

Monitoring of particulate PCDD/Fs in the air during four seasons in Seoul, Korea

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Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs)¹ are mainly produced as byproducts during artificial and natural combustion processes. After releases of PCDD/Fs from various sources, ambient air plays an important role as the transport media of atmospheric PCDD/Fs to other regions and environmental matrices. Therefore, the monitoring of PCDD/Fs in the air is important to explain the relationship between certain sources and around acceptors. Besides, PCDD/Fs in the air can be present in both particle and gas phases, and their existences can be changeable according to the meteorological conditions. Therefore, the long term monitoring of atmospheric PCDD/Fs can be said important to assess their fate and effect in the environment. In this sense, we tried to evaluate the variations of PCDD/F existence in different seasons throughout a year.

Materials and Methods

Eleven air samples were obtained during 2002-2003 in Seoul, Korea. A High volume air sampler with six stage impactor was used for the collection of atmospheric particles according to different particle sizes²; < 0.41, 0.41-0.73, 0.73-1.4, 1.4-2.1, 2.1-4.2, 4.2-10.2 and > 10.2 mm. Collecting air samples were tried to avoid rainy days and the Asian dust period. Before the sampling, polyurethane form (PUF) and glass fiber filter were pretreated to remove interferences. All samples were kept frozen at -20°C until analysis. PUF and GFF samples collected were processed separately for HRGC/HRMS analysis using a multiresidue method based on those used for PCDD/F analyses. For particulate matters, weight differences of filters between before and after air samplings represented the weigh of air particles. Sample preparation and analysis were performed according to the EPA 1613 method.

Results and Discussion

Particle size distribution: The total particle concentrations, ranged from 66.7 to 151.2 mg/m³, were averaged as 101.4 µg/m³. Although particulate matters were collected not so different ranges, the total concentrations in winter were higher than those in summer and particle levels were highest in spring. These results were consistent with the typical pattern of suspended particulate matters.³ However, their distributions in different particle sizes also were similar (Figure 1). The smallest particle size fraction (D_p < 0.41 mm) contained around 50% of total particles and about 20% of particles were found in the size range of 4.2-10.2 mm. The cumulative concentrations of less than 2 mm particle diameter were distributed over than 50%, which implies that the air in this region were affected by the artificial sources such as vehicles and combustion sources.⁴ The normalized distribution of particles with respect to particle size, however, showed bimodal distributions with peaks at 1.4-2.1 and 4.2-10.2 mm. This normalized distribution also showed urban characteristics of this region. However, during summer, the particles distributed a tri modal pattern with increase of particles ranged 0.41-0.73 mm. In winter, the portion of < 0.41 mm was relatively higher than other seasons, which was considered by the thermal processes.⁵

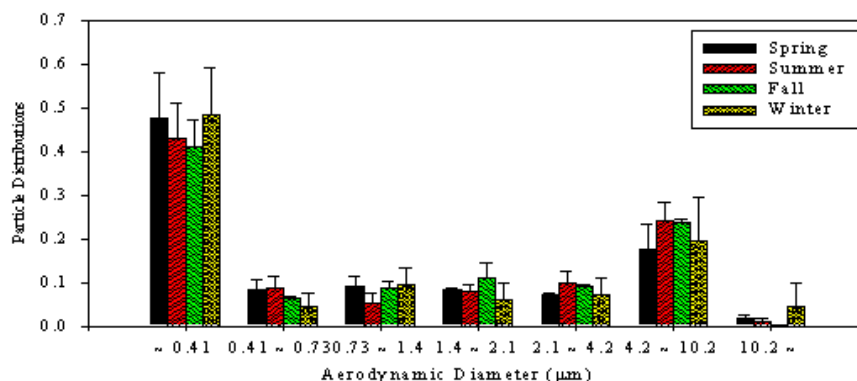


Figure 1. Seasonal variations of air particles in different particle sizes

PCDD/F distributions with particle sizes: Although the samples collected with impactor may not represent all PCDD/F levels in the air, especially lowchlorinated PCDD/Fs, the observed sum of PCDD/Fs in particle phase was averaged as 11.04 pg/m^3 ($2.44 \sim 25.43 \text{ pg/m}^3$). As Figure 2 shows, the presences of PCDD/Fs were more associated with the finest particle size ($< 0.41 \text{ mm}$) than those of any other particles.² Similar to the patterns of particulate matter, PCDD/Fs were found high levels in fall and winter, while the lowest levels of particulate PCDD/Fs were shown during summer. These differences are possibly due to the gasparticle partitioning of PCDD/Fs according to the cold temperature and the higher emissions by heating during winter.⁶

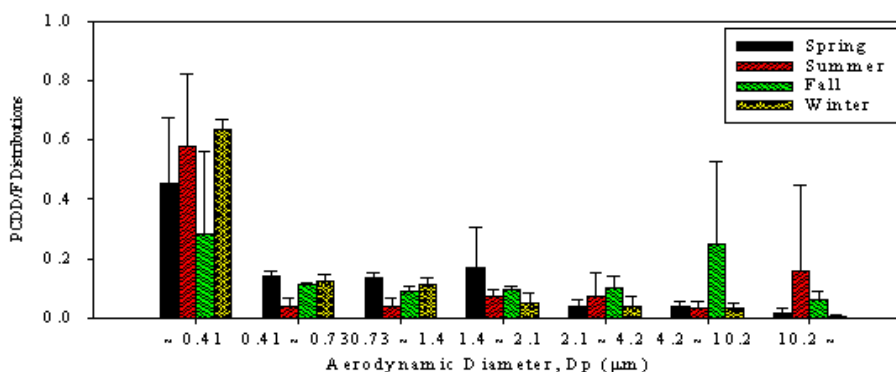


Figure 2. Seasonal variations of total particulate PCDD/Fs in different particle sizes

PCDD/F homologues had a specific pattern according to particle sizes; the fraction of lowchlorinated PCDD/Fs increased as the particle sizes increased and the opposite trend were observed in fine particles. This characteristic could be confirmed by the normalized distribution patterns and the results of principal component analysis (PCA). These trends have been found in previous studies, resulting from the different vapor pressures with chlorination degree.²

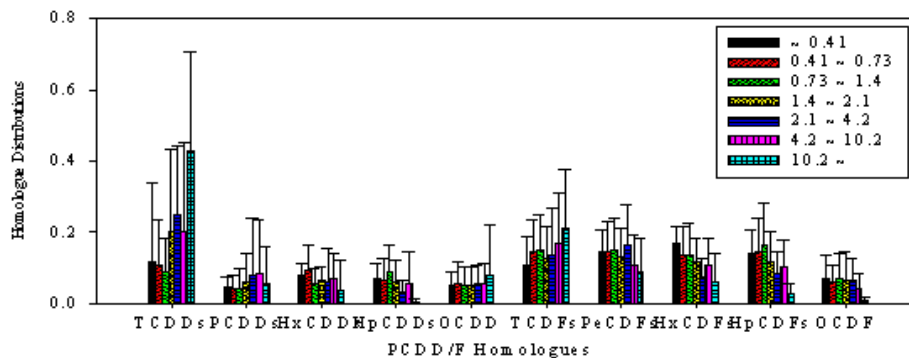


Figure 3. PCDD/F homologue profiles with particle size during a year

Homologue distributions as in Figure 3 were a little disordered in summer and fall. During the summer the concentrations of PCDD/Fs were smallest and the coarse particles ($> 10.2 \mu\text{m}$) also contained some PCDD/F homologues. Temperature might cause the different existences with particle phase; the average temperature during the air sampling was 24°C , while that in winter was around 0°C . The higher temperature brought about higher portion of vapor phase, and generally the negative correlation between temperature and total PCDD/F levels were found⁷. In our study, the vapor phase showed the PCDD/F concentrations ranged $0.52\text{--}7.50 \text{ pg}/\text{m}^3$. The concentrations of gaseous PCDD/Fs were associated with temperatures; the average level during summer was $5.62 \text{ pg}/\text{m}^3$, while in winter the PCDD/F concentrations had an average of $1.95 \text{ pg}/\text{m}^3$. Besides, photodegradation also could affect the PCDD/F distributions and this is more influenced to lowchlorinated compounds.¹ In this study the portions of these compounds (tetra-CDD/Fs) during summer were relatively smaller than other seasons. This suggests that meteorological conditions play an important role in the fate of PCDD/Fs.

Acknowledgements

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