

Atmospheric Deposition of Polychlorinated Dibenzo-*p*-dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) in Kanazawa, Japan

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The deposition processes of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in Kanazawa, Japan were studied by examination of the concentrations of PCDDs and PCDFs (PCDD/DFs) and their tetra- to octa-chlorinated homologues in the rain. The weighted mean deposition flux was 360 pg/m²/day [7.7 pg-toxicity equivalency quantity (TEQ)/m²/day]. Deposition fluxes obtained in this study were lower than the average value of Japan, suggesting that Kanazawa is a less polluted area. The seasons with the highest and next highest deposition fluxes were winter and spring, respectively, possibly due to the presence of an inversion layer in winter and spring that reduced the atmospheric dilution of pollutants. In addition, the ratio of PCDFs to total deposition flux in winter was larger than the ratios in the other seasons, possibly due to the burning of fossil fuels for residential heating. Deposition flux of each tetra- to octa-chlorinated homologue of PCDD/DFs was negatively correlated with surface temperature. Other meteorological parameters were positively correlated with almost all tetra- to octa-chlorinated homologues, except for heptachloro dibenzo-*p*-dioxins (HpCDDs) and octachloro dibenzo-*p*-dioxin (OCDD), possibly as a result of the photochemical reaction of pentachlorophenol (PCP), which produced mainly OCDD and traces of HpCDDs. In ambient air, the two most dominant homologues were tetrachloro dibenzo-*p*-dioxins (TeCDDs) and OCDD, while, in soil, the two most dominant homologues were OCDD and TeCDDs. The washout ratios increased with the increase in chlorine substitution. Thus, the difference in washout ratios between homologues might be one of the reasons for the difference of the homologue profile between the air and soil.

Key words — atmospheric deposition flux, washout ratio, homologue profile, meteorological factor, polychlorinated dibenzo-*p*-dioxin, polychlorinated dibenzofuran

INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are widespread environmental contaminants. These compounds are not created intentionally, but are produced inadvertently by a number of human activities and natural processes. Industrial or municipal waste incineration, manufacture and use of certain herbi-

cides^{1,2)} and pulp bleaching³⁾ are considered to be major sources of dioxins to the environment. Currently, the main source of PCDDs and PCDFs (PCDD/DFs) in Japan⁴⁾ is combustion at waste incinerators. However, PCDD/DFs were present as impurities in several herbicides that were previously used in paddy fields⁵⁾ and still remain in the fields and contaminate the aquatic environment.⁶⁾ Because the distribution of dioxins sources are different in each region, controlling the emission of dioxins will require understanding the contamination level and distribution processes of dioxins in each region.

The atmospheric transportation is the primary distribution pathway moving PCDD/DFs from emission sources to the terrestrial and aquatic environment. We previously showed that the composition of atmospheric PCDD/DFs was influenced by both combustion and soil suspensions,⁷⁾ while PCDD/DFs

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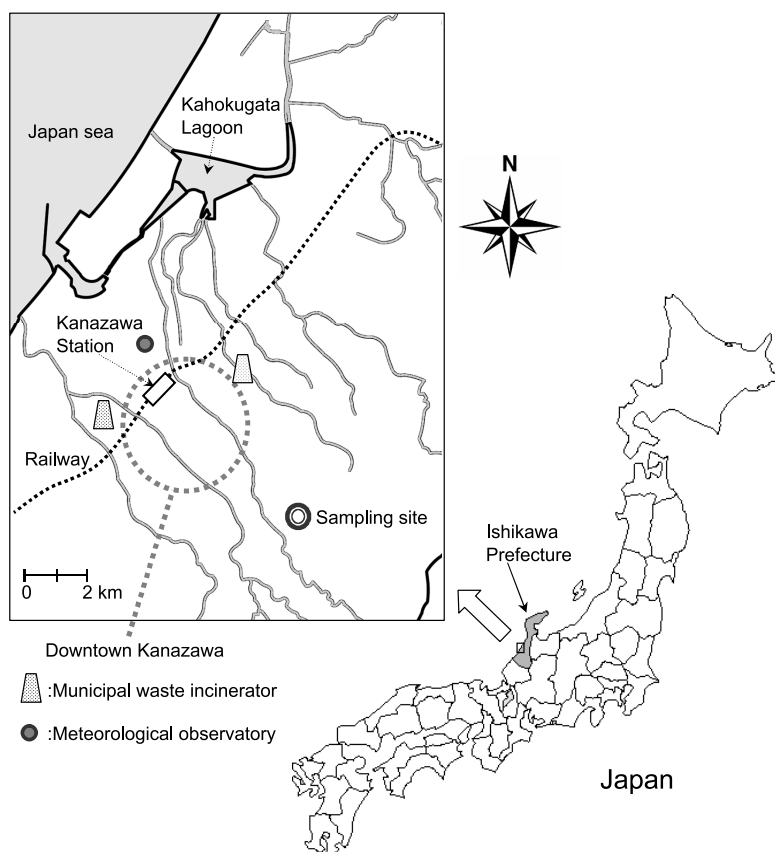


Fig. 1. Location of the Sampling Site

in soil are thought to be supplied by deposition from the atmosphere. Moreover, the gas/particle partition of atmospheric dioxins depends on the temperature.⁸⁾ Although the gas/particle partition ratio affects deposition from the atmosphere, few studies have examined the seasonal change of the atmospheric deposition flux (the atmospheric deposition of dioxins per unit area per unit time).

In the present study, we describe seasonal changes in the atmospheric PCDD/DFs deposition flux in Kanazawa, Japan and discuss the factors affecting these fluxes.

MATERIALS AND METHODS

Sample Collections — Our sampling site (Fig. 1) is the same place where ambient air samples were collected in our previous study.⁸⁾ This site is 6 km southeast from downtown Kanazawa (a city of 450000 people), and on a hill which rises about 100 m above sea level. The most frequent wind direction during the sampling period at this site was

from the south. The maximum and minimum temperature in this site were 24.8°C (in August) and 5.7°C (in January), and the annual mean temperature was 17.4°C. The monthly average precipitation at the sampling site was about 190 mm.

The mean concentration of atmospheric dioxins at the site was 0.021 pg-toxicity equivalency quantity (TEQ)/m³, which was similar to the average concentration of atmospheric dioxins in Ishikawa prefecture (0.028 pg-TEQ/m³; $n = 48$).⁹⁾ Thus the air sampled at this site was typical of Ishikawa. Because the concentration of atmospheric PCDD/DFs deposition is thought to be closely related to the concentration of atmospheric PCDD/DFs, we expected to collect typical deposition samples at this site.

Atmospheric depositions were collected using a 31 cm-diameter glass funnel connected to a 5 l amber glass bottle with a 1 cm-inner diameter Teflon tube, which collected mainly rain (wet depositions) but also dry depositions. This sampling apparatus was placed on the rooftop of a building and the top edge of this apparatus was 15 m above the ground. Atmospheric depositions were sampled about every

Table 1. Atmospheric Deposition Fluxes of PCDD/DFs on Kanazawa, Japan

Sampling period	2003/4/1– 4/4	4/4– 4/15	4/15– 4/22	4/22– 4/29	4/29– 5/6	5/6– 5/14	5/14– 5/21	5/21– 5/28– 6/4
Number of sampling days	3	11	7	7	7	8	6	8
Meteorological parameters ^{a)}								
Atmospheric pressure (hPa)	1009.5	1010.8	1014.2	1011.4	1010.6	1012.5	1007.3	1005.6
Surface temperature (°C)	9.9	11.2	13.7	15.0	17.0	17.8	17.1	20.5
Precipitation (mm)	19.5	70.5	65.0	61.0	28.5	46.0	16.5	17.0
Number of rainy days (day)	2	6	3	4	2	3	2	2
Deposition flux (pg/m ² /day)								
TeCDDs	68	43	64	11	14	50	4.3	5.0
PeCDDs	35	30	16	7.9	1.5	13	1.9	1.7
HxCDDs	46	52	22	13	5.2	N.D. ^{b)}	5.0	N.D. ^{b)}
HpCDDs	93	130	52	21	9.3	10	32	8.2
OCDD	230	460	170	42	9.1	23	120	26
PCDDs	470	710	320	95	39	96	170	41
TeCDFs	160	90	44	19	8.9	3.9	5.4	1.2
PeCDFs	120	77	37	17	5.8	4.2	3.4	1.9
HxCDFs	100	54	25	16	5.5	7.3	4.8	3.2
HpCDFs	61	43	26	16	8.5	4.8	3.0	4.0
OCDF	38	16	10	2.7	2.2	2.2	2.5	N.D. ^{b)}
PCDFs	480	280	140	70	31	22	19	10
Tota PCDD/DFs	950	990	460	160	70	120	180	51
WHO-TEQ (pg-TEQ/m ² /day)	11	12	5.2	1.3	0.29	1.1	0.50	0.075
	Mean deposition flux ^{c)}		PCDD/DFs		360 pg/m ² /day		WHO-TEQ	
					7.7 pg-TEQ/m ² /day			

^{a)} Meteorological factors were obtained from daily observations for the local meteorological observatory in Kanazawa. Atmospheric pressure and surface temperature were averaged in each sampling term. Precipitation and number of rainy days were sum total in each sampling term. ^{b)} N.D., Not detected. ^{c)} Weighted mean of all data. ^{d)} Multiply mean deposition flux by 365 days.

10 days on the average from April 2003 to January 2004. The sampling period was extended or shortened to compensate for low or high precipitation, respectively. A total 23 atmospheric deposition samples were collected (Table 1).

Pretreatment Procedure — Atmospheric depositions were pretreated as follows: each sample was trapped on a 90 mm diameter C18 (Octadecyl) Empore extraction disk (3M, St. Paul, MN, U.S.A.). The extraction disks were vacuum-dried in a desiccator, and soxhlet extracted with toluene for 20 hr. The soxhlet extractions were cleaned up as previously reported.⁸⁾ Briefly, each extract was solvent exchanged to hexane and this hexane solution was put on a multi-layered silica gel column with clean-up spike solutions. PCDD/DFs were eluted with 200 ml of hexane and fractionated with an active carbon-dispersed silica gel reversible column. The fractions were concentrated and spiked with 200 pg

of each of 4 ¹³C-labelled PCDFs (syringe spikes). Then, the volume was adjusted to 20 μ l with decane prior to GC/MS analysis.

GC/MS Analysis — The individual final solution was analyzed by high resolution-GC/high resolution-MS (HP-6890; Agilent, Wilmington, DE, U.S.A. + MS-700D; JEOL, Tokyo, Japan). Selected ion monitoring (SIM) measurements and determination of each isomer for PCDD/DFs were performed as we previously described.⁸⁾

Recovery rates of the clean-up spikes of all samples ranged from 50 to 120%.

TEQ values were calculated using WHO-TEF.¹⁰⁾ Atmospheric deposition flux refers to the total amount of deposited PCDD/DFs per m² per day.

Table 1. Continued

Sampling period	6/4– 6/18	6/18– 6/27	6/27– 7/4	7/4– 7/11	7/11– 7/18	7/18– 8/9	8/9– 8/20	8/20– 9/3
Number of sampling days	13	10	7	7	7	22	11	14
Meteorological parameters ^{a)}								
Atmospheric pressure (hPa)	1006.5	1002.6	1002.8	1004.3	1004.2	1004.3	1005.9	1008.1
Surface temperature (°C)	22.0	23.0	21.8	22.9	21.6	25.4	24.7	26.1
Precipitation (mm)	54.0	60.0	44.5	75.0	35.0	128.0	143.0	111.5
Number of rainy days (day)	6	6	6	7	4	11	9	8
Deposition flux (pg/m ² /day)								
TeCDDs	15	38	17	14	28	27	30	53
PeCDDs	3.9	7.2	3.4	3.5	9.8	15	19	27
HxCDDs	6.2	11	5.7	9.8	29	23	29	34
HpCDDs	13	12	8.2	27	15	28	36	32
OCDD	27	27	15	37	33	52	130	63
PCDDs	65	94	49	91	110	146	240	210
TeCDFs	6.8	19	12	19	32	38	27	42
PeCDFs	9.0	15	6.4	12	18	33	26	40
HxCDFs	7.7	14	8.1	8.9	19	29	26	42
HpCDFs	6.8	9.6	0.0	13	16	17	22	29
OCDF	4.2	N.D. ^{b)}	5.7	6.8	9.7	9.4	21	19
PCDFs	35	57	33	60	95	130	120	170
Tota PCDD/DFs	100	150	81	150	210	270	360	380
WHO-TEQ (pg-TEQ/m ² /day)	1.5	2.6	2.4	2.3	15	5.8	7.4	5.4
Sampling period	9/3– 9/7	9/7– 10/1	10/1– 10/17	12/1– 12/9	12/9– 12/18	12/18– 12/23	12/23– 2004/1/6	
Number of sampling days	4	24	16	8	9	5	14	
Meteorological parameters ^{a)}								
Atmospheric pressure (hPa)	1010.1	1009.1	1013.3	1016.7	1013.6	1010.2	1014.0	
Surface temperature (°C)	25.4	22.8	17.4	9.1	6.7	6.5	7.4	
Precipitation (mm)	26.0	55.0	60.5	65.5	125.5	43.0	110.0	
Number of rainy days (day)	2	10	6	6	9	5	14	
Deposition flux (pg/m ² /day)								
TeCDDs	19	15	10	110	73	46	80	
PeCDDs	15	4.7	7.7	69	53	36	91	
HxCDDs	21	7.8	16	120	67	51	120	
HpCDDs	28	7.1	21	120	73	44	120	
OCDD	60	23	44	220	110	60	150	
PCDDs	140	57	99	630	380	240	560	
TeCDFs	11	5.4	14	230	170	110	280	
PeCDFs	18	4.2	14	260	220	130	380	
HxCDFs	22	2.7	8.5	260	200	110	340	
HpCDFs	15	4.0	8.3	170	140	79	250	
OCDF	7.2	2.7	7.3	120	82	47	140	
PCDFs	73	19	52	1000	810	490	1400	
Tota PCDD/DFs	220	76	150	1700	1200	720	2000	
WHO-TEQ (pg-TEQ/m ² /day)	3.4	2.1	2.5	11	22	14	43	
	Annual Deposition ^{d)}			PCDD/DFs	130000 pg/m ² /year			
				WHO-TEQ	2800 pg-TEQ/m ² /year			

RESULTS AND DISCUSSION

Deposition of PCDDs and PCDFs

TEQ values of atmospheric deposition fluxes ranged from 0.075 to 43 pg-TEQ/m²/day (weighted mean 7.7 pg-TEQ/m²/day), and total concentrations of atmospheric deposition fluxes ranged from 31 to 2000 pg/m²/day (weighted mean 360 pg/m²/day) (Table 1). Using these values, the annual deposition flux was estimated to be 130000 pg/m²/year (2800 pg-TEQ/m²/year). Deposition fluxes of PCDD/DFs in Matsuyama (460000 people) in Japan,¹¹⁾ Bloomington (50000 people) in U.S.A. and Indianapolis (800000 people) in U.S.A.¹²⁾ were 790 (8.8 pg-TEQ/m²/day), 1000 and 1500 pg/m²/day, respectively. The deposition fluxes in Kanazawa were lower than those values.

In 1998, the Japanese Ministry of the Environment reported average domestic atmospheric deposition fluxes (in pg-TEQ/m²/day) of 25 at emission source sites, 19 in big cities, 18 in medium and small-sized cities and 4.1 at background sites.¹³⁾ Thus, our sampling site seemed less polluted with PCDD/DFs than medium and small-sized cities in Japan. However, because the yearly average concentrations of atmospheric dioxins in Japan have been decreasing year by year,⁴⁾ the average domestic atmospheric deposition fluxes may also have been decreasing.

Seasonality of Atmospheric Deposition Flux

The ratios of octachloro dibenzo-*p*-dioxin (OCDD) to the total PCDD/DFs in atmospheric deposition fluxes for spring, summer and autumn were higher than those in the air (Table 2). On the other hand, the ratios of TeCDDs in the deposition fluxes were lower than those in the air. The total deposition flux was highest in winter. In contrast, the total concentration of atmospheric PCDD/DFs was lowest in winter. The enhanced deposition in winter and spring may be due to the presence of inversion layers that reduced atmospheric dilution. The inversion layer that forms at low temperature in winter and early spring results in an increased concentration of suspended particulate matter (SPM) below the inversion layer.¹⁴⁾ However, the concentration of atmospheric PCDD/DFs in winter was low, possibly because pollutants in the air were removed efficiently by snow. Franz and Eisenreich¹⁵⁾ reported that SPM concentration in snow was more than 2 orders of magnitude higher than that in rain. Snow scavenges the particulate phase of atmospheric PCDD/DFs, and then the concentration in air de-

creases.

The concentration ratio of PCDFs to total PCDD/DFs in the deposition flux was higher in winter than that in other three seasons. The increase of PCDFs concentration ratio in the deposition flux in winter may be due to the combustion of fossil fuels (*e.g.* kerosene) for residential heating. PCDFs dominate over PCDDs in the burning of wood,¹⁶⁾ and the congener distribution of fossil fuel combustion was similar to that of wood combustion.¹⁷⁾ Therefore, the concentration ratio of PCDFs in deposition was considered to increase.

Meteorological Effects on Atmospheric Deposition Flux

The surface temperature showed a significant inverse correlation with deposition fluxes of all of the homologues and that of total PCDD/DFs, but the precipitations did not (Table 3). Most of the homologues were significantly positive correlated with the atmospheric pressure (except OCDD), and the ratio of rainy days [except heptachloro dibenzo-*p*-dioxins (HpCDDs), OCDD and PCDDs].

In winter, the atmospheric pressure is high in Kanazawa, but the surface temperature is low. The atmospheric inversion that is formed in winter might inhibit atmospheric mixing as mentioned above. The atmospheric pollutants are not diluted but remain for a long time, and then are washed out.

Another reason for the relationship between atmospheric deposition flux and temperature is that the ratio of particulate phase of PCDD/DFs in the air becomes high with decreasing in the temperature.⁸⁾ Because rain efficiently washes out the particulate phase of PCDD/DFs,¹⁸⁾ the increase of particulate phase of PCDD/DFs in the air is thought to result in the increase of PCDD/DFs deposition.

The atmospheric deposition fluxes were not correlated with total precipitation but they were correlated with the frequency of rainy days. In agreement with this observation, most of particles containing pollutants were found to be washed out from the atmosphere at the beginning of the each rain event.¹⁹⁾

In this study, the atmospheric deposition fluxes of HpCDDs and OCDD had weak or no correlations with meteorological factors. However, the deposition flux of heptachloro dibenzofurans (HpCDFs) and octachloro dibenzofuran (OCDF), which have the same number of chlorine substitutions as HpCDDs and OCDD, had high correlations. A possible reason for this difference is that HpCDDs and OCDD were generated by photochemical reactions

Table 2. Seasonal Deposition Fluxes of PCDD/DFs

Homologue	Deposition flux (pg/m ² /day) ^{a)}							
	Spring		Summer		Autumn		Winter	
	amount	(%)	amount	(%)	amount	(%)	amount	(%)
TeCDDs	27	(15.2)	14	(11.0)	9.2	(13.7)	65	(5.4)
PeCDDs	9.8	(4.0)	7.3	(5.8)	4.6	(5.8)	60	(4.5)
HxCDDs	14	(5.1)	11	(9.2)	6.9	(10.3)	81	(6.3)
HpCDDs	34	(12.5)	12	(9.4)	7.4	(11.3)	80	(6.2)
OCDD	100	(30.8)	27	(21.3)	16	(29.7)	120	(9.5)
PCDDs	190	(67.6)	71	(56.7)	45	(70.8)	400	(32.0)
TeCDFs	28	(9.1)	14	(12.1)	6.8	(7.7)	190	(14.4)
PeCDFs	23	(7.6)	13	(10.2)	6.6	(7.0)	240	(18.2)
HxCDFs	18	(7.1)	12	(9.8)	6.1	(4.9)	220	(16.7)
HpCDFs	15	(6.1)	8.5	(6.8)	4.8	(5.5)	160	(11.7)
OCDF	6.2	(2.5)	5.7	(4.5)	3.3	(4.0)	92	(7.0)
PCDFs	90	(32.4)	83	(43.3)	27	(29.2)	910	(68.0)
Total PCDD/DFs	280	(100)	120	(100)	72	(100)	1300	(100)
Homologue	Ambient air (pg/m ³) ^{b)}							
	Spring		Summer		Autumn		Winter	
	amount	(%)	amount	(%)	amount	(%)	amount	(%)
TeCDDs	0.84	(35.9)	0.45	(36.8)	0.45	(36.8)	0.16	(15.1)
PeCDDs	0.078	(3.4)	0.055	(4.5)	0.055	(4.5)	0.035	(3.7)
HxCDDs	0.091	(3.8)	0.057	(4.7)	0.057	(4.7)	0.041	(4.4)
HpCDDs	0.12	(5.0)	0.033	(2.6)	0.033	(2.6)	0.066	(5.7)
OCDD	0.25	(10.1)	0.084	(6.7)	0.084	(6.7)	0.25	(19.4)
PCDDs	1.37	(58.2)	0.68	(55.8)	0.68	(55.8)	0.55	(54.1)
TeCDFs	0.40	(16.9)	0.25	(20.4)	0.25	(20.4)	0.19	(21.8)
PeCDFs	0.25	(10.8)	0.16	(12.9)	0.16	(12.9)	0.12	(13.0)
HxCDFs	0.15	(6.4)	0.10	(8.0)	0.10	(8.0)	0.084	(9.3)
HpCDFs	0.13	(5.5)	0.029	(2.3)	0.029	(2.3)	0.047	(5.0)
OCDF	0.057	(2.3)	0.013	(1.1)	0.013	(1.1)	0.023	(2.4)
PCDFs	0.99	(41.8)	0.54	(44.2)	0.540	(44.2)	0.47	(45.9)
Total PCDD/DFs	2.4	(100)	1.2	(100)	1.2	(100)	1.0	(100)

Column of amount were weighted mean in each season. Column of (%) were ratio of individual homologue to total PCDD/DFs. a) This study. b) Ref. 8.

of PCP in the air. Baker and Hites²⁰⁾ suggested that some PCP can be converted in the atmosphere to OCDD, and to lesser amounts of HpCDDs by photochemical reactions. Changes of atmospheric conditions (*e.g.* changes in residual time, the concentration of PCP and the surface area of water droplets) accounted for the magnitude of HpCDDs and OCDD that were produced by the photochemical reactions. Therefore, the deposition fluxes of HpCDDs and OCDD, unlike those of the other homologues, were considered to be influenced by other factors such as the photochemical generations.

Washout Ratios

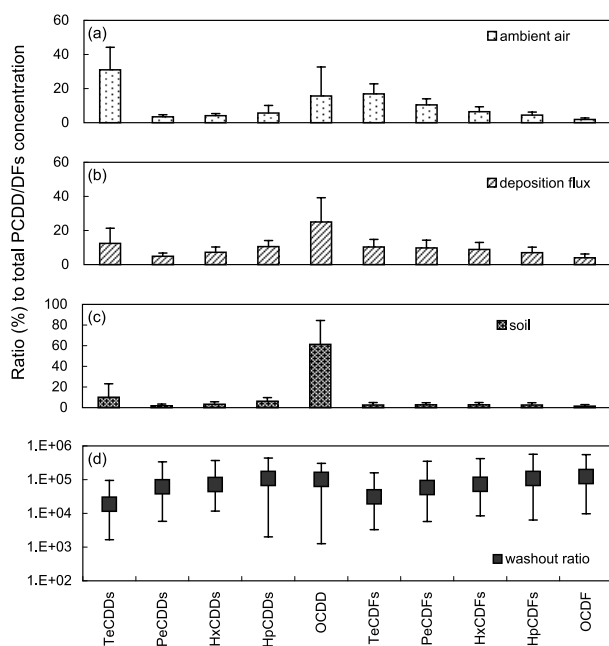
When a rain event occurs, atmospheric pollutants are removed from the air and transferred into the rain water as mentioned above. Washout ratios are expressed as the ratio of the concentration in the rain to that in the air.²¹⁾ We can regard this ratio as an indicator of pollutant-scavenging ability of the air.

Figure 2 shows the average concentration ratio of homologues of (a) ambient air, (b) atmospheric deposition flux, (c) soil, and (d) washout ratios. The homologue profile of soil samples were based on the average concentrations in 34 soil samples that we previously determined.²²⁾ TeCDDs was the domi-

Table 3. Correlation between Atmospheric Deposition Flux and Meteorological Factors^{a)}

Homologue	Atmospheric pressure (hPa)	Surface temperature (°C)	Precipitations (mm)	Ratio of rainy days ^{b)}
TeCDDs	0.53*	-0.75**	0.23	0.46*
PeCDDs	0.53*	-0.76**	0.35	0.60**
HxCDDs	0.51*	-0.77**	0.35	0.62**
HpCDDs	0.47*	-0.76**	0.18	0.38
OCDD	0.32	-0.56*	0.04	0.09
PCDDs	0.47*	-0.75**	0.18	0.34
TeCDFs	0.49*	-0.79**	0.28	0.60**
PeCDFs	0.49*	-0.74**	0.34	0.62**
HxCDFs	0.49*	-0.73**	0.35	0.62**
HpCDFs	0.50*	-0.72**	0.36	0.61**
OCDF	0.50*	-0.72**	0.37	0.64**
PCDFs	0.50*	-0.74**	0.34	0.62**
Total PCDD/DFs	0.52*	-0.80**	0.30	0.55*

a) Meteorological factors were obtained from daily observations for the local meteorological observatory in Kanazawa. b) The number of rainy days divided by that of sampling days in each sampling period. Significant at * $p < 0.05$. Significant at ** $p < 0.01$.

**Fig. 2.** Concentration Ratio of Homologues of (a) Ambient Air, (b) Deposition Flux, (c) Soil and (d) Washout Ratio

Homologue profiles of (a), (b) and (c) were based on Ref. 8, this study and Ref. 20, respectively. In (a) to (c), bar represents S.D. In (d), each box and bar represent mean and range, respectively.

nant homologue in ambient air [Fig. 2(a)], while OCDD was the dominant homologue in the atmospheric deposition flux [Fig. 2(b)] and in soil [Fig. 2(c)]. The washout ratios increased with the increase in chlorine substitution. This result indicates

that highly chlorinated PCDD/DFs (*i.e.* HpCDD/DFs and OCDD/DF) were more efficiently scavenged from ambient air than less chlorinated PCDD/DFs. Thus, the difference in washout ratios between the homologues might be one of the reasons for the difference in the homologue profiles of the air and the soil.

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