

PARAMETERS CHARACTERIZING ATMOSPHERIC BEHAVIOR OF PCDDs/PCDFs

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Introduction

The current major source of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) is considered to be combustion processes¹. These persistent compounds could be transported over wide areas. Understanding the atmospheric behavior of PCDDs/PCDFs is important for exposure assessment and the prediction of the effectiveness of emission control measures for combustion. In this study, the atmospheric existence forms and dry/wet depositions of PCDDs/PCDFs were investigated to obtain the parameters characterizing atmospheric behavior, which can be used for a computerized environmental model simulation, such as gas-particle partition coefficient, particle size distribution, washout ratio, and dry deposition velocity.

Materials and Methods

Sample collection

Sampling was conducted on the roof of a building at Yokohama National University during the period of Oct. 1998 – Mar. 2000.

Air samples for gas-particle partition coefficients were collected by a high volume air sampler (DHV-1000S, Shibata Scientific Technology) equipped with a quartz fiber filter (QFF) to collect particulate compounds and two polyurethane foam plugs (PUFs) to collect gas phase compounds. Each sample was collected for 48 h at a flow rate of 566 L/min. The samples were collected about twice a month ($n=22$).

Air samples for particle size distributions were collected using an Andersen high volume air sampler (AH-600, Shibata Scientific Technology). The atmospheric particles were separated according to their aerodynamic diameters into five fractions (<1.1, 1.1-2, 2-3.3, 3.3-7, >7 μm) by the impactor of the Andersen sampler. Each sample was collected for 72 h at a flow rate of 566 L/min. The samples were collected seasonally ($n=4$).

Dry deposition samples were collected on a thin layer of water (1.15 m² of total surface area) in four stainless steel vats. Dry deposition sampling and air sampling were performed simultaneously for 48 h (or 72 h) each time. The samples were collected about once a month ($n=12$).

Wet deposition samples were collected with a rain sampler that consisted of a glass funnel with 45 cm inner diameter and a glass bottle. When the rain sensor detected rain, the cover on the funnel would open to collect rainwater. Each sample mostly represented a single rain event. The samples for a single rain event were collected about once a month ($n=10$).

Sample analysis

QFFs and PUFs were separately analyzed. They were extracted with toluene by using a Soxhlet/Dean-Stark extractor for 16 hours. Deposition samples were filtered through a glass fiber

filter and a solid phase extraction disk (ENVI-18 DSK 90mm, Supelco). The filter and the disk were extracted twice with acetone and twice with toluene using an accelerated solvent extraction method (ASE-200, Dionex).

The extracts were cleaned by sulfuric acid / silica gel column chromatography (or treated with concentrated sulfuric acid and cleaned by silica gel column chromatography) and activated-carbon-impregnated silica gel column chromatography for further cleanup, and injected into an HRGC/HRMS (HP6890, Hewlett-Packard and Autospec-Ultima, Micromass) for analysis. Tetra- to octachlorinated PCDD/PCDF congeners were measured using a DB-5 column (60 m, J&W Scientific).

Results and Discussion

Gas-particle partitioning

PCDDs/PCDFs in air exist in either the gas phase or the particulate phase, and the two phases behave differently. Gas-particle partition coefficients (K_p) and the fractions of compounds associated with the particulate phase (ϕ) were calculated by,

$$K_p = C_p / TSP / C_g \quad (1)$$

$$\phi = C_p / (C_p + C_g) = K_p \times TSP / (K_p \times TSP + 1), \quad (2)$$

respectively, where C_p and C_g are the atmospheric concentrations of a compound in the particulate phase and the gas phase, respectively, and TSP stands for total suspended particles in $\mu\text{g}/\text{m}^3$ ^{2, 3}. The analyte concentrations on QFF and PUF were approximately considered as C_p and C_g , respectively and a mean TSP value of $53.1 \mu\text{g}/\text{m}^3$ was used in all calculations. The partition depended on the ambient temperature, T , as shown in Figures 1 and 2. Based on the approximate linear relationships of Figure 1, the curves in Figure 2 were obtained. The values of K_p for the hepta- and octachlorinated compounds were estimated from those of K_p for the tetra- to hexachlorinated compounds by using the linear relationships between $\log K_p$ and $\log P_l$ (the subcooled liquid vapor pressures)^{4, 5}.

About half of the tetrachlorinated compounds existed in the gas phase at a temperature of 5°C , whereas hepta- and octachlorinated compounds existed almost entirely in the particulate phase under 30°C . The partition of penta- and hexachlorinated compounds strongly depends on the ambient temperature. These differences in partition determine the atmospheric behavior such as the rate of atmospheric deposition processes and degradation.

Particle size distribution

A difference in particle size distribution among homologues was observed (Table 1: average values in four samples). The largest amounts of hexa- to octachlorinated compounds existed in small particles, whereas the less chlorinated compounds were widely distributed from small to large particles. This trend was found similar to those reported for other locations^{6, 7}.

Dry deposition

The ratio of dry deposition flux to air concentration of a compound is often defined as deposition velocity.

$$F_p = V_p \times C_p \quad (3)$$

where F_p is the particulate phase dry deposition flux and V_p is the dry deposition velocity for the particulate phase⁸.

The gas phase dry deposition flux depends on the difference in concentration of a compound between the deposition surface and the atmosphere. Assuming that equilibrium was reached between the gas phase in the atmosphere and the dissolved phase in the water in stainless steel vats, F_p was obtained by subtraction of the dissolved amount which was calculated using Henry's Law

constants⁹, from the observed deposition fluxes.

The obtained values of V_p had large variations (Table 2). The values of V_p increased as the average wind speed increased during the sampling period.

The deposition velocities are determined as a function of particle diameter. The values of V_p for aerosol particles of approximately 0.1-1 μm in diameter are generally the minimum of those of particles of all sizes⁸. The difference in V_p among homologues can be explained by the difference in particulate size distribution among homologues (Table 1).

Wet deposition

Efficiencies of gas and particle washouts (W_p and W_g) from the atmosphere by precipitation are empirically defined as:

$$C_{rain} = W_p \times C_p + W_g \times C_g, \quad (4)$$

where C_{rain} is the concentration of a compound in precipitation¹⁰. W_g is approximately obtained by using Henry's Law constant (H), assuming an equilibrium is reached between raindrops and the gas phase in the atmosphere such that

$$W_g = R \times T/H, \quad (5)$$

where R is the gas constant¹⁰. Since air and rain concentrations were not measured simultaneously, the values of C_p and C_g were estimated from the air concentration data based on the ambient temperature and the wind speed during the rain-sampling period.

The obtained values of W_p were higher than those of W_g (Table 3), suggesting that the efficiencies of washouts from the atmosphere by precipitation are higher in the particulate phase than in the gas phase. As with dry deposition velocities, the scavenging collection efficiencies for aerosol particles of approximately 1 μm in diameter are generally the minimum values¹¹. Therefore, the difference in W_p among homologues can be explained by the difference in particulate size distribution among homologues (Table 1).

Acknowledgments

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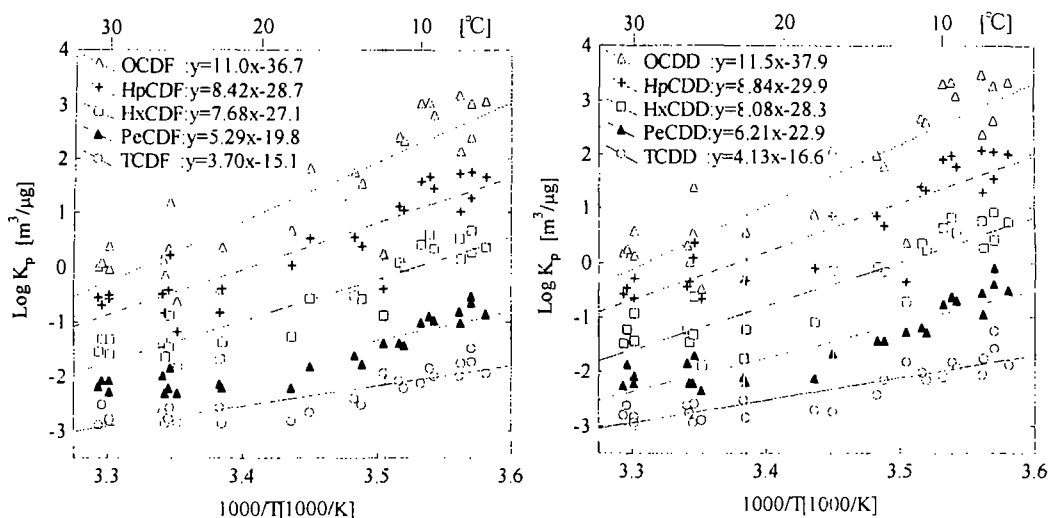


Figure 1. Plot of $\log K_p$ vs $1000/T$.

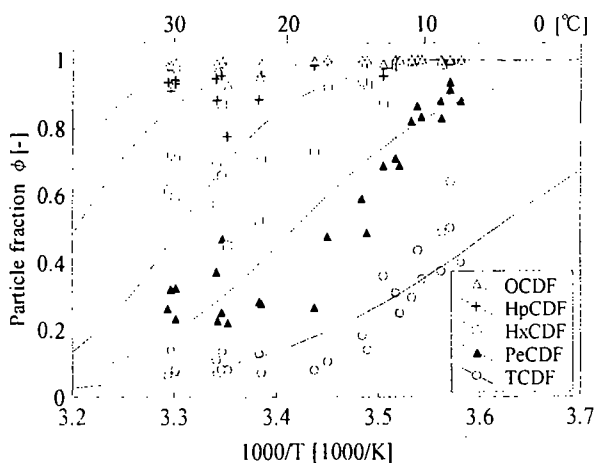


Figure 2. Plot of ϕ vs $1000/T$ (PCDFs).

Table 1. Fractions of PCDDs/PCDFs in the investigated size ranges of atmospheric particles (average values in four samples) [%]

aerodynamic diameter [μm]	>7.0	3.3-7	2-3.3	1.1-2	<1.1
TCDF	12.8	13.2	13.0	15.6	45.4
PeCDF	7.6	8.2	8.6	12.3	63.2
HxCDF	4.6	5.4	6.1	9.8	74.1
HpCDF	2.9	3.4	4.0	7.2	82.5
OCDF	2.8	3.2	3.7	7.3	83.0
TCDD	15.7	14.4	14.0	16.8	39.1
PeCDD	8.8	8.7	8.9	12.9	60.7
HxCDD	5.3	5.9	6.9	10.6	71.3
HpCDD	2.9	4.6	6.1	9.2	77.2
OCDD	3.4	6.7	7.3	11.2	71.5

Table 2. Dry deposition velocities of PCDDs/PCDFs in the particulate phase, V_p , [cm/s]

	Average	Geomean	Max.	Min.
TCDF	0.72	0.43	3.3	0.12
PeCDF	0.34	0.17	1.7	0.052
HxCDF	0.17	0.089	0.81	0.030
HpCDF	0.17	0.078	0.96	0.024
OCDF	0.22	0.10	1.2	0.021
TCDD	1.2	0.78	4.2	0.17
PeCDD	0.53	0.29	1.9	0.080
HxCDD	0.32	0.19	1.1	0.062
HpCDD	0.33	0.21	1.3	0.065
OCDD	0.67	0.39	2.7	0.072

Table 3. Washout ratios of PCDDs/PCDFs in the particulate phase, W_p , and in the gas phase, W_g , [-] $\times 1000$

	W_p				W_g (25°C)
	Average	Geomean	Max.	Min.	
TCDF	100	92	140	34	1.3
PeCDF	48	41	85	16	1.8
HxCDF	32	26	87	10	2.2
HpCDF	34	25	110	10	2.4
OCDF	42	25	180	9.1	3.1
TCDD	120	110	250	47	2.6
PeCDD	55	46	120	19	3.4
HxCDD	38	33	84	12	4.4
HpCDD	48	39	130	16	5.3
OCDD	74	66	160	28	4.7

The values of W_g were obtained by using Henry's Law constants of compounds⁹ according to equation (5).