# LEVELS OF DIOXIN CONGENERS IN SOIL SAMPLES FROM VARIOUS SITES IN BUSAN, REP. OF KOREA

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**Abstract**

In this study, the range of dioxin concentration and mean concentration of dioxin congeners in soil samples according to the land use were determined. Soil samples were collected in May 2006 in period of about 4 weeks from various sampling sites(23 sites) distributed through the Busan city. Each concentration in soil samples ranged from 0.417 to 156.153 pg I-TEQ/g, with a mean value of 20.032 pg I-TEQ/g. The mean concentration in metal refinery areas was higher than any other area, with 86.204 pg I-TEQ/g, followed by waste incinerator area with 34.705 pg I-TEQ/g. The majority of soil samples had the same dioxin congener profiling despite the wide range of dioxin concentration. The concentration of PCDFs was higher than that of PCDDs in all areas by about 2.5 – 4 times. Especially the contribution rates of penta+hexa CDF in metal refinery area, waste incinerator area, factory area, scrap iron loading area, waste landfill area, metal mine area and wastewater incoming area were 61.4, 66.4, 64.4, 66.4, 63.2, 63.8 and 72.2 %, respectively. From these results, it was judged that penta CDF and hexa CDF were major contributors of soil samples in Busan city, Rep. of Korea.

**Introduction**

Dioxins are persistent organic pollutants(POPs) which are stable to photochemical, chemical and biological decomposition[1]. And dioxins are not especially produced, but are formed as by-products in the process of certain human activities, i.e. industrial processes, fossil fuel combustion, or waste destruction[2]. In general, dioxins emitted by incinerators exist in gaseous and particle phase according to the ambient temperature and vapor pressure of dioxin congeners. And dioxins released in the atmosphere return to the soil, plants or organisms by dry or wet deposition process and finally accumulate to human beings through food chains. 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, automobils and so on. In this paper, the mean concentrations and congener profilings of dioxins in soil samples divided by land use were examined to grasp the degree of dioxin pollution.

**Materials and Methods**

Sampling sites and time :

The soil samples that used in this study were obtained from 23 sites in Busan city, Rep. of Korea and were collected in May 2006 in period of about 4 weeks from various sampling sites distributed through the city. Every soil sample was the surface soil(about 5 cm of sampling depth) and collected by 5 point mixture method. 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. And the collected soil samples were air dried, sieved(2 mm mesh) and homogenized.

Analytical methods & instrumentation :

The US-EPA method[3], ISO method[4] and JIS method[5] were used for preparation and instrument analysis of all soil samples. Approximatly 40-50 g of each sample were weighed and mixed with anhydrous sodium sulfate in thimble filter to obtain homogeneity and eliminate moisture within samples. The samples were spiked with 10 ul of mixture of 15 congeners $^{13}C_{12}$-2,3,7,8-substituted dioxins(Wellington EPA-1613LCS, USA) and were extracted by soxhlet extraction with toluene for 24 hours.

To cleanup sample extracts, various column chromatographies such as multi layer silica column, alumina column and carbon column were used. The carbon column chromatography was carried out as occasion demands, for example samples with many interferences. Multi layer silica column, alumina column and carbon column were used according to the JIS method and ISO method.

Dioxins analysis was conducted by a 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. The mass spectrometer was operated in electron impact mode at 35 electron voltage, in the selected ion monitoring mode and with a resolution of over 10,000 at 10% valley. Table 1 shows the conditions of gas chromatograph and mass spectrometry.

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℃ |

The identification and quantification of each dioxin congeners were performed by the isotop dilution method using relative response factors previously obtained from five standard solution(Wellington EPA-1613CVS, USA). At the beginning of each day of analysis, HRGC/HRMS system performance was verified for all dioxin congeners and labeled compounds with CS3 calibration verification standard solution(Wellington EPA-1613CS3, USA).

The each recovery of dioxin congeners was always in the range 50-120%.

**Results and Discussion**

The range of dioxin concentration and mean concentration of dioxin congeners in soil samples according to the land use were shown in Table 1 and 2.

Table 1summarized mean dioxin concentration as international TEQ(I-TEQ) of 7 areas(23 sites) samples. Each concentration in soil samples ranged from 0.417 to 156.153 pg I-TEQ/g, with a mean value of 20.032 pg I-TEQ/g. It can be observed that the local variation is very considerable. Domingo J. L. et al also reported that despite the broad range in observed I-TEQ, profiles of individual 2,3,7,8-substituted congener concentrations were quit similar[6]. The mean concentration in metal refinery areas(MR) was higher than any other area, with 86.204 pg I-TEQ/g, followed by waste incinerator areas(WI, 34.705 pg I-TEQ/g). And then, the concentrations of the other areas were high in order of FA(5.791 pg I-TEQ/g), SIL(3.489 pg I-TEQ/g), WL(3.403 pg I-TEQ/g), MM(1.111 pg I-TEQ/g) and WWI(0.482 pg I-TEQ/g).

The mean concentration of dioxin congeners in soil samples according to the land use was shown in Table 2. In the case of MR areas, the distribution of dioxin congener show that penta CDF among all congeners was the highest with 33.992 pg I-TEQ/g followed by hexa CDF with 18.909 pg I-TEQ/g. The contribution rates of penta and hexa CDF were 39.4 and 21.9 %, respectively. On the other hand, the contribution rate of PCDD was lower than that of PCDF, with 27.5 %. Penta and hexa CDD were higher detected than any other PCDD congener similar to that of PCDFs, but the distribution rates of them were relatively low by 8.9 and 8.5 %, respectively. This was similar to the results of soil performed by Karell M. et al. that congener profile of raw concentration (not I-TEQ) was clearly dominated by the OCDD, but that of I-TEQ was dominated by the 2,3,4,7,8-Penta CDF[7]. The distributions in other areas were very similar to that of MA area. The concentration of PCDFs was higher than that of PCDDs in all 7 areas by about 2.5 – 4 times. Especially the contribution rates of penta CDF + hexa CDF in MR, WI, FA, SIL, WL, MM and WWI area were very high with 61.4, 66.4, 64.4, 66.4, 63.2, 63.8 and

72.2 %, respectively.

Consequently, the majority of soil samples had a wide difference of dioxin concentration but the same congener profiling. And the high levels of dioxin in MR, WI and FA areas have been affected by stack gas from waste incinerator and factories[6]. From these results, contrary to the results of other studies performed by Pai-Sheng C et al. and Stefano C. et al., it is judged that penta CDF and hexa CDF are major contributors of soil samples in Busan city, South Korea[8,9].

**References**

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Table 2. The range of dioxin concentration in soil samples.

| | Sites | Site number | Concentration (pg I-TEQ/g) |
|---|---|---|---|
| 1 | Metal refinery area (MR) | 3 | 5.764 - 96.096 (86.204) |
| 2 | Waste incinerator area (WI) | 3 | 1.696 – 77.786 (34.705) |
| 3 | Factories area (FA) | 6 | 0.972 - 19.212 (5.791) |
| 4 | Scrap iron loading area (SIL) | 1 | 3.489 |
| 5 | Waste landfill area (WL) | 5 | 0.796 – 12.418 (3.403) |
| 6 | Metal mine area (MM) | 2 | 0.417 - 1.804 (1.111) |
| 7 | Wastewater incoming area (WWI) | 1 | 0.482 |

Table 3. Mean concentration of dioxin congneners in soil samples according to the land use.

(unit : pg I-TEQ/g)

| No. | Congeners | Sampling areas | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | MR | WI | FA | SIL | WL | MM | WWI |
| | **Tetra CDF** | **6.840** | **0.663** | **0.257** | **0.129** | **0.197** | **0.070** | **0.022** |
| 1 | 2378 | 6.840 | 0.663 | 0.257 | 0.129 | 0.197 | 0.070 | 0.022 |
| | **Penta CDF** | **33.992** | **11.384** | **2.173** | **1.124** | **1.306** | **0.437** | **0.197** |
| 2 | 12378 | 3.160 | 0.889 | 0.212 | 0.133 | 0.110 | 0.041 | 0.025 |
| 3 | 23478 | 30.832 | 10.495 | 1.961 | 0.991 | 1.196 | 0.396 | 0.172 |
| | **Hexa CDF** | **18.909** | **11.643** | **1.556** | **1.194** | **0.845** | **0.272** | **0.151** |
| 4 | 123478 | 7.087 | 3.925 | 0.513 | 0.609 | 0.337 | 0.099 | 0.067 |
| 5 | 123678 | 5.479 | 3.014 | 0.427 | 0.373 | 0.252 | 0.077 | 0.041 |
| 6 | 234678 | 5.829 | 4.333 | 0.571 | 0.212 | 0.240 | 0.096 | 0.043 |
| 7 | 123789 | 0.515 | 0.371 | 0.045 | 0.000 | 0.015 | 0.000 | 0.000 |
| | **Hepta CDF** | **2.535** | **3.060** | **0.369** | **0.323** | **0.114** | **0.051** | **0.018** |
| 8 | 1234678 | 2.226 | 2.638 | 0.346 | 0.294 | 0.102 | 0.049 | 0.018 |
| 9 | 1234789 | 0.309 | 0.422 | 0.022 | 0.029 | 0.012 | 0.002 | 0.000 |
| | **Octa CDF** | **0.228** | **0.387** | **0.035** | **0.028** | **0.007** | **0.007** | **0.002** |
| 10 | OCDF | 0.228 | 0.387 | 0.035 | 0.028 | 0.007 | 0.007 | 0.002 |
| | **Tetra CDD** | **3.943** | **0.842** | **0.189** | **0.000** | **0.119** | **0.000** | **0.000** |
| 11 | 2378 | 3.943 | 0.842 | 0.189 | 0.000 | 0.119 | 0.000 | 0.000 |
| | **Penta CDD** | **7.685** | **1.966** | **0.480** | **0.299** | **0.331** | **0.083** | **0.000** |
| 12 | 12378 | 7.685 | 1.966 | 0.480 | 0.299 | 0.331 | 0.083 | 0.000 |
| | **Hexa CDD** | **7.368** | **3.251** | **0.391** | **0.146** | **0.301** | **0.095** | **0.034** |
| 13 | 123478 | 1.456 | 0.549 | 0.072 | 0.000 | 0.059 | 0.017 | 0.000 |
| 14 | 123678 | 3.291 | 0.978 | 0.167 | 0.146 | 0.136 | 0.043 | 0.019 |
| 15 | 123789 | 2.621 | 1.725 | 0.152 | 0.000 | 0.106 | 0.036 | 0.015 |
| | **Hepta CDD** | **3.398** | **1.067** | **0.181** | **0.133** | **0.115** | **0.045** | **0.024** |
| 16 | 1234678 | 3.398 | 1.067 | 0.181 | 0.133 | 0.115 | 0.045 | 0.024 |
| | **Octa CDD** | **1.305** | **0.443** | **0.160** | **0.113** | **0.067** | **0.051** | **0.033** |
| 17 | OCDD | 1.305 | 0.443 | 0.160 | 0.113 | 0.067 | 0.051 | 0.033 |
| | **Total PCDF** | **62.505** | **27.136** | **4.390** | **2.798** | **2.469** | **0.837** | **0.390** |
| | **Total PCDD** | **23.699** | **7.569** | **1.401** | **0.691** | **0.934** | **0.274** | **0.091** |
| | **Total PCDF+PCDD** | **86.204** | **34.705** | **5.791** | **3.489** | **3.403** | **1.111** | **0.482** |