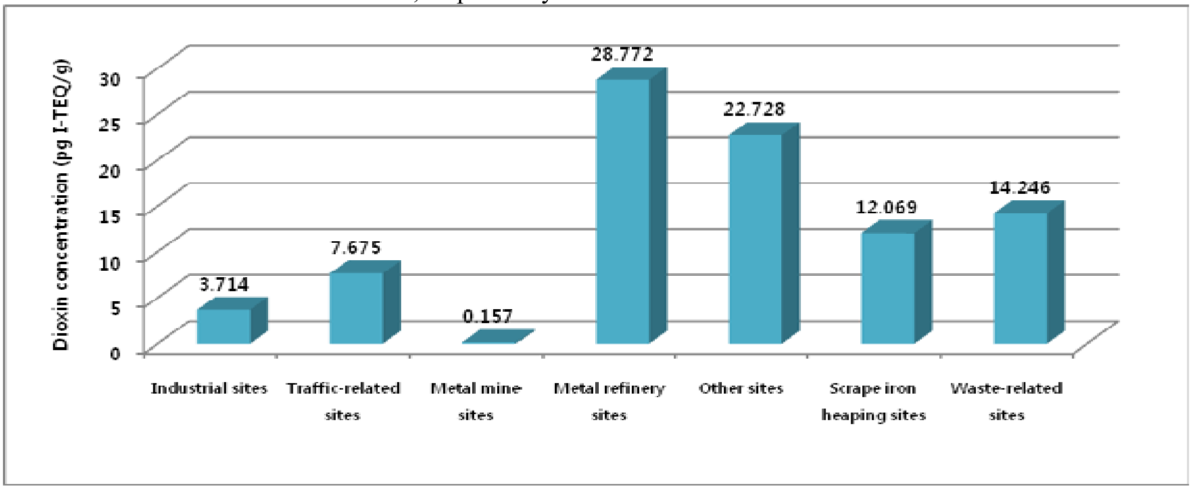

Fig. 2. Mean concentration of dioxin according to the group of pollution source.

Table 2. Mean concentrations and contribution rates of dioxin congeners in all investigated sites

	Congeners	Real values		TEQ values	
		Conc. (pg/g)	Contribution (%)	Conc.(pg-TEQ/g)	Contribution (%)
1	2378-TCDF	5.108	1.3	0.549	4.6
2	12378-PeCDF	7.350	1.9	0.402	3.4
3	23478-PeCDF	8.193	2.1	**4.376**	**36.7**
4	123478-HxCDF	9.982	2.5	1.049	8.8
5	123678-HxCDF	7.767	2.0	0.823	6.9
6	234678-HxCDF	7.322	1.9	0.768	6.4
7	123789-HxCDF	0.304	0.1	0.033	0.3
8	1234678-HpCDF	31.691	8.1	0.328	2.8
9	1234789-HpCDF	4.614	1.2	0.048	0.4
10	OCDF	40.570	10.3	0.041	0.3
	PCDF	**122.901**	**31.3**	**8.417**	**70.6**
11	2378-TCDD	0.355	0.1	0.406	3.4
12	12378-PeCDD	2.513	0.6	1.354	11.3
13	123478-HxCDD	1.638	0.4	0.180	1.5
14	123678-HxCDD	4.510	1.2	0.481	4.0
15	123789-HxCDD	3.591	0.9	0.388	3.3
16	1234678-HpCDD	47.440	12.1	0.488	4.1
17	OCDD	**209.192**	**53.3**	0.214	1.8
	PCDD	**269.239**	**68.7**	**3.512**	**29.4**
	Total	**392.140**	**100.0**	**11.929**	**100.0**

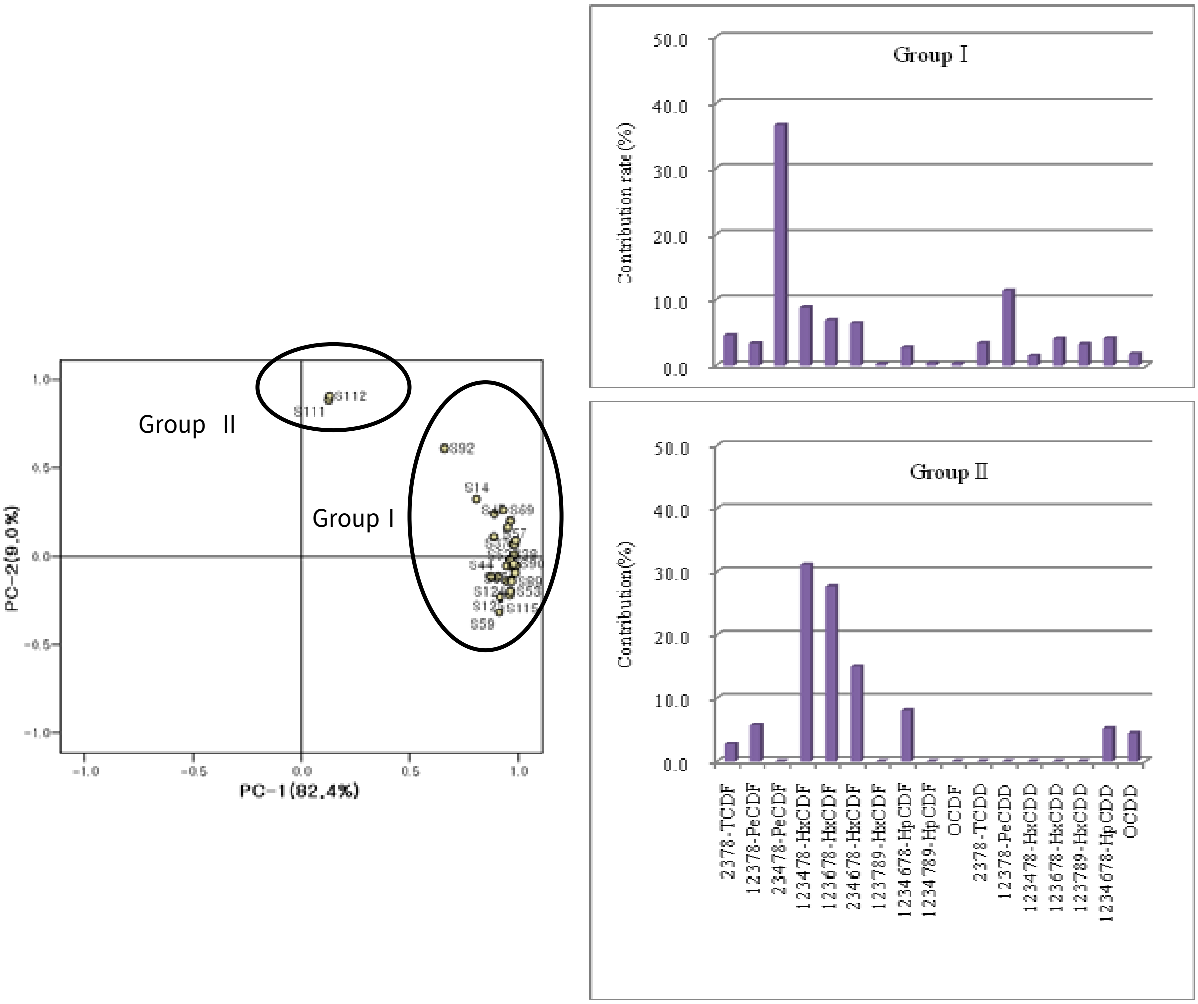

Fig. 3. Principal component plot of dioxin congener profile(International TEQ ; I-TEQ) in soil samples.

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