

Comparison of Compositions of Polychlorinated Dibenzop-dioxins (PCDDs) and Dibenzofurans (PCDFs) in Air and Soil Samples Collected in Ishikawa

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Dioxins are present as impurities in agrochemicals applied to the soil. To examine the possibility that dioxins end up in the atmosphere, we compare the homologue composition and some characteristic isomer distributions of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in air and soil samples collected at sites in Ishikawa Prefecture, Japan. Tetrachloro dibenzo-*p*-dioxin (TeCDD) was the most abundant PCDD homologue in the air samples, while octachloro dibenzo-*p*-dioxin (OCDD) was the most abundant PCDD homologue in the soil samples. However, at several site, the most predominant homologue in the soil sample was not OCDD but TeCDD. The mean ratio of TeCDDs to PCDDs in the air samples was significantly smaller in winter than in other seasons, but no such seasonal variation was observed in the distribution of PCDF homologues. The abundance of PCDF homologues was inversely related to the number of chlorine substitutions in the air samples. The contribution of each toxic isomer (2,3,7,8-chlorine-substituted) to the total toxicity equivalency quantity (TEQ) in the air samples tended to be intermediate between their contributions to the TEQs in the soil and cinder samples. This result suggested that the air samples were influenced by both soil/dust suspension and combustion. In order to clarify the contributions of agrochemicals to dioxins in the air, we focused on the ratios of several characteristic isomers that are indicators of agrochemicals (chloronitrophen: CNP and pentachlorophenol: PCP) to their homologues. Significant decreases in the ratios of the isomers to their homologues in the air samples were observed only in winter, probably as a result of suppression of dust suspension by the snow cover. Therefore, the contribution of combustion to the dioxin concentration in the air was thought to be relatively large in winter.

Key words — polychlorinated dibenzo-*p*-dioxin, polychlorinated dibenzofuran, agrochemical, homologue, isomer, combustion

INTRODUCTION

The origin of dioxins in environmental samples can be inferred from the composition of their homologues and isomers.¹⁾ Analysis of dated sediment core samples has shown that the main source of dioxins has changed with time.²⁾ Prominent sources of dioxins in the environment include combustion sources as well as impurities of several agrochemicals that had been widely used in the past and such agrochemical-origin dioxins are still present in soil and sedi-

ment.^{3,4)} In general, soil and sediment samples contain a limited number of predominant dioxin isomers of largely agrochemical origin,⁵⁾ while combustion-origin samples contain almost all isomers. Therefore, it is useful to focus on the ratios of these isomers to their homologues for evaluating the contributions of the agrochemicals.

Large amounts of agrochemicals have been used in Japanese paddy fields in the past several decades. Among them were the herbicides pentachlorophenol (PCP) and chloronitrophen (CNP), which contained dioxins as impurities.⁶⁾ Dioxins with high chlorine contents, such as hepta- and octachloro dibenzo-*p*-dioxins (HpCDDs and OCDD) and heptachloro dibenzofurans (HpCDFs), are indicators of PCP contamination,^{5,7,8)} while 1,3,6,8- and 1,3,7,9-

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tetrachloro dibenzo-*p*-dioxins (1,3,6,8- and 1,3,7,9-TeCDDs) and 2,4,6,8-tetrachloro dibenzofuran (2,4,6,8-TeCDF) are the typical isomers that are known as impurities of CNP.^{6,9,10} The present paddy soil are still contaminated with dioxins originating from the above two herbicides.^{10,11} However, it is unclear whether the soil agrochemicals have affected other parts of the environment.

Air and soil probably influence each other through wet/dry deposition and wind-driven dust suspension.¹² In this study, we examine the homologue and some characteristic isomer composition of dioxins in environmental air and soil samples to determine the relative contribution of the combustion and agrochemicals to atmospheric dioxins. Especially, we show that agrochemicals make an important contribution to atmospheric dioxin.

MATERIALS AND METHODS

Chemicals — Two standard mixed solutions (DF-A10 series and PCB-A10 series) were purchased from Wellington Laboratories (Ontario, Canada). The DF-A10 series consisted of 23 native and 25 ¹³C-labelled polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/DFs), including 17 2,3,7,8-chlorine-substituted isomers. The PCB-A10 series consisted of 14 native and 18 ¹³C-labelled polychlorinated biphenyl (PCB), including 12 coplanar polychlorinated biphenyl (co-PCB) isomers. These two solutions were used to make working curves for determining 17 2,3,7,8-chlorine-substituted PCDD/DFs and 12 co-PCBs.

Clean up spike solution for PCDD/DFs (NK-LCS-P) and for co-PCBs (PCB-LCS-A200), syringe spike solution for PCDD/DFs (DF-IS-L200) and for co-PCBs (PCB-IS-B100) and sampling spike solution for PCDD/DFs (DF-IS-A40) and for co-PCBs (PCB-SS-A20) are all from Wellington Laboratories.

Each constituent of multi-layered silica gel column for clean up of the crude extracts of samples was obtained from Wako Pure Chemicals (Osaka, Japan). Active carbon-dispersed silica gel for separating PCDD/DFs from co-PCBs was purchased from Kanto Kagaku (Tokyo, Japan). Hexane, toluene, dichloromethane and other organic solvents used in the sample pretreatments were from Kanto Kagaku and were of dioxin-analysis grade.

Sampling — Air samples were collected at twelve sites in Ishikawa Prefecture in central Honshu

Island, Japan in all four seasons in 2000 and 2001 (Fig. 1). The main topographic feature of Ishikawa Prefecture is the Noto Peninsula, which juts into the Sea of Japan. The population of Ishikawa Prefecture is about 1200000. Kanazawa, the capitol city of the prefecture (population about 450000), is a commercial city but it has only a few large-scale sources of dioxins, such as industrial waste incinerators. In order to monitor the environmental samples with sufficiently high levels of dioxins, we collected air samples near several conspicuous sources that are located in cities and towns other than Kanazawa.

Air sample were collected with high-volume air samplers (HV-700F; Sibata, Tokyo, Japan) at a flow rate of 700 l/min for 24 hr. The particulate phase of dioxin was collected on quartz fiber filters, while the gaseous phase of dioxin was adsorbed in two polyurethane foam (PUF) plugs attached to the high-volume air samplers. The quartz fiber filters were combusted at *ca.* 600°C overnight and sealed in aluminum foil in desiccators prior to use. The PUF plugs were pre-extracted in acetone with a soxhlet apparatus for 20 hr, vacuum-dried, and also sealed in aluminum foil in desiccators. Before the start of sampling, each filter was spiked with 1000 pg of ¹³C-labelled 1,2,3,4-TeCDD (DF-IS-A40) and ¹³C-labelled 3,3',4,5'-TeCB (PCB-SS-A20).

Soil samples were collected from three undisturbed sites (*e.g.*, schoolyards, shrines, playgrounds) within several hundred meters of each air-sampling site, air-dried at room temperature, and screened with 2 mm mesh strainers. Thus, we obtained 48 air samples and 36 soil samples.

Analytical Methods — Air and soil samples were pretreated according to procedures published by the Ministry of Environment, Japan with minor modifications. The quartz fiber filter and PUF of each air sample were soxhlet extracted for 20 hr in toluene and in acetone, respectively. The extract from the filter was stirred into the extract from PUF, and then the solution was evaporated to near dryness with a rotary evaporator. The residues obtained were redissolved in 10 ml of hexane. Screened soil samples (*ca.* 60 g) were soxhlet extracted for 20 hr in toluene with copper chips to eliminate sulfur contamination. The extract was also concentrated to near dryness with a rotary evaporator and then redissolved in 10 ml of hexane again.

Half of the volume of the above hexane solution of the air or soil sample was put through a multi-layered silica gel column with clean up spike solutions (NK-LCS-P + PCB-LCS-A200), including

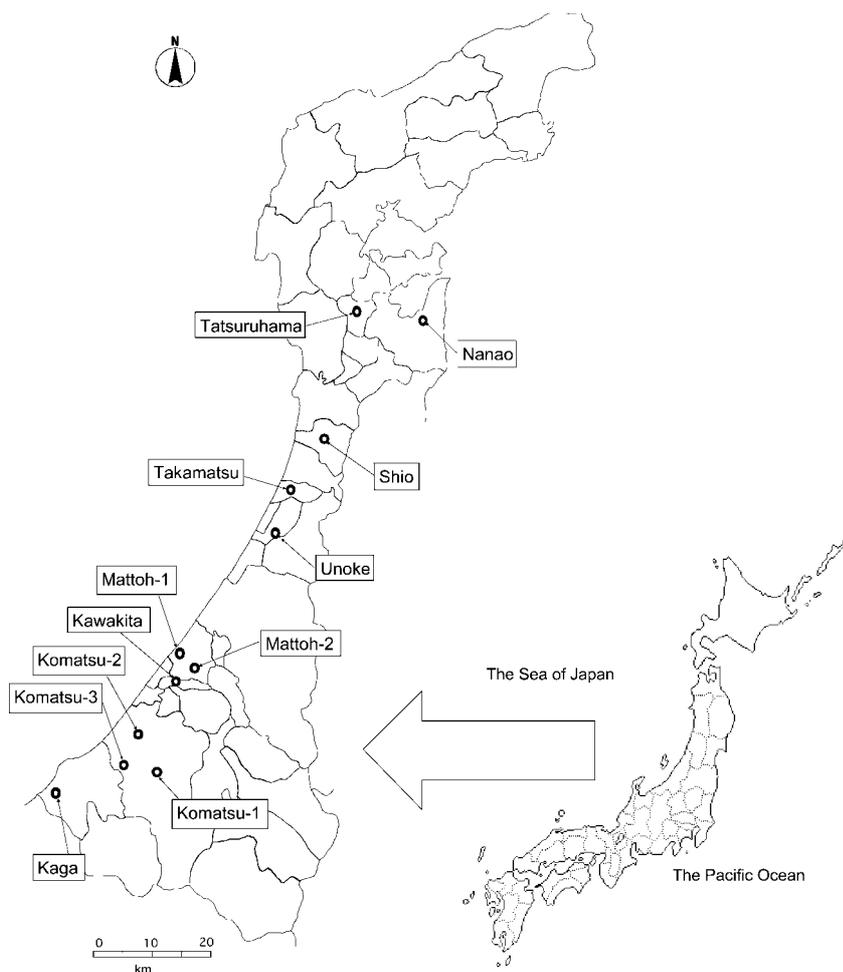


Fig. 1. Air-Sampling Sites in Ishikawa Prefecture, Japan

500 pg of 17 ^{13}C -labelled 2,3,7,8-chlorine-substituted PCDD/DFs and 12 ^{13}C -labelled co-PCBs. The layers of the column consisted of (starting from bottom) 1 g anhydrous Na_2SO_4 , 0.9 g silica gel, 3 g 2% KOH/silica gel, 0.9 g silica gel, 4.5 g 44% H_2SO_4 /silica gel, 6 g 22% H_2SO_4 /silica gel, 0.9 g silica gel, 3 g 10% AgNO_3 /silica gel and 1 g anhydrous Na_2SO_4 . If necessary, the above hexane solution was treated with concentrated H_2SO_4 before it was loading onto the column. PCDD/DFs and co-PCBs were fractionated with active carbon-dispersed silica gel columns. The final PCDD/DFs fraction was eluted with *ca.* 250 ml of toluene and the resulted solutions were concentrated to 50 μl .

The sample solutions were spiked with 500 pg of each of four kinds of ^{13}C -labelled PCDFs (syringe spikes) to enable calculation of recovery rates of clean up spikes, and 1 μl of the final solutions was injected into a high resolution GC/MS (HP-6890; Hewlett Packard, Wilmington, DE, U.S.A. + MS-

700D; JEOL, Tokyo, Japan). SIM measurement was performed with a fused silica capillary column SP-2331 (60 m \times 0.32 mm i.d., 0.20 μm film thickness; Supelco, Bellefonte, PA, U.S.A.) for analysis of TeCDD/DFs, PeCDD/DFs, and HxCDD/DFs (except 1,2,3,7,8,9-HxCDF) and with a DB-17 capillary column (30 m \times 0.32 mm i.d., 0.25 μm film thickness; Agilent Technologies, Wilmington, DE, U.S.A.) for analysis of HpCDD/DFs, OCDD/DF and 1,2,3,7,8,9-HxCDF. The chromatograms were analyzed with the computer software "Diok Ver. 2" (JEOL) for dioxins data analysis. The concentrations of each isomer of the samples and the recovery rates of the spikes added were also calculated. The recovery rates of clean up spikes of all the samples were in the range of 50% to 120% according to the measurement manual published by the Ministry of Environment, Japan.

RESULTS AND DISCUSSION

General Remarks on the Concentrations of Dioxins

The atmospheric concentration of dioxins, including co-PCBs, ranged from 0.0079 pg-TEQ/m³ to 0.54 pg-TEQ/m³. The highest concentration was obtained at Kawakita in winter. This site was strongly influenced by an industrial waste incinerator, which was several hundred meters upwind of the air-sampling site, under the most frequent wind direction in winter. Yearly average concentration was highest at Komatsu-2 site (0.18 pg-TEQ/m³), which was on a roof of the building of the sewage disposal plant near downtown Komatsu.

The concentration of dioxins in soil (including co-PCBs) ranged from 0.0076 pg-TEQ/g to 8.6 pg-TEQ/g. The soil-sampling point of the highest concentration was a shrine near the Mattoh-1 air-sampling site. The second and the third highest concentrations were also observed at shrines near the Mattoh-1 and Tatsuruhama air-sampling sites, respectively. These higher concentrations might be partly due to frequent, small-scale combustions during religious ceremonies at the shrines.

Homologue Profiles in the Air and the Soil Samples

The seasonal variation of atmospheric PCDD/DF composition obtained from the air samples is shown in Fig. 2. The ratio of PCDFs to PCDDs+PCDFs was significantly larger in winter than that in the other seasons. PCDFs occupied about 30% of PCDDs+PCDFs in spring, summer and autumn, while the ratio of PCDFs increased to about 55% of PCDDs+PCDFs in winter. The higher abundance of PCDFs than PCDDs in winter might be due to an increase in combustion of fossil fuels.¹³⁾

Figure 3 shows the seasonal variations in the relative levels of five PCDD homologues and five PCDF homologues (expressed as percents of the total PCDDs and total PCDFs, respectively) in the air samples. The contribution of TeCDDs to the total PCDDs was considerably larger than the contributions of the other PCDDs in all seasons, although it was not as great in winter. On the other hand, the contributions of the PCDF homologues gradually decreased with increasing number of chlorine substitutions in each season. No seasonal change was observed in the profile of the PCDF homologues.

The homologue distribution of PCDD/DFs in the soil samples is shown in Table 1. OCDD was the

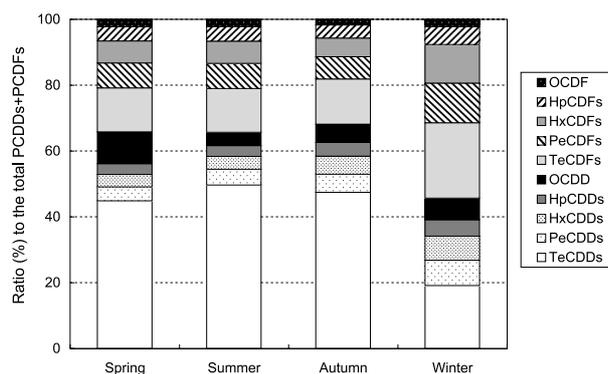


Fig. 2. Seasonal Variation of PCDD/DFs Composition in Air

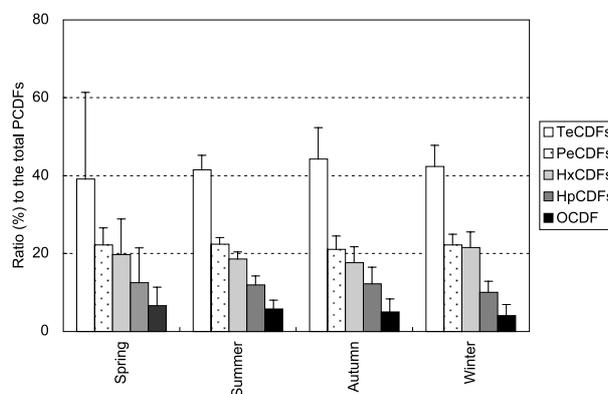
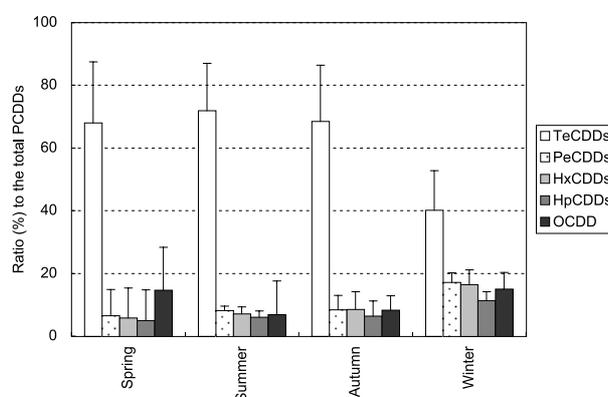


Fig. 3. Seasonal Variation of Homologue Profiles of PCDD/DFs in Air

Each box and vertical bar represent mean and S.D., respectively.

homologue that made the greatest contribution to PCDDs+PCDFs in the soil samples. This result well agreed with the results of previous studies and may be due to the remaining influence of PCP herbicide.^{8,11,14)} The homologue compositions of the soil samples varied widely among the sampling points. For examples, the standard deviations (S.D.) of the ratios of TeCDDs and OCDD to the total

Table 1. Homologue Distribution of PCDD/DFs in the Soil Samples (%)

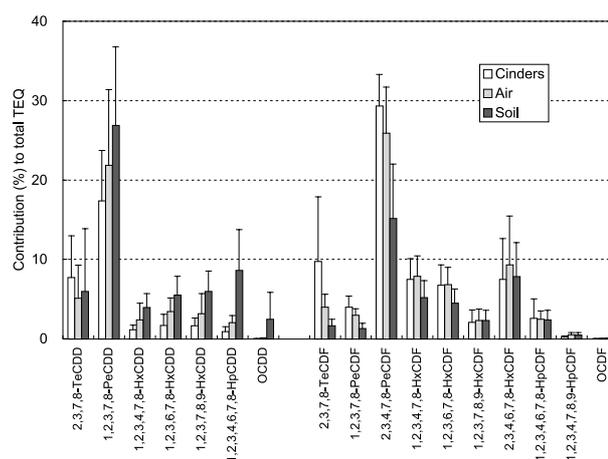
Compound	mean \pm S.D.
TeCDDs	22.8 \pm 25.1
PeCDDs	3.8 \pm 2.6
HxCDDs	3.7 \pm 2.8
HpCDDs	6.3 \pm 3.5
OCDD	50.6 \pm 29.3
Total PCDDs	87.3 \pm 12.8
TeCDFs	2.6 \pm 2.2
PeCDFs	2.3 \pm 2.2
HxCDFs	3.2 \pm 3.4
HpCDFs	2.8 \pm 3.6
OCDF	1.7 \pm 2.4
Total PCDFs	12.7 \pm 12.8
PCDDs+PCDFs	100.0 \pm 0.0

PCDDs+PCDFs in the soil samples were 25% and 29%, respectively. The wide range of values might be due to differences in the integrated amounts of agrochemicals applied in different regions. In a few areas (Mattoh and Kawakita), the predominant homologue of PCDD/DFs in the soil was not OCDD but TeCDDs. It should be noted that a singular distribution of TeCDD isomers was also observed in soil samples collected in the above areas.

Contributions of Isomers to the Toxicity Equivalency Quantity (TEQ)

The toxicities of PCDD/DFs are, in general, evaluated by the toxicity equivalency quantity (TEQ), which is the sum total of the products of the concentrations of the 2,3,7,8-chlorine-substituted isomers and their toxicity equivalency factors (TEF). Isomers that mainly contribute to the total TEQ of the combustion-origin samples are different from those of the agrochemical-influenced samples.¹⁵⁾ Therefore, it is useful to examine which isomers predominantly contribute to the TEQ.

Figure 4 shows the contributions of the 2,3,7,8-chlorine-substituted isomers to the total TEQ in both the air and soil samples. It also shows the contributions of these toxic isomers in cinders samples collected from 12 industrial waste incinerators. 1,2,3,7,8-PeCDD was the largest contributor to the TEQ and was followed by 2,3,4,7,8-PeCDF and 1,2,3,4,6,7,8-HpCDD in the soil samples. Among these specific isomers, 1,2,3,7,8-PeCDD and 1,2,3,4,6,7,8-HpCDD are said to be the two major

**Fig. 4.** Contribution of 2,3,7,8-Chlorine Substituted Isomers to TEQ

Each box and vertical bar represent mean and S.D., respectively.

toxic (2,3,7,8-chlorine-substituted) isomers that were emitted from CNP and PCP herbicides, respectively.^{5,6)} On the other hand, 2,3,4,7,8-PeCDF was the largest contributor to the TEQ and was followed by 1,2,3,7,8-PeCDD and 2,3,7,8-TeCDF in the cinders samples, which are thought to be pure combustion-origin samples. The contribution of the isomers to the TEQ in the air samples was intermediate between their contributions to the soil and cinders. This suggests that the environmental air was influenced by both combustion and soil/dust suspension.

Specific Isomer Composition in the Air and Soil Samples

The isomer profile of PCDD/DFs, in general, varies greatly among the kind of environmental media. Though the toxicity of dioxins is usually expressed as the TEQ, the composition analysis of non-2,3,7,8-chlorine-substituted isomers is needed to infer the contributions of pollution sources.^{10,11)} For example, the isomer distributions of TeCDDs, PeCDDs, TeCDFs and HpCDFs in the combustion-origin samples and in the agrochemical-influenced samples are quite different, while, in general, those of HxCDDs and HxCDFs are not.⁵⁾

The % ratios of main isomers to TeCDDs, PeCDDs, TeCDFs and HpCDFs in the air, soil and cinder samples are shown in Table 2. 1,3,6,8- and 1,3,7,9-TeCDDs are formed by the reaction of two 2,4,6-trichlorophenol (2,4,6-TrCP) molecules, which is a raw material of CNP synthesis.⁶⁾ 1,3,6,8-TeCDD was the most abundant isomer in TeCDDs in both the air and soil samples ($\geq 50\%$). However, the

Table 2. Main Isomer Composition Ratios of TeCDDs, PeCDDs, TeCDFs and HpCDFs in Soil, Air and Cinders Samples (%)

Compound	Soil		Air				Cinders
	mean \pm S.D.	Spring	Summer	Autumn	Winter	mean \pm S.D.	
		mean \pm S.D.	mean \pm S.D.	mean \pm S.D.	mean \pm S.D.		mean \pm S.D.
1,3,6,8-TeCDD	54.7 \pm 17.6	69.8 \pm 3.0	60.1 \pm 14.7	61.7 \pm 8.4	51.3 \pm 8.4	21.2 \pm 5.9	
1,3,7,9-TeCDD	19.9 \pm 6.4	20.6 \pm 1.5	16.7 \pm 4.1	16.8 \pm 3.8	17.7 \pm 1.9	13.1 \pm 3.4	
2,3,7,8-TeCDD	0.4 \pm 0.5	0.1 \pm 0.1	0.2 \pm 0.1	0.1 \pm 0.0	0.4 \pm 0.3	2.6 \pm 2.2	
1,2,4,6,8-PeCDD	22.6 \pm 4.8	30.0 \pm 3.7	32.9 \pm 5.7	26.9 \pm 3.4	30.2 \pm 8.8	26.9 \pm 6.8	
1,2,3,6,8-PeCDD	35.8 \pm 14.0	27.6 \pm 7.9	30.0 \pm 8.9	29.7 \pm 7.0	22.3 \pm 6.0	17.8 \pm 2.4	
1,2,3,7,9-PeCDD	16.7 \pm 2.9	14.7 \pm 3.9	14.0 \pm 2.2	14.8 \pm 2.4	12.7 \pm 4.6	13.2 \pm 1.2	
1,2,3,7,8-PeCDD	4.3 \pm 2.9	3.2 \pm 0.9	3.7 \pm 1.5	3.6 \pm 1.2	5.0 \pm 3.2	6.1 \pm 2.5	
1,2,7,8-TeCDF	3.9 \pm 1.6	8.2 \pm 3.6	4.4 \pm 1.2	4.4 \pm 0.9	5.7 \pm 3.0	5.1 \pm 1.5	
2,4,6,8-TeCDF	25.3 \pm 15.1	17.7 \pm 3.1	17.6 \pm 8.5	15.4 \pm 2.8	11.4 \pm 2.4	9.2 \pm 2.4	
2,4,6,7-TeCDF	7.8 \pm 4.0	5.6 \pm 1.2	5.1 \pm 1.0	6.1 \pm 2.4	5.3 \pm 0.7	4.8 \pm 1.6	
2,3,7,8-TeCDF	3.4 \pm 1.6	2.0 \pm 0.3	2.5 \pm 0.8	2.3 \pm 0.9	2.5 \pm 0.9	3.1 \pm 2.2	
1,2,3,4,6,7,8-HpCDF	48.6 \pm 8.4	58.7 \pm 4.0	48.7 \pm 5.8	55.0 \pm 6.7	54.9 \pm 6.8	65.8 \pm 3.1	
1,2,3,4,6,7,9-HpCDF	13.2 \pm 4.0	17.1 \pm 1.1	17.3 \pm 3.4	15.6 \pm 3.3	15.6 \pm 6.4	9.7 \pm 1.1	
1,2,3,4,6,8,9-HpCDF	24.0 \pm 9.1	14.6 \pm 2.5	13.6 \pm 8.1	16.0 \pm 5.6	15.2 \pm 6.1	6.9 \pm 1.8	
1,2,3,4,7,8,9-HpCDF	9.5 \pm 4.1	9.6 \pm 2.7	11.2 \pm 3.6	11.2 \pm 5.2	10.7 \pm 5.0	5.6 \pm 1.2	

1,3,6,8-TeCDD/TeCDDs ratios in the cinder samples were significantly lower (21%) than the ratios of the air and soil samples. The 1,3,6,8-TeCDD/TeCDDs ratio in the air samples did not change much with the season, and its yearly average was close to that of the soil samples. The 1,3,7,9-TeCDD/TeCDDs ratio in the air (17–21%) was also close to the ratio in the soil regardless of the season. Therefore, in view of the ratios of the above two major isomers to TeCDDs, the air might be more strongly influenced by soil suspension than by combustion. The S.D. values of 1,3,6,8-TeCDD/TeCDDs and 1,3,7,9-TeCDD/TeCDDs were significantly larger in the soil samples than in the air samples. This was mainly due to the low ratios (about 20% for 1,3,6,8-TeCDD/TeCDDs and lower than 10% for 1,3,7,9-TeCDD/TeCDDs) of the above two isomers to TeCDDs at the Mattoh and Kawakita sites, where the predominant homologue in the soil was not OCDD but TeCDD. An industrial waste incinerator and a municipal waste incinerator, which were located upwind of the sampling sites, might have affected the soil samples as a result of long-term depositions.^{15–17)}

The difference in the main isomer distribution of PeCDDs between the air and soil was clearer than that of TeCDDs (Table 2). The ratio of 1,2,3,6,8-PeCDD to PeCDDs was the highest (36%), followed by 1,2,4,6,8-PeCDD (23%) and 1,2,3,7,9-PeCDD (17%) in the soil samples. The ratios of 1,2,3,6,8-

PeCDD and 1,2,4,6,8-PeCDD in the air samples were almost the same (about 30%) in spring, summer and autumn. A different order of the isomer ratios was observed in the air samples only in winter, *i.e.*, the ratio of 1,2,4,6,8-PeCDD to PeCDDs was the highest (30%), followed by 1,2,3,6,8-PeCDD (22%) and 1,2,3,7,9-PeCDD (13%). 1,2,3,6,8- and 1,2,3,7,9-PeCDDs are formed from 2,4,6-TrCP and 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP). 2,3,4,6-TeCP is formed by the chlorination of 2,4,6-TrCP through its synthesis.⁶⁾ The winter pattern of the main isomers of PeCDDs in the air was similar to those in the cinders. In view of the distribution of the major isomers of PeCDDs, the contribution of soil/dust suspension was comparatively smaller in winter in the air samples. Because the ground surface was covered with snow during the air-sampling periods in winter at most of the sampling sites in Ishikawa Prefecture, the soil/dust suspension from the surface might have been suppressed in winter.¹⁸⁾ In addition, the amount of the emission of combustion-origin dioxins from many sources, such as domestic heating, was larger in winter.¹⁹⁾ In fact, at several sites in Kanazawa, the ratio of coarse airborne particulates, which mainly originated from suspended soil, to the total amount of airborne particulates was reduced in winter.²⁰⁾

Environmental samples that have a trace of CNP herbicide usually show the characteristic SIM chro-

matogram of TeCDFs. Among the many isomers of TeCDFs in such samples, 2,4,6,8-TeCDF is usually the only one that is outstanding.^{5,11} In the combustion-origin samples, however, the concentrations of each of these isomers were almost the same. Then, we calculated the 2,4,6,8-TeCDF/TeCDFs ratios of the air and soil samples to estimate the contribution of the CNP. As shown in Table 2, the 2,4,6,8-TeCDF/TeCDFs ratio in the soil samples was remarkably high (25%), the ratio in the cinder samples was low (9%) and the ratios in the air samples were intermediate (11–18%). Interestingly, the ratio of 2,4,6,8-TeCDF to TeCDFs was significantly reduced only in winter. This result also suggested that the effect of soil/dust suspension was reduced in winter and the contribution of combustion was relatively increased in winter instead.

Although the above-mentioned TeCDDs, PeCDDs and TeCDFs include some specific isomers that indicate remaining CNP contamination, highly chlorinated PCDD/DFs are the impurities of PCP herbicide.^{6,7} Then, we focus on 1,2,3,4,6,8,9-HpCDFs, which can be formed from PCP and 2,3,4,6-TeCP.⁶ This isomer is, in general, abundant in sediment and in river water²⁻⁴) but it is not so abundant in combustion-origin samples. As shown in Table 2, the ratio of 1,2,3,4,6,7,8-HpCDF to HpCDFs was the highest (66%) in the cinder samples. The ratio of 1,2,3,4,6,7,8-HpCDF (49–59%) was also the highest in the air sample in every season (Table 2). The other 3 isomers, including 1,2,3,4,6,8,9-HpCDF, were only minor constituents among HpCDFs in both the air and cinders. The ratio of 1,2,3,4,6,7,8-HpCDF to HpCDFs (49%) was indeed the highest in the soil samples again, although the ratio of 1,2,3,4,6,8,9-HpCDF to HpCDFs was remarkably high (24%). Therefore, we can say that PCP contamination is present in the soil but not in the air. The fact that the S.D. value of the ratio of 1,2,3,4,6,8,9-HpCDF to HpCDFs was considerably large (9%) suggested that the application of PCP varied widely among the soil-sampling points. In fact, the HpCDF isomer distribution patterns of several soil samples were quite similar to the pattern of the air samples.

In conclusion, we determined the relative contributions of combustion and agrochemicals remaining in the soil to the dioxin composition in the air through the analysis of homologue and specific isomers of PCDD/DFs. Especially, the contribution of soil/dust suspension to the composition of atmospheric dioxins decreased in winter in the area of

Ishikawa Prefecture, but the relative contribution of combustion increased in winter instead. In the present study, each air sample was collected for 24 hr. We are currently conducting 7-day air sampling at a flow rate of 100 l/min in order to reduce the daily variation of the atmospheric concentrations. Preliminary results from the 7-day air sampling also showed that the relative contribution of combustion to the air increased only in winter.

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