Distribution of Polychlorinated Dibenzo-*p*-Dioxins and Dibenzofurans in Various Sizes of Airborne Particles

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Introduction

With regard to the atmospheric behavior of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/DFs), it is known that at least 75% of the PCDDs/DFs are attached to particles[1], so it is important to investigate the various properties of the particles combined with the PCDDs/DFs. The transport and deposition of particles can be described as a function of particle size. Large particles (aerodynamic diameters d_{ae}>10μm) have short residence times in the atmosphere, while smaller size particles reside for a long time in the atmosphere and long range transport is expected. In general, atmospheric particles in urban air have two peaks in their distribution, one peak consists of large size particles, mostly attributed to the natural source such as soil particles, and the other peak corresponds to the small size particles (d_{ae}<1μm), mainly produced through incineration. It is quite natural that atmospheric PCDDs/DFs mainly exists on the small particles, but recently, it became apparent that the soil in Japan involves a large amount of PCDDs/DFs and possibility plays a significant role as an uptake pathway [2] by plants, the volatilization of PCDDs/DFs from the soil surface may raise the concentration in the leaf of the plants. Therefore, the contribution of PCDDs/DFs from soil should be assumed as a source.

Knowledge on the size distributions of particles emitted from various sources and the distribution of PCDDs/DFs over the particle is important in order to reveal the mechanism of removing of PCDDs/DFs from the atmosphere and the cycle of PCDDs/DFs between the ground and atmosphere.

There are only a few studies[3] on the particle size distribution of PCDDs/DFs, so we investigated the distribution of PCDDs/DFs from large to small particles using Andersen high volume air sampling system.

Experimental

Airborne particles at three sites were collected on a quartz fiber filter (QFF) according to particle size using an Andersen high volume air sampler, and PCDDs/DFs in these particles were measured. Sampling was performed by passage through the QFF at an air flow rate of 566 l/min for 48-72 hours at sites A and B in 1988 and at site C in 1992. The atmospheric particles were separated into five fractions by the impactor according to their aerodynamic diameters. The following size ranges were sampled and are subsequently referred to as stages 1 to 5:>7, 7-3.3, 3.3-2, 2-1.1, and <1.1μm. Site A was located in an urban area and site B was an industrial area while site C was a rural area more than 6 km away from a major incineration site. Before use, the QFFs were precleaned by baking them for 6 hours at 600°C. Weights of the particles collected on the QFFs were measured after allowing them to stand for 48 hours in the room kept at a constant temperature (20°C) and humidity (50%) before and after sampling. The QFFs were then extracted with acetone in a Soxhlet extractor for 24 hours. The extracts were fortified with ten kinds of ^{13}C-

labeled PCDDs/PCDFs as internal quantification standards. The extracts were washed with concentrated sulfuric acid and purified on a silica gel column, and on an alumina column. The PCDDs/DFs were analyzed by an HRGC/HRMS technique using a Finnigan MAT-90 mass spectrometer (Finnigan MAT, Germany) directly interfaced with a Varian Model 3400 gas chromatograph. The GC was equipped with a splitless injector and a SP-2331 capillary column for the PCDDs/DFs. For analysis of the *hepta-*, *octa*-CDDs and CDFs, an OV-17 capillary column was used. During the GC/MS data acquisition, perfluorokerosene was bled into the mass spectrometer to obtain high accuracy mass assignments at 8000 to 10000 mass resolution. Two ions of a molecular cluster were recorded.

Result and Discussion

Table 1 presents the amounts of PCDDs/DFs collected on each stage and Fig. 1 shows the size distribution curves of the PCDDs/DFs concentration (pg/m^3) fitted by a spline function. Fig. 2 is the concentration calculated as pg/g on each stage. The PCDDs/DFs isomer patterns for each sample were very similar for all five stages at the three sites, showing a fly ash pattern.

The largest amounts of PCDDs/DFs were found on particles with a d_{ae} of less than 1.1μm that accounted for over 50% of the total PCDDs/DFs. *Hexa*-CDD and *hepta*-CDD were dominant in total PCDDs on the particles of $d_{ae}<1.1\mu m$, and *hepta*-CDF and *octa*-CDF in total PCDFs, which was the same tendency at all three sites. The PCDDs/DFs congener patterns were different in each stage as shown in Fig. 2. Most of *hexa-* to *octa*-CDDs/DFs existed on small particles, whereas the less chlorinated DDs/DFs were widely distributed from the small to large size particles. Consequently, the PCDDs/DFs congener pattern on the larger particles showed a pattern similar to the gaseous pattern of atmospheric PCDDs/DFs. From these findings, it is assumed that large particles emitted from incinerators such as a municipal waste incinerator have a gas phase pattern of PCDDs/DFs, or soil particles as the result of wind erosion contributed to the distribution of PCDDs/DFs on the larger particles, otherwise, gaseous PCDDs/DFs volatilized from the soil surface influenced the measurements. In either case, this fact should be investigated furthermore to determine the source.

As shown in Fig. 2, the concentrations (pg/g) of PCDDs/DFs congeners showed roughly the same level on each stage of $d_{ae}<2\mu m$. It may be suggested that particles of $d_{ae}<1.1\mu m$ coagulated with each other and formed the large particles, thus keeping their same composition.

TEQs (toxic equivalents) were calculated using I-TEF. Table 2 shows the TEQs with respect to particle size. PCDDs/DFs on particles of $d_{ae}<1.1\mu m$ contributed mostly to the toxicity, providing over 47% of the total TEQ loading. PCDFs showed about twice as much concentration as PCDDs in the total TEQs.

It is well known that large particles are mainly removed by dry deposition from the atmosphere. Thus, these results can be considered as an explanation for congener profile in determining the PCDDs/DFs congeners during dry deposition.

References

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Table 1 Amounts of PCDDs/DFs congeners (pg) with respect to particle sizes
(Stage 1 to 5:
>7 , 7-3.3, 3.3-2, 2-1.1, <1.1 μm)

Site A	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	total	pg/m^3	<1.1μm/total
TeCDD	458	372	425	352	770	2378	0.9	32%
PeCDD	283	348	404	349	1355	2739	1.1	49
HxCDD	208	389	397	667	4194	5855	2.3	72
HpCDD	322	794	918	1722	9048	12804	4.9	71
OCDD	192	516	591	856	3831	5987	2.3	64
totalPCDD	1460	2418	2737	3945	19198	29758	11.5	65
TeCDF	812	615	687	864	2464	5442	2.1	45%
PeCDF	746	935	880	997	4494	8053	3.1	56
HxCDF	422	554	694	1260	6072	9003	3.5	67
HpCDF	158	278	382	878	6028	7724	3.0	78
OCDF	37	41	112	262	3261	3713	1.4	88
totalPCDF	2175	2423	2756	4261	22319	33935	13.1	66

Site B	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	total	pg/m^3	<1.1μm/total
TeCDD	689	456	407	536	1470	3559	1.1	41%
PeCDD	158	190	263	306	2016	2933	0.9	69
HxCDD	200	228	349	520	4964	6260	2.0	79
HpCDD	129	120	266	565	3501	4580	1.5	76
OCDD	615	493	322	566	2467	4463	1.4	55
totalPCDD	1791	1487	1606	2493	14418	21794	7.0	66
TeCDF	634	467	502	503	2348	4454	1.4	53%
PeCDF	490	389	534	732	4052	6196	2.0	65
HxCDF	293	166	440	787	5284	6970	2.3	76
HpCDF	130	139	259	415	3284	4228	1.4	78
OCDF	46	42	183	230	1503	2004	0.6	75
totalPCDF	1593	1203	1918	2667	16470	23852	7.7	69

Site C	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	total	pg/m^3	<1.1μm/total
TeCDD	969	862	981	948	982	4742	1.8	21%
PeCDD	424	628	577	718	1395	3742	1.4	37
HxCDD	192	197	272	550	2542	3754	1.4	68
HpCDD	150	244	239	664	4054	5351	2.1	76
OCDD	52	88	104	200	747	1191	0.5	63
totalPCDD	1787	2021	2174	3079	9720	18781	7.2	52
TeCDF	366	449	244	433	926	2418	0.9	38%
PeCDF	473	388	573	595	1684	3713	1.4	45
HxCDF	453	386	474	759	3010	5082	2.0	59
HpCDF	228	211	296	639	3797	5171	2.0	73
OCDF	60	46	94	401	2163	2764	1.1	78
totalPCDF	1580	1480	1681	2827	11580	19148	7.4	60

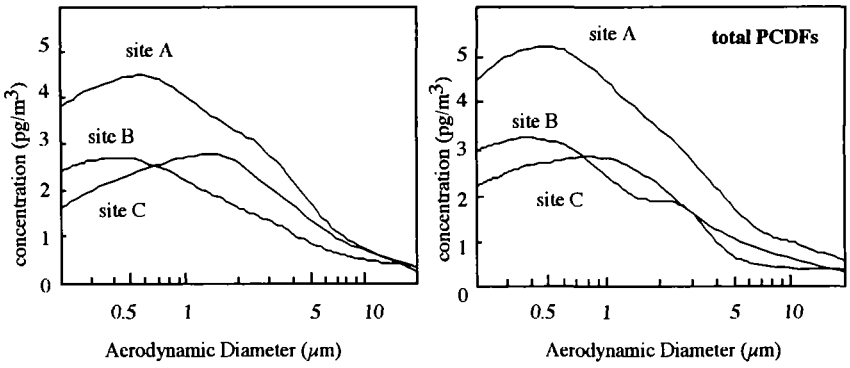

Fig.1 Size distribution curves of PCDDs/DFs concentrations

Table 2 TEQs of PCDDs/DFs (pg) with respect to particle size
(Stage 1 to 5:
>7 , 7-3.3, 3.3-2, 2-1.1, <1.1 μm)

Site A	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	total	pg/m^3	<1.1μm/total
total PCDDs	19	21	17	36	155	249	0.10	62%
total PCDFs	36	39	49	78	379	581	0.22	65
total DDs/DFs	55	60	67	114	535	830	0.32	64

Site B	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	total	pg/m^3	<1.1μm/total
total PCDDs	10	10	9	16	177	221	0.07	80%
total PCDFs	25	16	38	72	442	592	0.19	75
total DDs/DFs	34	26	46	87	619	813	0.26	76

Site C	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	total	pg/m^3	<1.1μm/total
total PCDDs	15	25	54	31	62	186	0.07	33%
total PCDFs	29	22	32	51	172	307	0.12	56
total DDs/DFs	45	47	86	82	234	493	0.19	47

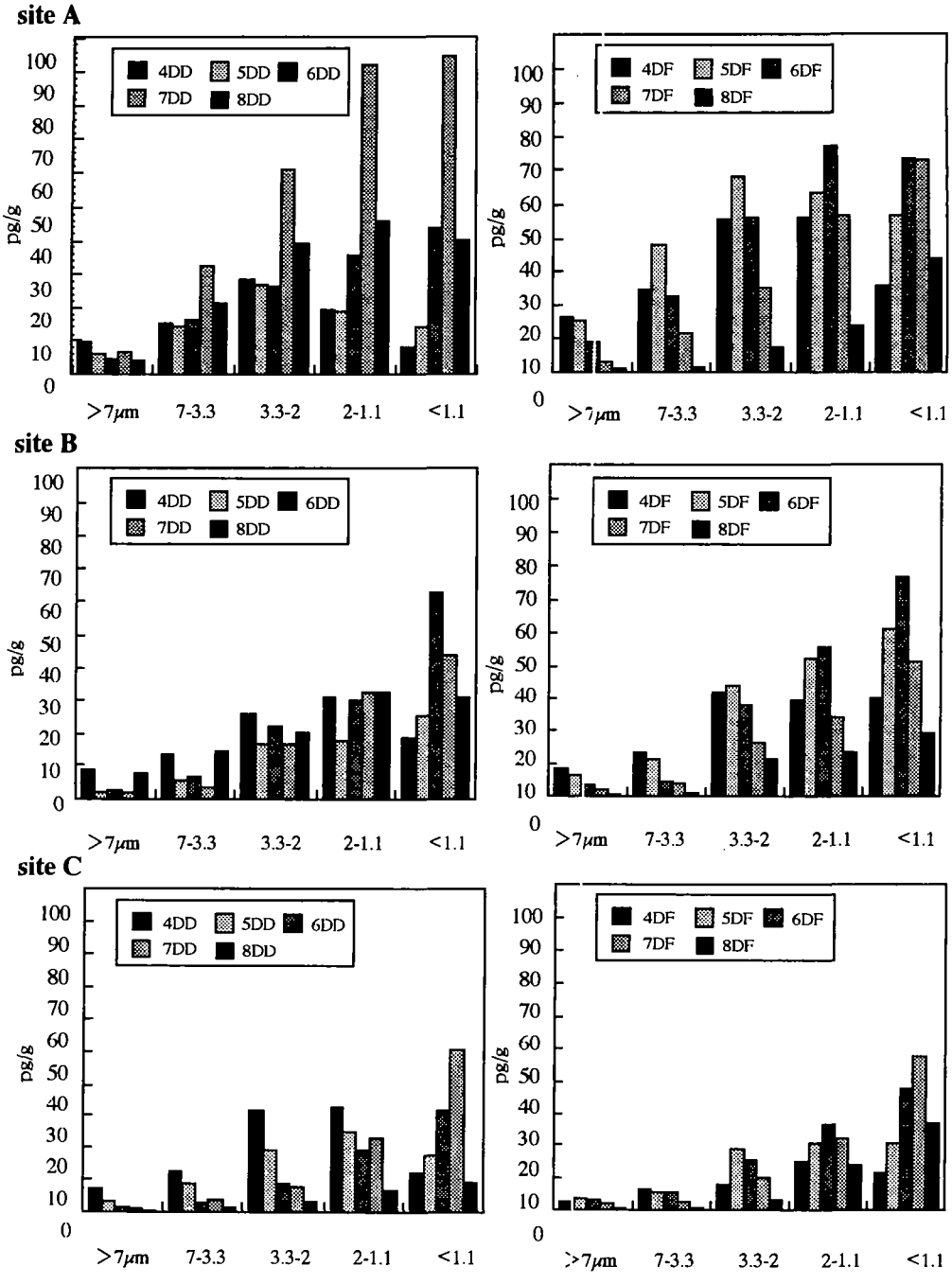

Fig.2 Concentration profiles of the PCDDs/DFs congeners (pg/g) with respect to particle size at sites A, B and C