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Seasonal Concentrations and Compositions of PCDDs/DFs in Atmospheric Environment

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INTRODUCTION

It is well known that the sources of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are municipal waste incinerators, paper and pulp mills, steel mills, sewage sludge, chlorinated chemicals and so on. Atmosphere is the most important media for PCDDs/DFs contamination because PCDDs/DFs are emitted directly and transported over long distance. These compounds have been deposited in many environmental components, such as land and aquatic environment. Finally, PCDDs/DFs are taken up by organisms and causes harmful effects to ecosystem. Therefore, it is important to understand the environmental fate of PCDDs/DFs in atmosphere.

On the present study, Matsuyama, Japan, was chosen because two municipal waste incinerators and large number of small sized incinerators are located. Burning of the waste, such as plastics and papers, in both incinerators is the major source for the PCDDs/DFs and they were serious impact on the air quality of Matsuyama.

This study provides base-line data of PCDDs/DFs concentrations in Matsuyama. Air samples from Ehime University, Matsuyama, were analyzed for PCDDs/DFs. The residue levels and patterns of PCDDs/DFs in ambient air as well as the relationship between air and deposition (dry and wet) are discussed in this study.

EXPERIMENTAL

Sampling

Sample were set up at the roof of Ehime university's building located in Matsuyama, Japan, and were collected from August 1996 to February 1997. Polyurethane foam plug (PUF, Model HA, Achilles Co. Ltd., Japan, diameter 35 mm, length 50 mm, density $20 \pm 1.6 \text{ kg/m}^3$) was used as adsorbent for collection of PCDDs/DFs. PUF plugs were precleaned with acetone and toluene in a Soxhlet extractor (500mL) for 30 hours. These extracts were concentrated to 100 μL and used

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to check the contamination. Three dried PUF plugs were packed in a glass column (i.d. 35 mm, length 160 mm) and set into the stainless steel shelter to keep it away from the rain. Air samples were taken over 5-7 days with two air pumps (Model AP-240Z, IWAKI Co. Ltd., Japan) giving volumes ranging from about 500 to 700m³ (flow rate 27-33 L/min.) and these six PUF plugs were combined as one sample.

Analysis

PCDDs/DFs adsorbed on six PUF plugs were Soxhlet extracted with acetone and toluene (500mL) for 24 hours. The extract was concentrated to 1 mL. The sample was diluted with hexane and interfering substances in the extract was removed by sulfuric acid. Then, silica gel and activated carbon column chromatography were carried out for purification and separation. The purified extract was concentrated to 50 μ L before analysis by GC-MS. All samples were analyzed by HRGC-HRMS (JEOL SX102A - HP5890 II) equipped with a CHROMPACK CP-Cil 88 for Dioxins.

RESULTS and DISCUSSION

Concentrations and Compositions of PCDDs/DFs in Ambient Air

Figure 1 shows the concentrations of PCDDs/DFs in ambient air samples from Matsuyama, Japan. The concentrations of PCDDs and PCDFs were ranged from 10.7 to 1.54 pg/m³ and from 16.0 to 2.67 pg/m³ during this sampling period, respectively. No seasonal variation of PCDDs/DFs concentrations was observed. Eitzer and Hites¹⁾ also found no seasonal variation effect. In this study, no seasonal variation on the percent composition of PCDFs to total PCDDs/DFs for each air sample was observed. These values were ranged from 49.7 to 70.2% (Average 62.1%). However, it was found that the percent composition of low chlorinated PCDDs/DFs congeners slightly increased during August and September (Figure 2). This may indicate that gasified PCDDs/DFs from soil and plants contribute to the variation during August and September.

Secondly, we calculated 2,3,7,8-TeCDD toxic equivalents (TEQ) using I-TEF (International Toxic Equivalency Factor) to evaluate human exposure by air. TEQ were ranged from 0.277 to 0.076 pg/m³. The average of TEQ was 0.157 pg/m³. Daily intake of TEQ from the air was estimated to 2.4 pg/day based on 15m³ for breath per person in a day. Kurokawa et al.²⁾ analyzed ambient air collected from Hukuoka, Japan. They confirmed high contribution of PCDFs to TEQ. In this study, it was found that PCDFs were also major contributors to TEQ and its percentage was 72.3%. 2,3,4,7,8-PeCDF was the most important contributor to TEQ in the 17 toxic 2,3,7,8-substituted isomers.

Relationships between Ambient Air and Deposition (Dry and Wet)

We analyzed PCDDs/DFs in dry and wet deposition from 1995 to 1996³⁾. Therefore, sampling period of ambient air is not same with the sampling period for dry and wet deposition. However, we use these data in order to clarify fate of PCDDs/DFs in atmospheric environment, because no seasonal variation of PCDDs/DFs in ambient air was observed.

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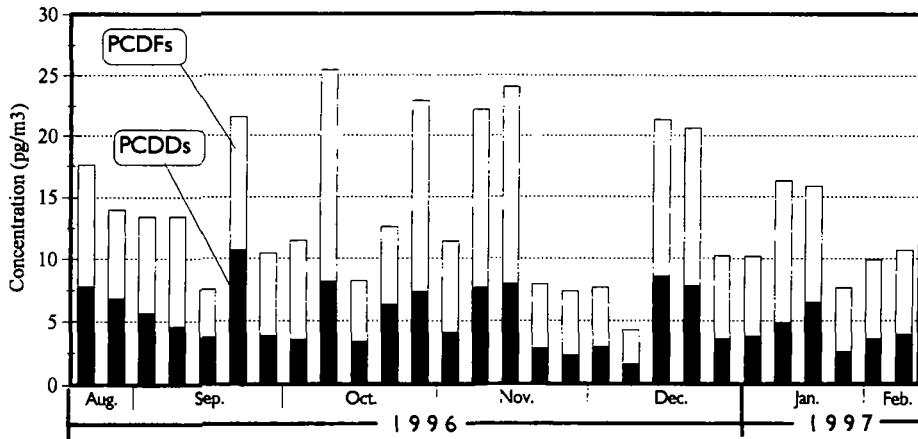


Figure 1. Concentrations (pg/m³) of PCDDs/DFs in Ambient Air

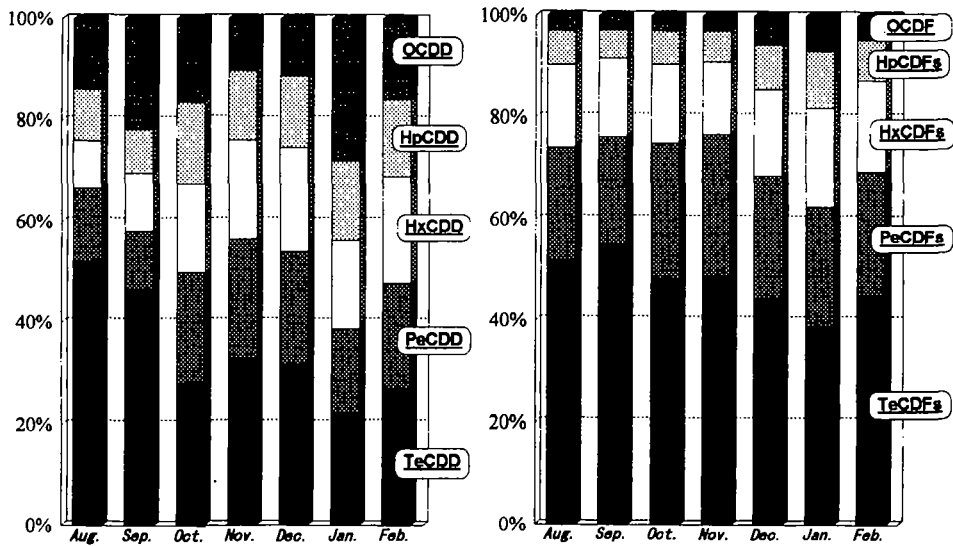


Figure 2. Congener Composition of PCDDs/DFs in Ambient Air

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Relationship between Air and Dry Deposition

Deposition velocity (Vd) was calculated for each PCDDs/DFs congener in every month by
 $Vd = Df / Ca$

Df ; Dry Deposition Flux (g/cm²/sec)

Ca ; Average Concentration of Ambient Air (g/cm³)

Deposition velocity is defined as removal of PCDDs/DFs from atmosphere and this was calculated from the data obtained from August to February. The results are shown in Table 1. These were ranged from 0.0041 to 0.40 cm/sec and slightly lower than the values calculated by Koester and Hites⁴. With a few exceptions, deposition velocities of PCDFs were slightly higher than those of PCDDs. It is known that vapor pressure of PCDFs isomers is higher than that of PCDDs isomers, comparison with both same chlorinated isomers⁵. Figure 3 shows the relationship between deposition velocity and vapor pressure of PCDDs/DFs congeners⁷ and other organochlorines, such as DDTs, HCHs and chlordane compounds (CHLs)⁶. The strong correlation between deposition velocity and vapor pressure of each compound were observed (r=0.79). It appears to be highly dependent on their affinity to particles. Further, Table 1 shows clearly that high chlorinated congeners, such as HpCDDs, OCDD and OCDF, were removed with high efficiency from atmosphere than low chlorinated congeners. Furthermore, in cold season, such as January and February, PCDDs/DFs were removed with more high efficiency than in warm season such as August. Figure 4 shows the relationship between deposition velocity of total PCDDs/DFs in each air sample and the average temperature during representative sampling period. There was no significant (r=0.64) relationship between deposition velocity of total PCDDs/DFs and average temperature. We also noted that rather high dry deposition flux of these compounds were found during cold season (i.e. January and February) than the warm season (i.e. July and August). It suggests that the relative abundance of particle-bound PCDDs/DFs in atmosphere were increased during cold weather conditions and were removed efficiently from atmosphere.

Relationship between Air and Wet Deposition

Scavenging Ratio (Sr) was calculated for each PCDDs/DFs congener in every month by
 $Sr = Cw / Ca$

Cw ; Concentrations in Wet Deposition (pg/m³)

Ca ; Average Concentrations of Ambient Air (pg/m³)

Table 2 shows calculated scavenging ratios of samples collected from August to February. These ratios were ranged from 1100 to 320000 and were concurrent with the values calculated by Koester and Hites⁴. As is the case with deposition velocity, with a few exceptions, the scavenging ratios of high chlorinated congeners were higher than those of low chlorinated congeners. The scavenging ratios derived from the samples collected at cold season were higher than those of warm season. Moreover, the scavenging ratios of PCDDs were slightly higher than those of PCDFs. It is expected that these facts depend on affinity between PCDDs/DFs and particles. Figure 5 shows the relationship between scavenging ratio of total PCDDs/DFs in each

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air sample and the average temperature during each air sampled period. Scavenging ratios of total PCDDs/DFs were also related to the average temperature ($r=0.52$). It suggests that the relative abundance of particle-bound PCDDs/DFs were increased under cold weather conditions and removed efficiently from atmosphere by rain as same processes of dry deposition.

LITERATURE CITED

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Table 1. Deposition Velocity (cm/sec) of PCDDs/DFs Congeners

	August	September	October	November	December	January	February
TeCDDs	0.010	0.028	0.039	0.048	0.10	0.20	0.28
PeCDDs	0.009	0.053	0.017	0.035	0.050	0.076	0.14
HxCDDs	0.019	0.055	0.018	0.081	0.046	0.067	0.093
HpCDDs	0.026	0.074	0.028	0.24	0.070	0.096	0.25
OCDD	0.033	0.031	0.040	0.30	0.13	0.13	0.33
TeCDFs	0.0041	0.013	0.0078	0.017	0.029	0.041	0.099
PeCDFs	0.0079	0.026	0.011	0.038	0.036	0.041	0.12
HxCDFs	0.019	0.030	0.017	0.077	0.050	0.033	0.090
HpCDFs	0.0075	0.037	0.013	0.14	0.031	0.031	0.013
OCDF	-	-	-	0.090	-	0.068	0.32

Table 2. Scavenging Ratio of PCDDs/DFs Congeners

	August	September	October	November	December	January	February
TeCDDs	2300	3600	9700	7000	27000	14000	38000
PeCDDs	2800	9300	8800	7700	26000	9800	30000
HxCDDs	6400	11000	15000	14000	44000	21000	46000
HpCDDs	16000	31000	31000	59000	130000	45000	160000
OCDD	11000	17000	45000	130000	220000	46000	320000
TeCDFs	1100	2200	3700	2900	14000	5000	19000
PeCDFs	1900	6100	9700	6700	26000	7900	33000
HxCDFs	3900	10325	19000	20000	52000	11000	56000
HpCDFs	3500	15000	21000	23000	68000	20000	91000
OCDF	-	-	-	-	-	43000	200000

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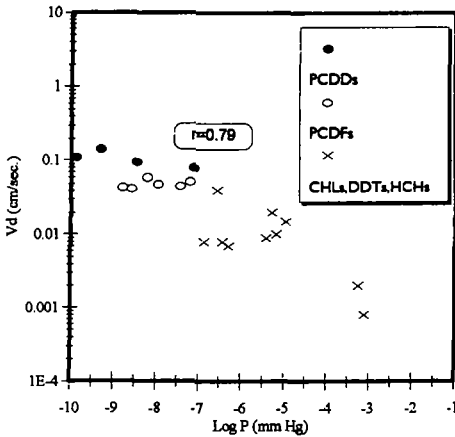


Figure 3. Relationships between Vapor Pressure and Deposition Velocity of PCDDs/DFs and Other Organochlorines

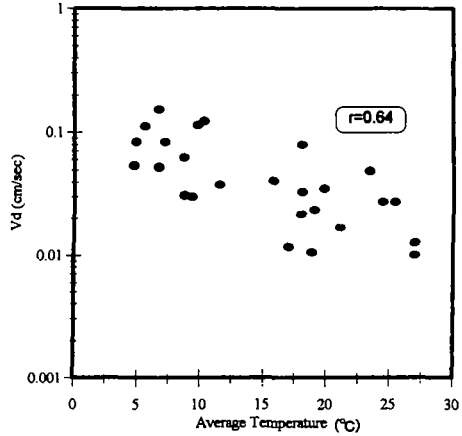


Figure 4. Relationships between Deposition Velocity of total PCDDs/DFs and Average Temperature

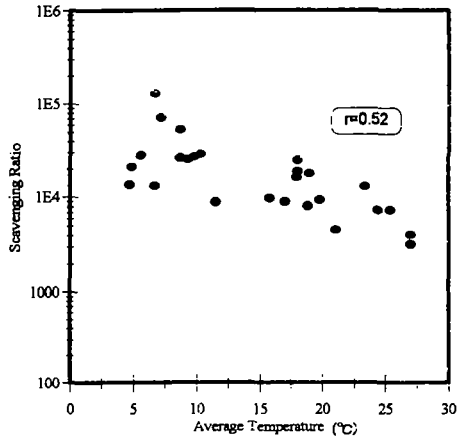


Figure 5. Relationships between Scavenging Ratio of total PCDDs/DFs and Average Temperature