TEMPORAL AND SPATIAL DISTRIBUTION CHARACTERISTICS OF DIOXINS IN ENVIRONMENTAL MEDIA, SOUTH KOREA

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Introduction

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/DFs) and coplanar polychlorinated biphenyls (co-PCBs) are ubiquitous pollutants in environmental samples and belong to the persistent organic pollutants (POPs) with bioaccumulation, toxicity, persistence, and long range transportation. These contaminants are unintentionally formed as by-products from artificial activities such as incineration, power generation, metallurgical processes, and other many processes. Also PCDD/DFs and co-PCBs are still detected as very low level in environmental media such as the air, soil, sediment, and water (S. K. Shin., et al. 2011).

These works were investigated for assessing of temporal and spatial levels from environmental samples, correlation among the others media with weather conditions, their possible sources, and it compared with those of other countries.

Materials and methods

Air samples were collected from 37 sites across South Korea over 4 seasons in 2009. Sampling regions were classified as 7 industrials, 22 residential areas, and 8 rural areas. Sites were selected considering emission sources, population density, and long range transport possibility. Sampling was conducted at 24hr with high volume air sampler, which was consists of QFF (Quartz Fiber Filter), 2 PUFs (Poly Urethane Form) and ACF (Activated Carbon Filter) during 3 days. Total volume of air sample was roughly 1,000 m³ with flow rate of 700 L/min (S. K. Shin., et al. 2011; KMoE. 2010).

Other samples were collected from 57 sites for surface soil (0 ~ 10 cm) on spring, 30 sites for bottom sediment (0 ~ 10 cm) on fall by using of grab sampler, 72 sites for water on spring and fall by using of water sampler. The collected samples were placed in cleaned amber glass bottles and refrigerated at 4 °C until analysis.

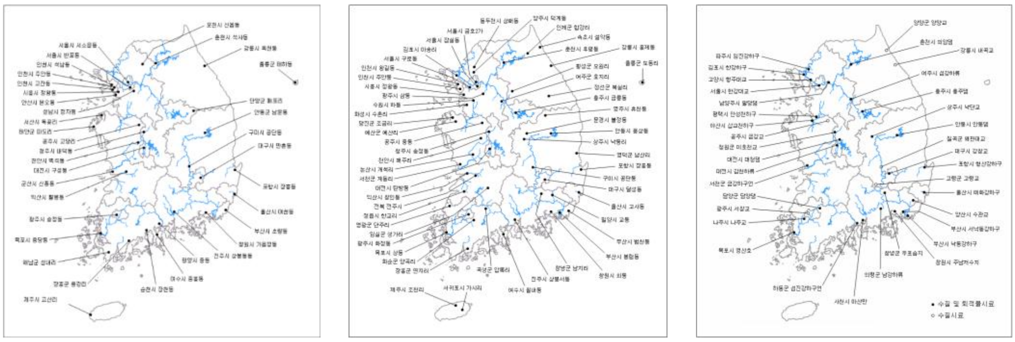
The dioxin compounds for analysis were toxic 17 PCDD/PCDFs isomers, 12 co-PCBs (#77, #81, #105, #114, #118, #123, #126, #156, #157, #167, #169 and #189). Procedure of sample analysis was treated, extracted, clean-up, concentrated and analyzed by the Korea official testing method for POPs analysis.

Briefly, after spiked with $^{13}C_{12}$-labeled PCDD/Fs and co-PCBs internal standards, each sample and a recovery standard were extracted by a soxhlet extractor with solvent such as dichloromethane. Then the extracts were washed with concentrated H_2SO_4 followed by hexane saturated H_2O. Sample clean-up was performed using a silica and alumina column. Finally $^{13}C_{12}$-labeled syringe recovery standards (Wellington EPA1613 ISS and WPISS) were added to the concentrated samples before instrumental analysis. All compounds were analyzed by high-resolution gas-chromatography/high-resolution-mass-spectrometry (HRGC/HRMS). A SP-2331 column (60 m, 0.32 mm id, 0.25μm) was used for PCDD/Fs and a DB-5MS column (60 m, 0.25 mm id, 0.25μm) for co-PCBs (S. K. Shin., et al. 2011; J. S. Park., et al. 2011; KMoE. 2010).

The temperature programs of the GC were as follows: (1) for PCDD/Fs, initial hold at 120 °C for 1 min, increase at 10 °C/min to 200 °C, hold for 2 min, then increase at 3 °C/min to 260 °C, hold for 20 min; (2) for co-PCBs, initial hold at 150 °C for 1 min, increase at 20 °C/min to 185 °C, hold for 3 min, increase at 6 °C/min to 245 °C, hold for 3 min, then increase at 6 °C/min to 290 °C, hold for 10 min. 1μL of each sample was injected at temperatures of 260 °C and 280 °C for PCDD/Fs and co-PCBs, respectively. The MS was operated under positive EI conditions (32 eV) with a resolution of 10 000 mass-to-charge ratio (m/z). Data were collected in selected ion monitoring (SIM) mode. TEQ calculation was done using international TEFs (PCDD/Fs) and WHO TEFs (co-PCBs). Several steps were taken to obtain data that would allow an assessment of the accuracy and reliability of the data (S. K. Shin., et al. 2011; J. S. Park., et al. 2011; KMoE. 2010).

Before sampling, Wellington EPA1613 CSS and Wellington EPA1668 CS were added as sampling recovery internal standards for PCDD/Fs and co-PCBs. Prior to extraction, Wellington EPA1613 LCS and Wellington WP-LCS were added as clean-up internal standards for PCDD/Fs and co-PCBs. The average recoveries of

PCDD/Fs (50–120%) and co-PCBs (51–120%) for all samples were in accordance with the Korean official method and EPA guideline. Field blank, method blank (one a batch) and glassware blank were analyzed and the target compounds not detected. The values below the limit of detection (LOD, 0.050 pg/m^3, 0.5 pg/L, 1 pg/g for air, water, soil and sediment respectively) were noted as ''ND'' (not detected) (S. K. Shin., et al. 2011; KMoE. 2010).

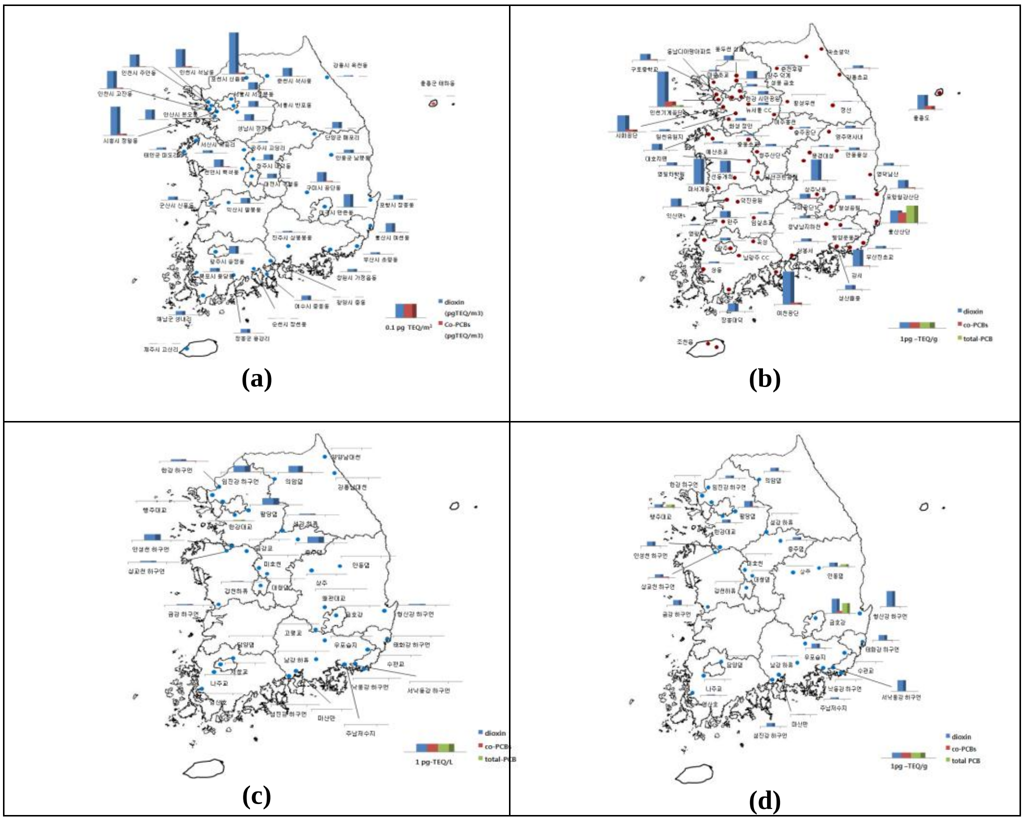


(a) (b) (c)

Fig. 1. Sampling site of POPs monitoring in Korea (a) air, (b) soil, (c) water and sediment.

Results and discussion

Average concentrations of PCDD/Fs and co-PCBs were detected 0.051 ± 0.060 pg I-TEQ/m^3, 0.002 ± 0.003 pg WHO-TEQ/m^3 at this monitoring in Korean air, reapectively. The total of mean concentration PCDD/Fs and co-PCBs was detected 0.053 ± 0.062 pg TEQ/m^3 (KMoE. 2010).



(a) (b) (c) (d)

Fig. 2. Spatial distribution (average) level of dioxins in Korea (a) air, (b) soil, (c) water, (d) sediment

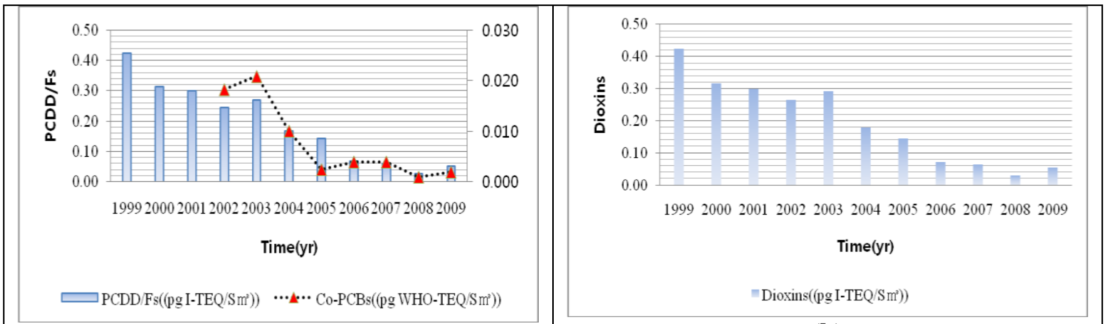
In the national survey (from 1999 to 2008), mean level of atmospheric PCDD/Fs have been investigated from 0.045 to 0.425 pg TEQ/m^3, and concentration of this 2009 survey was very low level, compared to last surveys and Korean air quality standards (0.6 pg TEQ/m^3). Also most atmospheric PCDD/Fs level of residential and industrial points were observed higher than those of rural sites. Some industrial sites showed higher levels of PCDD/Fs and co-PCBs than the residential and background region. The PCDD/Fs and co-PCBs levels in Korean atmosphere were similar to that of other countries. The levels of spatial distributions of PCDD/Fs in an ambient air reveal that those were founded to be the highest in the north- western region (close to Seoul, Si-hung industry of Inchon city and Pocheon industrial area) of South Korea and consistent with previous studies such as impacts of anthropogenic and unknown emission sources, concentrated or scattered with industrial facilities (KMoE. 2009; KMoE. 2010; Loren H. R., et al., 2005).

The cause of a decreasing trend of PCDD/Fs and co-PCBs in air, because the Korean government has strongly regulated dioxin emission criteria from metropolitan solid waste incineration facilities since 1997 (over 50 ton/day, change an old 0.5 to a new 0.1 ng I-TEQ/m^3) which were extended to small incinerators became the major point source of dioxin emission in Korea, and reinforced the regulation in 2006 (below 2 ton/hour, change an old 40 to a new 10 ng I-TEQ/m^3), closed to mostly small waste incinerators, resulting in much decreasing weight of emission. Also biannually national dioxin emission inventories from waste treatment facilities were announced from 2001 to 2009 (decrease from 880 to 48 g I-TEQ/yr in incineration facilities, decrease from 123 to 78 g I-TEQ/yr in non-incineration facilities). As a result, the contribution to atmospheric PCDD/Fs from incinerators has decreased from 88% to 38% during 2001 and 2009. In 2009, the amount of dioxin emissions to the air in Korea was estimated about 126 g, which means a decrease of 88% compared to 2001. Those decreasing amounts of atmospheric emissions of PCDD/Fs and PCBs mostly contributed to the decreasing trend of atmospheric levels (KMoE. 2012).

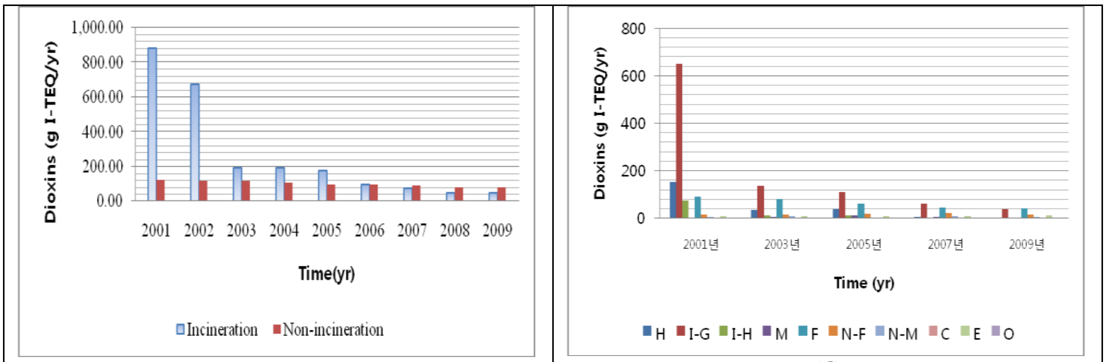
For the purpose of comparison of seasonal variations in air, it compared with average values using the statistic method such as one way ANOVA (analysis of variance, factor "season"). As a result of ANOVA, $p = 0.052$ appear as statistically significant at the 95% confidence level ($p > 0.05$). The difference of mean concentration of atmospheric PCDD/Fs and co-PCBs was not significant. The concentration of PCDD/Fs (0.074 pg TEQ/m^3 in winter) was higher concentration than in other seasons, in fact, that it does not different the average concentration of other seasons (KMoE. 2010).

For the high regions of dioxin in the northern part of South Korea, more continuous monitoring should be need to determine the cause and emission source.

Compared with air samples, other Korean environmental samples (soil, sediment, water etc.) also show low levels that are similar to other countries of environmental media and many variations between the other sampling sites and time. Fluctuation of PCDD/Fs and co-PCBs data in soil survey is considered to be effective that near emission source, wind direction, rain fall, temperature, mixing height etc. Dioxins in the river and lake water of domestic country was conducted from 1999 to 2007 in the residual environmental endocrine disruptors survey, the result of PCDD/Fs monitoring was revealed to 0.001 ~ 1.073 pg TEQ/L (0.165 pg TEQ/L) and did not differ significantly. In addition, co-PCBs showed to ND ~ 0.075 pg TEQ/L (0.005 pg TEQ/L), which were similar to other countries. In 2009, result of survey in sediment observed to 0.001 ~ 3.828 pg TEQ/g (0.860 pg TEQ/g) and did not differ significantly. In addition, co-PCBs showed to ND ~ 0.572 pg TEQ/g (0.078 pg TEQ/g), which were similar to other countries, and the 2008 survey results is similar to that of 2009 survey (KMoE. 2009; KMoE. 2010).



(a) (b)



(c) (d)

Fig. 3. Annual variations of level in Korea (1999-2009) (a) PCDD/Fs, (b) dioxin, (c) emission of dioxin (KMoE. 2009; KMoE. 2010; NIER. 2008), (d) biannually national dioxin inventories in several emission sources (H; household, I-G; incineration general, I-H; incineration hazardous, M; medical waste, N-F; nonferrous, N-M; nonmetal, C; chemistry, E; energy, O; others (KMoE. 2012)

1. Average concentrations of PCDD/Fs and co-PCBs in air were detected 0.051, 0.002 pg TEQ/m^3 relatively in 2009, which were low compared to similar concentrations of other countries in Asia. These results were equal to tenth level of air quality standards (0.6 pg TEQ/m^3), and were very as low as results (from 0.045 to 0.425) in 10 years ago.
2. PCDD/Fs and co-PCBs were relatively high in Inchon and Siheng region with a heavily industrial complex from 0.127 to 0.205, 0.007 to 0.012, respectively. Particularly, the highest concentration in Pocheon, Gyonggi province appeared 0.304 around the study area, the focus of ongoing monitoring and emission management facilities will be needed.
3. The average concentration of PCDD/Fs and co-PCBs in water samples was shown to 0.165, 0.005 pg TEQ/L which are similar to international levels respectively. The levels in soil (2.280, 0.246 pg TEQ/g) were similar to findings in 2008, but according to the sampling sites, results were great variation. Detection levels were low compared to some other countries in Asia. The mean level of PCDD/Fs and co-PCBs in sediment was detected to 0.860, 0.078 pg TEQ/g respectively and were lower than the international level.
4. Elevated PCDD/Fs and co-PCBs observed at residential and industrial regions indicate a potential contribution and impacts of artificial sources. The mean level of PCDD/Fs and co-PCBs showed small seasonal variations ($p = 0.052$, $\alpha = 0.05$). But the atmospheric PCDD/Fs and co-PCBs in Korea shown rapidly decreased during the last 10 years (1999-2009), demonstrating the efficiency of stricter regulations, closing of small incinerators, and improvements of facilities.

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