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Annual and seasonal variations in atmospheric PCDDs/PCDFs and dioxin-like PCBs levels in satellite cities of Seoul, Korea during 2003–2009

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HIGHLIGHTS

- Long-term variations of atmospheric PCDD, PCDF, and dl-PCB are presented.
- Measurements were made at six neighboring cities of Seoul from 2003 to 2009.
- Annual averages were decreased with the most apparent change in 2006.
- PCDFs were reduced more effectively than PCDDs, leading to increase in PCDD/PCDF ratio.
- It confirms the efficacy of the reinforced national regulation enacted in 2006.

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ABSTRACT

Long-term measurements of atmospheric polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (dl-PCBs) were conducted in six satellite cities of Seoul, the capital of South Korea, from January 2003 to December 2009. Of the six sites, three were located in residential areas (Suwon, Anyang, and Seongnam) and the other three were in industrial areas (Ansan, Bucheon, and Siheung). For the 7 years, the average concentrations of PCDDs/PCDFs and dl-PCBs were higher at industrial sites than those at residential sites, and their lowest and highest concentrations were 0.113 ± 0.073 pg international toxicity equivalency quantity (I-TEQ) m^{-3} and 0.0071 ± 0.0040 pg World Health Organization (WHO)-TEQ m^{-3} at Seongnam and 0.625 ± 0.597 pg I-TEQ m^{-3} and 0.0376 ± 0.0285 pg WHO-TEQ m^{-3} at Ansan, respectively. The annual averages of these compounds tended to decrease from 2003 to 2009, with the most apparent change in 2006 when the regulation of dioxin emission standard was reinforced for flue gas from incineration facilities. Complying with the reinforced standard, the concentrations of PCDFs were reduced more effectively than those of PCDDs, leading to increase in ratios of PCDDs to PCDFs since 2006. Additionally, a seasonal tendency was observed for PCDDs/PCDFs with higher concentrations in winter than summer, which was opposite for dl-PCBs. This seasonal difference suggests their sources such as combustion processes and volatilization and the influence of synoptic-scale circulation. The congener profiles indicated that 1,2,3,4,6,7,8-HpCDF, OCDF, OCDD, and 1,2,3,4,6,7,8-HpCDD were the most abundant, comprising 65.0% of the 17 toxic 2,3,7,8-substituted PCDDs/PCDFs mass. The three congeners of 2,3′,4,4′,5-PeCB, 2,3,3′,4,4′-PeCB, and 3,3′,4,4′-TeCB comprised 75.9% of the 12 dl-PCBs.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (dl-PCBs) are highly toxic (Cleverly et al., 2007; Correa et al., 2004). Of the 210 PCDD/PCDF compounds (75 PCDDs and 135 PCDFs), only 17 congeners (7 PCDDs and 10 PCDFs), which have chlorines in the 2, 3, 7, and 8 positions, together with 12 congeners of the 209 PCBs, have toxicity that disrupts the endocrine system of humans and causes different cancers. A toxicity equivalency factor (TEF) was developed such that the TEF of each congener is assigned relatively to the most toxic 2,3,7,8-TCDD, which is given the reference value of

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1 to compare their toxicity and implement regulatory control. Then, the total toxicity equivalency quantity (TEQ) of a PCDD/PCDF mixture can be calculated by multiplying the concentrations of each compound by its respective TEF and adding them together (the international toxicity equivalence factors [I-TEF] for PCDDs/PCDFs and the World Health Organization TEF [WHO_{1998}-TEF during 2003–2006 and WHO_{2005}-TEF afterward] for the dl-PCBs) (Van den Berg et al., 2006).

PCDDs/PCDFs and dl-PCBs are ubiquitous in air, water, soil, sediment, plants, and animals and are released as byproducts during various thermal processes of combustion, incineration, and metal smelting (Abad et al., 2007; Cleverly et al., 2007; H. Li et al., 2008; Y. Li et al., 2008; Venier et al., 2009; Xu et al., 2009). dl-PCBs originate from commercial PCBs used previously and from municipal waste incineration (Kurokawa et al., 1996). PCDDs/PCDFs and dl-PCBs are chemically stable in the environment. These compounds bind to organic carbon in atmospheric particles, soil particles, and sediments and readily bio-accumulate in the ecosystem via the food chain (Kim et al., 2005; Raun et al., 2005; Venier et al., 2009). Air concentrations of PCDDs/PCDFs and dl-PCBs are controlled by emissions, dry and wet deposition, and chemical processes such as photochemical oxidation and vapor/particle partitioning, as well as physical processes such as dilution and long-range transport.

For dioxins and PCBs, monitoring programs are crucial, through which long-term and reliable data should be provided for environmental policy making and implementation and the evaluation of its efficacy. In Korea, the Ministry of Environment and National Institute of Environmental Research started a nationwide program in 1999 to monitor and test levels of PCDDs/PCDFs, dl-PCBs, and other endocrine disrupting chemicals in ambient air, river, soil, and sediment. Subsequently, Gyeonggi Institute Health and Environment took the initiative in atmospheric PCDD/PCDF research and established observation stations on the outskirts of Seoul (Kim et al., 2007). These sites are characterized by the highest population and number of cars, thereby being environmentally conscious and addressing a series of pollution issues. The measurement data from these stations have provided baseline information for understanding the characteristics of atmospheric PCDDs/PCDFs and dl-PCBs and revising national regulations.

The objectives of this study were to determine the concentrations and congener profiles of atmospheric PCDDs/PCDFs and dl-PCBs in major satellite cities of Seoul in Korea and to identify their spatial and temporal characteristics.

2. Materials and methods

2.1. Sampling

Atmospheric measurements of PCDDs/PCDFs and dl-PCBs were carried out at six satellite cities of Seoul, the capital of South Korea, from June 2003 to September 2009 (Table 1 and Fig. 1). Samples were usually collected bimonthly until 2006 and seasonally afterward (Tables 2 and 3). As a result, 191 samples were taken and analyzed in this study. The six stations are located in Suwon, Anyang, and Seongnam as residential areas and Ansan, Bucheon, and Siheung as industrial areas. These are major neighboring cities of Seoul and located in Gyeonggi Province that occupies 10,183 km^2 (10% of the whole county) with a population of 11 million (21% of the whole population), and 15,460 industrial facilities (The Provincial Office of Gyeonggi, 2010). The former three cities house over 20% of the population of Gyeonggi Province. The air pollutants emitted from Ansan, Bucheon, and Siheung comprise >25% of those emitted by the entire province. These sites were designated as national ambient air quality standard monitoring stations and operated by the local government of Gyeonggi Province. Therefore, continuous measurement data are available for gaseous and particulate pollutants such as O_3, NO_x, CO, SO_2, and PM_{10} and meteorological parameters such as temperature, humidity, and wind speed and direction in addition to PCDD/PCDF and dl-PCB concentrations.

Table 1
Sampling sites.

Sampling site	Population (person)	Location	Land use
Suwon	1,090,678	N 37° 17′ 01″ E 127° 00′ 36″	Residential area
Seongnam	958,349	N 37° 22′ 58″ E 127° 07′ 08″	
Anyang	627,330	N 37° 22′ 52″ E 126°57′09″	
Bucheon	882,037	N 37° 31′12″ E 126° 46′ 25″	Industrial area
Ansan	741,073	N 37° 18′ 19″ E 126° 47′ 18″	
Siheung	408,164	N 37° 20′ 48″ E 126° 44′ 24″	

2.2. Sampling procedure

Air sampling was carried out using a high volume air sampler (HV-1000F, Sibata, Soka-City, Saitama, Japan) in compliance with Environmental Protection Agency (EPA) Method TO-9A. Samplers were installed on the roofs of buildings to avoid the influence of ground dust. Each sampler collected approximately 1000–1600 m^3 of air at 400 L min^{-1} for 2–4 days. Under this condition, there was likely to be no sampling artifact due to breakthrough, based on the previous studies (Tysklind et al., 1993; Correa et al., 2004; Martínez et al., 2006; Lee et al., 2008).

Particulate matter and gas-phase compounds were separately collected on quartz fiber filters and two polyurethane foam (PUF) plugs, respectively. Quartz filters were pre-baked at 800 °C for 4 h, and PUF plugs were pre-cleaned with toluene over 24 h using a Soxhlet extractor. Prior to sampling, PUF plugs were spiked with [$^{37}Cl_4$]2,3,7,8-T_4CDD standard (ED-2522, CIL, Andover, MA, USA or EPA-1613CSS, Wellington, ONT, Canada) to estimate sampling performance and extraction efficiency.

2.3. Analytical methods

The concentrations of PCDDs/PCDFs and dl-PCBs were determined with EPA Method 1613 and EPA 1668B, which specify preparation, extraction, detection, and quantification procedures utilizing the isotope dilution technique, internal standard calibration, high resolution capillary column gas chromatography (HRGC) coupled with high resolution mass spectrometry (HRMS). After the samples were collected, PCDDs/PCDFs and dl-PCBs were extracted from the filters and PUF plugs together with 800 mL of toluene in a Soxhlet apparatus over 24 h. The extract was subsequently refluxed with hexane and cleaned up using the acid/base method followed by silica gel and alumina columns. After extraction, 1 ng $^{13}C_{12}$-labeled standards were added to each extract to quantify the target compounds: EDF-8999 (CIL) or EPA-1613LCS (Wellington) for PCDDs/PCDFs and WP-LCS (Wellington) for dl-PCBs. After cleanup, the purified extracts were concentrated to approximately 50 μL and spiked with 1 ng of internal standard: EDF-5999 (CIL) or EPA-1613ISS (Wellington) for PCDDs/PCDFs and WP-ISS for dl-PCBs.