

UPTAKE RATE OF DIOXINS AND DIOXIN LIKE POLYCHLORINATED BIPHENYLS BY POLY URETHANE FORM DISK PASSIVE AIR SAMPLER IN GYEONGGI-DO, SOUTH KOREA

Heo JW^{1*}, Lee GW²

¹Gyeonggi-do Institute of Health and Environment, 95, Pajangcheon-ro, Jangan-gu, Suwon-si, Korea; ²Hankuk University of Foreign Studies, 81, Oedae-ro, Mohyeon-myeon, Cheoin-gu, Yongin-si, Korea

Introduction

Atmospheric transport is the primary global distribution pathway moving polychlorinated dibenzo-p-dioxins and dibenzo furans (PCDDs/Fs) and dioxin-like polychlorinated biphenyls (dl-PCBs) from atmospheric emission sources via deposition to terrestrial and aquatic ecosystems¹. Therefore, the monitoring of Persistent organic pollutants (POPs) in the atmosphere is necessary to gain a better knowledge of factors that control their environmental concentration, fate and transport and to assess the spatial and temporal distribution of atmospheric PCDDs/Fs and dl-PCBs. Traditionally, monitoring of PCDD/Fs and dl-PCBs in the atmosphere has used the active air samplers (AASs), which require electric power to operate the flow pump. These samplers are relatively expensive and cannot easily deploy for large scale air monitoring and at certain locations.

To address these limitations, it has been suggested that alternative air monitoring could be performed employing passive air samplers (PASs). PASs are easy to deploy, cost-effective, and simple to operate because they detect only chemical compounds that diffuse in and are deposited from the air. PASs offer considerable potential as a monitoring tool, especially for multi-point sampling over large remote areas.

Owing to low concentration of PCDD/Fs and dl-PCBs PASs require long sampling times in the atmosphere to quantify these chemicals. This means that the average concentration of PCDDs/Fs and dl-PCBs over a certain period time is determined; this is referred to as the time-weighted average (TWA) concentration.

Previous studies of PASs focused mainly on gas-phase compounds (e.g., polychlorinated biphenyls (PCBs))² because the kinetic uptake theory for PASs is mainly based on chemical diffusion and the partitioning of gas-phase compounds entering the sampling medium. Not much research into PASs for particle-associated chemicals has been performed, especially for PCDDs/Fs and polycyclic aromatic hydrocarbons (PAHs).

In this study, we conducted a field assessment of a PAS for PCDDs/Fs and dl-PCBs, which have high K_{OA} values and relatively high toxicity. To calibrate the polyurethane foam (PUF)-based PASs, we deployed them alongside AASs to obtain the field uptake rate and determined the conditions necessary to maintain linear uptake of PCDDs/Fs and dl-PCBs in the PAS in order to estimate their atmospheric concentrations.

Material and methods

An AAS and five PASs were deployed at Suwon and Ansan of air pollutants observatory in Gyeonggi-do. Suwon city is at the center of Gyeonggi-do and is defined as an urban-residential area with a population of approximately one million. After establishment of the National Banwol industrial complex in 1987, Ansan city became the largest industrial development area in Gyeonggi-do and is defined as an industrial area. Air sampling of PCDDs/Fs and dl-PCBs was performed with an AAS (HV-700F, Sibata, Japan). The AAS was equipped with a quartz filter (QF) (20 cm × 25 cm) and PUF plugs (length 5 cm, diameter 9.0 cm), and was operated at a flow rate 100 L/min over a week-long period to derive the uptake rate. The volume of air aspirated per sample per week was in the range 940~1423 m³.

Starting in February 2010, AAS samples in Suwon and Ansan were collected for 370 days and 173 days, respectively. Typhoon (7th) Kompasu struck central South Korea early on September 3, 2010, causing massive power outages along the west coast. The air-pollutant observatory in Ansan was damaged due to the tropical storm, and inevitably, we had to stop PAS sampling at the Ansan site.

After collection, PUF and quartz filters were placed in solvent-rinsed alumina foil envelopes, which were then put in polyethylene zipper bags and stored in freezer prior to extraction. The five PUF-disk (14 cm diameter, 1.2 cm thickness) PASs (TE-200-PAS, Tisch environmental Inc.) were deployed together with AAS during sampling periods. The PASs were sheltered by two stainless bowls to prevent direct the deposition of coarse-sized particles and to minimize the influence wind speed on the outdoor sampling rate. To maintain linear uptake phase of

PCDDs/Fs and dl-PCBs in the PAS, samplers were deployed within 80 days. Comparing the long-term and short-term data of PAS, we computed the acceptable period to ensure linear uptake was maintained under various metrological conditions.

All samples (PUF plugs, filter, PUF disk) were extracted using toluene by Soxhlet over a 24-h period. The $^{13}\text{C}_{12}$ -labelled surrogate standards (EPA-1613LCS, 68B-LCS, Wellington Laboratories, Canada) were spiked on each sample prior to extraction. The volume of sample extract was reduced to 20 mL by rotary evaporator (R205, Buchi) and divided into two parts for PCDDs/Fs and dl-PCBs. PCDDs/Fs and dl-PCBs were conducted according to US EPA 1613 and 1668B protocol, respectively. Before air sampling, PUF disk and plugs were cleaned with acetone. Laboratory blank was analyzed for every sampling event, and only highly chlorinated congeners were detected.

Results

Active air sampler - Concentration of PCDDs/Fs and dl-PCBs in the ambient

The total concentration of Σ PCDD/F and Σ dl-PCB based on the ambient TEQ in Suwon and Ansan ranged from 0.037 to 0.300 pg-TEQm^{-3} (mean value, 0.108 pg-TEQm^{-3}) and from 0.171 to 0.635 pg-TEQm^{-3} (mean value, 0.386 pg-TEQm^{-3}), respectively. The Ansan (industrial) area showed relatively high PCDD/F concentrations of 0.153~0.613 pg I-TEQ m^{-3} . These values are higher than those at the Suwon sites, confirming the existence of sources of PCDDs/Fs and dl-PCBs in the industrial area. The ambient concentration of PCDDs/Fs in Ansan was similar to those in other industrialized Asian countries^{3,4} and was higher than those in Europe^{2,5-8}. More than 80% of PCDDs/Fs ($\text{Cl}_{4-8}\text{DD/Fs}$) were associated with the particulate phase.

The average value for Σ dl-PCB in Suwon was 2.294 pgm^{-3} with an average of 0.006 pg-WHO TEQm^{-3} ; these data are approximately two-times lower than that in the Ansan area (4.380 pg m^{-3}). Owing to industrial areas such as Ansan being affected by potential contamination sources of PCDDs/Fs and dl-PCBs, the dl-PCB level in Ansan showed higher values than in Suwon. PCB-118 (33.4~60.0%) had the highest concentration at all sites. At both sites, the main TEQ contributors were PCB126, accounting for more than 88% of the dl-PCB TEQ in all samplers. These results are similar to those of previous studies^{3,9}. In the summer season, dl-PCBs were present mainly in the gas phase and had the highest concentration at all sites.

Congener profile of PCDDs/Fs and dl-PCBs in active and passive air samplers

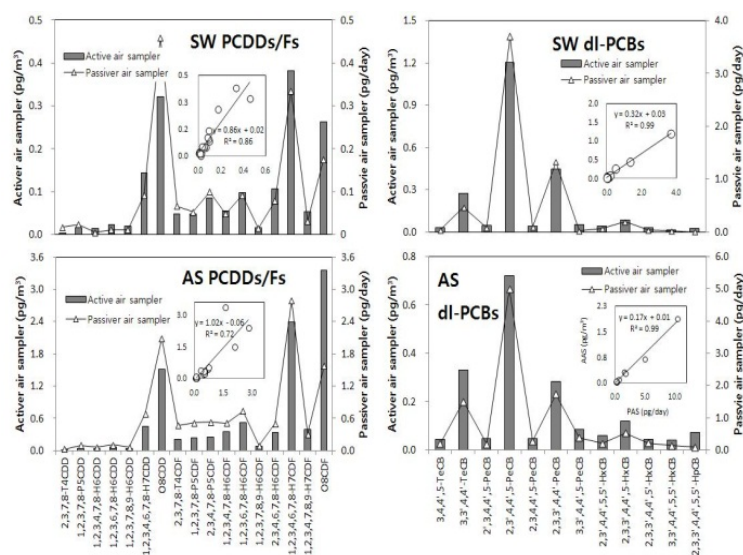


Fig. 1 Comparison between profile congeners of 2,3,7,8 PCDDs/Fs and dl-PBCs results from AAS (pgm^{-3}) PAS (pg/day)

of particle-bound PCDDs/Fs were found on small particles with aerodynamic diameters (D_p) of less than 1.5 μm ^{11,12}. Thus, a relatively high correlation coefficient ($R^2 > 0.72$) was observed, although PCDDs/Fs were associated with particulate matters.

A comparison of the congener profiles of 2,3,7,8-substituted PCDDs/Fs and dl-PBCs from the AAS (pgm^{-3}) and PAS ($\text{pg/exposure time (day)}$) is presented in Fig. 1. Since PAS sampling theory is based on the diffusion of gas-phase chemicals to a collecting medium, dl-PCBs, which are mainly in the gas phase, exhibited a high coefficient of correlation ($R^2 = 0.99$) in the comparison of the AAS and PAS congener distributions (Fig. 1).

Ultra-fine particle ($<0.1\mu\text{m}$) move through the atmosphere much like gases, and adhere to/become trapped by sampler and previous studies reported that about 10% of the ambient particles are sampled by the PUF disk¹⁰ and likely

represent the finest particle components. In general, smaller particles have a high PCDD/F content and the largest amounts

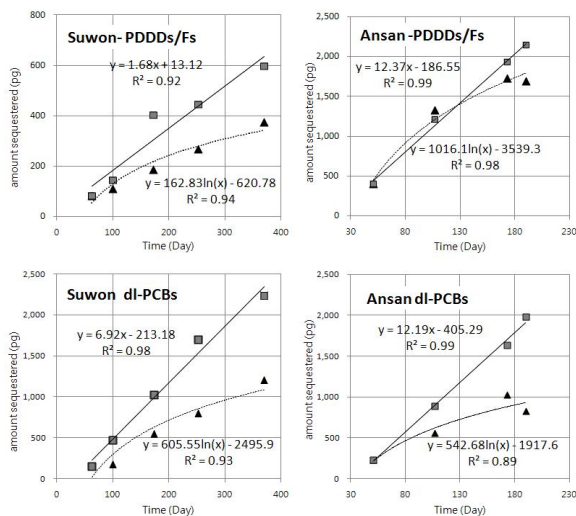


Fig. 2 Profile of amount sequestered PCDDs/Fs and dl-PCBs for individual and accumulated PUF PAS

Uptake rate

To evaluate the feasibility of the PAS as an environmental monitoring tool for POPs, the uptake rate or sampling rate is required as calibration data. These sampling rates are usually determined using the laboratory as an indoor reference site. During the linear adsorption stage, the sampling rate for PCDDs/Fs and dl-PCBs can be calculated according to the following simple equation (1) according to the theory of PASs^{13, 14}. The equivalent sampler volume (V_{eq}) for the exposure time of the PAS was calculated as

$$V_{eq}(m^3) = C_{PUF} / C_A = k_A A_{PUF} \text{ Time} = R (=k_A A_{PUF}) \text{ Time} \quad (1)$$

where C_{PUF} (pg/samplers) is the PUF-disk concentration, C_A (obtained from the AAS; pg/m³) is the mean air concentration (gas + particle phase), k_A (m s⁻¹) is their-side mass-transfer velocity, A_{PUF} (m²) is the exposed surface area of the PUF disk, Time (day) is the exposure time of the PUF-disk PAS. The slope of the linear regression plots of V_{eq} (Y-axis) and Time (X-axis) was defined as the sampling rate (R , m³ d⁻¹). In this study, linear uptake was assumed throughout the exposure time (<80 days) and also congeners at very low concentrations were excluded. The aforementioned studies of uptake rate primarily focused on gas-phase chemicals such as PCBs, polybrominated diphenyl ethers (PBDE), and polychlorinated naphthalenes (PCNs)¹³⁻¹⁶. Studies of uptake rate of particle associated chemicals such like PCDDs/Fs and high molecular weight PAHs are a few². The uptake rate of PCDDs/Fs in Suwon ranged between 0.46 and 1.57 m³ d⁻¹ with a mean value of 1.01 m³ d⁻¹, which were slightly lower than the uptake rate in Ansan (0.14–2.47 m³ d⁻¹; mean, 1.72 m³ d⁻¹). The levels measured in this study are in agreement with those reported in similar studies (mean value, 1.7 m³ d⁻¹).

Generally, to assess the PCB level using PAS, an uptake rate of 3–4 m³ d⁻¹ has been used in field studies^{3, 17-19}. However, the average uptake rate of dl-PCBs with high K_{OA} in Suwon and Ansan was 1.84 m³ d⁻¹ (0.43–3.36 m³ d⁻¹) and 2.15 m³ d⁻¹ (1.34–3.08 m³ d⁻¹), respectively, and the uptake rates measured in this study were lower than those reported in similar studies owing to only dl-PCBs with high K_{OA} being considered. The reported uptake rate (~1–2 m³ d⁻¹) for compounds with higher K_{OA} and particle-associated compounds was lower than that for other compounds¹⁶.

PCDDs/Fs are mainly in the particle phase, and at supercooled liquid vapor pressure (P_L) below 10⁻⁴ and high log K_{OA} > 10, the uptake rate (or V_{eq}) and its variation for PCDDs/Fs are generally lower than those for dl-PCBs, despite different sampling sites. The uptake rate of PCDDs/Fs with high log K_{OA} values greater than 10 are generally about two-times lower than that of dl-PCB compounds. The difference in uptake rate between PCDDs/Fs and dl-PCBs is more likely due to the combined effect of environmental conditions (presence of emission sources, etc.) and the physicochemical properties of the target compounds, such as gas/particle partitioning. With increasing temperature dl-PCBs partition preferentially to the gas phase and the sampling rate

The period of linear adsorption stage

To accurately estimate the target chemical atmospheric concentration, the PAS should maintain linear uptake conditions in the field. Hence, it is important to calculate the period over which linear adsorption of the target compounds continues. Previous studies have suggested that a sampling rate of chemicals with octanol-air partitioning coefficient (K_{OA}) > 8.5 remains linear over 100 days at a few m³/day^{2, 13}. The linear uptake stage was fairly long for the PCDDs/Fs and dl-PCBs (t_{25} : time to reach 25% saturation) at about 290 days for PUF under indoor conditions¹³. Data obtained from the individual PASs deployed for less than 80 days were compared with accumulated data from PASs collected consecutively at all sites (Fig. 2). The accumulation of dl-PCBs in the samplers started to deviate from linear uptake after about 90 days and the period to maintain linear uptake was shorter than that for PCDDs/Fs (ca. 100 days).

varies slightly due to substantially increased adsorption to the PUF media. Therefore, the variation in gas/particle partitioning depending on temperature probably plays an important role in the difference in uptake rate. From these results, compound-specific differences in passive sampling rates of PCDDs/Fs and dl-PCBs imply that different uptake rates should be used to acquire more accurate concentrations depending on the target compounds, with uptake rates of about 1.38 and 2.0 m³ d⁻¹ applied here for PCDDs/Fs and dl-PCBs. In order to validate the uptake rate, PAS accumulated values were calculated using the obtained uptake rate values for the average individual PCDDs/Fs and dl-PCB congeners and were compared with those from the AAS (Fig.3). In the Fig.3, the concentrations from PASs exposed for longer periods showed good agreement with the average concentration from the AAS, showing a good match generally within a factor of 2–3. It was demonstrated that PASs offer a feasible alternative to AASs in the field.

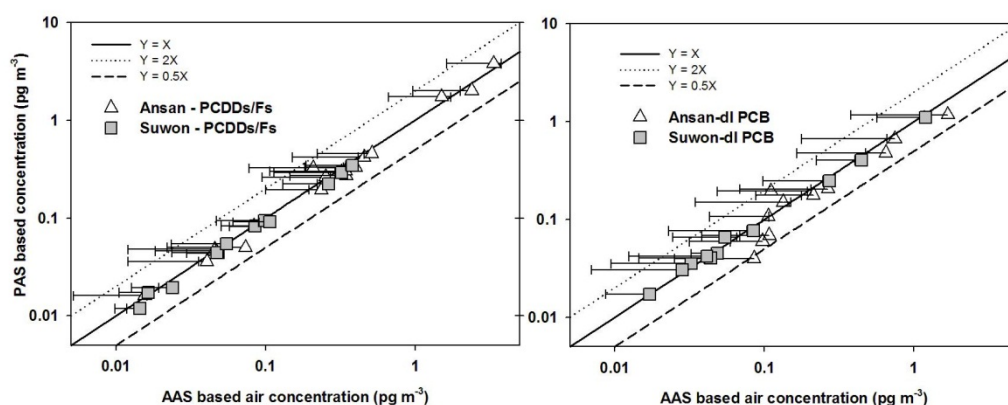


Fig. 3 Plot of various PCDDs/Fs and dl-PCBs measured using AAS and PAS at Suwon and Ansan

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