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Nationwide monitoring of atmospheric PCDD/Fs and dioxin-like PCBs in South Korea

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ABSTRACT

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (DL-PCBs) were measured in ambient air samples collected from different parts of South Korea in 2008, and the measured levels were used for assessing the spatial and temporal distribution of atmospheric PCDDFs and DL-PCBs in South Korea. The average concentrations of atmospheric PCDD/Fs and DL-PCBs among the 37 sites were 28 fg I-TEQ m^{-3} (ND ∼ 617) and 1 fg WHO-TEQ m^{-3} (ND ∼ 0.016). Elevated atmospheric levels of PCDD/Fs and DL-PCBs observed at residential/industrial sites and in the north-west of Korea, indicated a potential contribution and impacts of anthropogenic sources of PCDD/Fs and DL-PCBs. These levels were similar or lower than those previously reported in other ambient air surveys. Average concentrations of PCDD/Fs showed small seasonal variations (ANOVA analysis, $p = 0.144$). The highest concentrations of PCDD/Fs were observed during winter, followed by spring, autumn and summer. Atmospheric PCDD/Fs and DL-PCBs in South Korea rapidly decreased during the last 10 years (1998–2008), demonstrating the efficiency of stricter regulations and the application of best available technologies/best environmental practices at emission sources. Comparison of the congener profiles and principal component analysis showed that current atmospheric PCDD/Fs are mostly influenced by industrial sources and PCBs from old commercial PCB uses. Nationwide POPs monitoring will continue and allows an effective evaluation of the implementation of the Stockholm Convention on POPs.

1. Introduction

After Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) are classified and regulated as persistent organic pollutants (POPs) under the Stockholm Convention on POPs in 2004 (UNEP, 2001), the monitoring of POPs has become a serious issue in many countries because of their toxicological effects and associated adverse health implications. PCDD/Fs are one of the most toxic chemical groups known to science exhibiting carcinogenicity, immunotoxicity, reproductive and developmental effects in mammals and interfering with regulatory hormones in humans. PCDD/Fs are formed as unintentional by-products in certain processes and activities, and may also be introduced into processes as contaminants in raw materials. PCDD/Fs released to the atmosphere are mainly from anthropogenic activities, including waste incineration, power/energy generation, other high-temperature sources, metallurgical processes, and chemical-industrial sources. PCBs from a simplified source can be divided into two main classes: intentional chemicals produced in the chemical industries, and unintentionally *de novo* synthesized by-products during thermal processes. The production and consumption of global PCBs for industrial purposes are relatively well established. So far, numerous atmospheric monitoring studies on programs on POPs were conducted using high volume air samples (HVAS) or passive air samplers on global (Pozo et al., 2009) and regional-scale (Li et al., 2010). The number of PCDD/Fs and PCBs studies in the Korean environment (Lee et al., 2007; Choi et al., 2009) has recently increased thanks to a series of global initiatives on POPs and an increasing concern about the risks that these chemicals pose to human health and the environment.

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PCDD/Fs monitoring in environmental samples have been conducted in South Korea since the late 1990s. The Ministry of Environment, Korea (MOE) published the first national PCDD/F air emission inventory in 2005 (KMOE, 2010). And a decreasing trend of PCDD/F levels has been observed in environmental samples (Lee et al., 2007; Moon et al., 2009; KMOE, 2010); and biota samples (Kim et al., 2008b). The emissions of PCBs caused by *de novo* synthesis are not believed to contribute significantly to the global historical PCB mass balance (Breivik et al., 2002). The relative importance of atmospheric emissions from various source categories is not known with considerable uncertainty (Breivik et al., 2004). Kim et al.(2005) reported that Korean ambient air was more influenced by combustion processes than the ambient air of Japan and also the effect of PCB commercial products was relatively small. In addition, they found that highly chlorinated homologues (7–10 Cl) were detected only in the Korean industrial areas. PCB levels in iron and steel complexes in South Korea have been reported to be higher than those in residential areas, indicating that iron and steel complexes are probably an important source of PCBs (Kang et al., 2009). Emissions of PCBs from iron and steel complexes are expected because these complexes use various thermal processes that may synthesize PCBs incidentally. The previous monitoring of atmospheric PCDD/Fs and PCBs in South Korea mainly focused on the ambient environment of a potential source or a restricted region and only few studies have been conducted on national scale atmospheric PCDD/F levels using active air sampling in South Korea, no such evaluation has been performed in South Korea. This is the first national field study to investigate levels and spatial distributions of atmospheric PCDD/Fs and dioxin-like PCBs (DL-PCBs) across South Korea, moreover the seasonal and temporal distribution were evaluated. Furthermore, we tried to identify the potential major sources of high PCDD/F levels in South Korea. Based on these results governments could effectively evaluate the implementation of the Stockholm Convention on POPs and establish comprehensive reductive countermeasures for PCDD/Fs and PCBs.

2. Experimental

2.1. Air sampling

Ambient air samples were collected from 37 sites across South Korea (Fig. S1) over four consecutive sampling periods in 2008 (Period 1, January–February; Period 2, April–May; Period 3, July–August; Period 4, October–November). Different sampling sites were classified as industrial (7 sites), residential (22 sites) and rural sites (8 sites) (Table S1). Sampling sites were selected considering emission source distribution, population density, and long rage transport potential of PCDD/Fs and PCBs. So that the representativeness of air samples is assured as far as possible and both the effect of source emissions to the ambient environment and the spatial distribution of emission sources are reflected. A typical air sampling was composed of 24 h sampling using high volume air sampler on three consecutive days. Total sampling volume of air was approximately 1000 m^3 per sample and an air flow rate of 700 L min^{-1} was used. The results obtained by the analysis shall be the average of the three consecutive days' data.

2.2. Analysis of PCDD/Fs and DL-PCBs

The target compounds for analysis were seventeen toxic PCDD/F isomers and 12 DL-PCBs (#77, #81, #105, #114, #118, #123, #126, #156, #157, #167, #169 and #189). Extraction, clean-up, and analysis of air samples were conducted according to the ''Korean official method of POPs analysis''. Briefly, after spiking with $^{13}C_{12}$-labeled PCDD/Fs and DL-PCBs internal standards, each sample and a recovery standard were solvent extracted in a Soxhlet apparatus with DCM. 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 Wellington WP-ISS) were added to the concentrated samples prior to 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 i.d., 0.25 μm) was used for PCDD/Fs and a DB-5MS column (60 m, 0.25 mm i.d., 0.25 μm) for DL-PCBs. 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^{-1} to 200 °C, hold for 2 min, then increase at 3 °C·min^{-1} to 260 °C, hold for 20 min; (2) for DL-PCBs, initial hold at 150 °C for 1 min, increase at 20 °C min^{-1} to 185 °C, hold for 3 min, increase at 6 °C min^{-1} to 245 °C, hold for 3 min, then increase at 6 °C min^{-1} to 290 °C, hold for 10 min. One microliter of each sample was injected at temperatures of 260 °C and 280 °C for PCDD/Fs and DL-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 (DL-PCBs).

2.3. Quality assurance/quality control

Several steps were taken to obtain data that would allow an assessment of the accuracy and reliability of the data. Prior to sampling, Wellington EPA1613 CSS and Wellington EPA1668 CS were added as sampling recovery internal standards for PCDD/Fs and DL-PCBs. Prior to extraction, Wellington EPA1613 LCS and Wellington WP-LCS were added as clean-up internal standards for PCDD/Fs and DL-PCBs. The average recoveries of PCDD/Fs (50–119%) and DL-PCBs (50–120%) in all samples were in accordance with the Korean official method and EPA guideline. Field blank, method blank (one per batch) and glassware blanks were analyzed and the target compounds not detected. The values below the limit of detection (LOD, 50 fg m^{-3}) were noted as ''ND'' (not detected).

3. Results and discussion

3.1. Levels and spatial distribution

The average concentrations of PCDD/Fs in ambient air samples from the 37 sites ranged from ND to 617 fg I-TEQ m^{-3}, with an average of 28 fg I-TEQ m^{-3} (Fig. 1a). Compared with rural sites, atmospheric PCDD/Fs concentrations were obviously elevated at residential/industrial sites. Although some industrial sites showed higher levels of PCDD/Fs and PCBs than the residential and background areas, the PCDD/F and PCB levels in the South Korean atmosphere were similar to that of other countries (Table S3) and much lower than the Korean atmospheric PCDD/Fs standard (600 fg TEQ m^{-3}), except for one sample collected during the winter period (Site: Re7). Spatial distributions of atmospheric PCDD/Fs (Fig 2) show that the levels of atmospheric PCDD/Fs were found to be the highest in the north-west area of South Korea (Re7: 617 fg I-TEQm^{-3}, I2: 269 fg I-TEQ m^{-3}, Re3: 145 fg I-TEQ m^{-3}). These sites are close to Seoul, the biggest city of South Korea, where half of the total Korean population lives, indicating potential contributions and impacts of anthropogenic sources of PCDD/Fs. This is consistent with previous studies (Venier et al., 2009). Among the sampling sites of high PCDD/F levels, site R7 is located north-east of Seoul city, near the demilitarized zone (DMZ) in the 38th parallel in South Korea. There are no large industrial sources or known