POLYCHLORINATED DIBENZODIOXINS AND POLYCHLORINATED DIBENZOFURANS IN INCINERATOR ASHES IN THE ASIA-PACIFIC REGION

Mami Niida[1], Ryoko Kudo[2], Erina Nakanose[2], Manabu Oizumi[3], Mizuki Sakai[3], Jun Kobayashi[3], Kinumi Fukumura[3], Hideo Kajihara[3] and Yukio Takahashi[2]

1. The Japan Offspring Fund, 2-5-2 Kojimachi, Chiyoda-ku, Tokyo, 102-0083, Japan
2. Faculty of Technology, Niigata University, Ikarashi 2-no-cho, Niigata City, 950-2181, Japan
3. Graduate School of Science and Technology, Niigata University, Niigata City, 950-2181, Japan

Introduction

Since Olie and coworkers found in 1977 that fly ashes produced from municipal waste incinerators contained polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)[1], studies on dioxins (PCDD/Fs and PCBs) from solid wastes incineration have been carried out and it has been found that incinerators are a major source of dioxins in the environment. As a result, various countermeasures have been taken in developed countries to reduce dioxin production.

However, the information available on dioxins components in ash is still insufficient. In addition, in developing countries, combustion of solid wastes is still carried out mostly in open fields without measures to control the production of dioxins. Therefore, in this study, ashes from solid waste incinerators and dumping sites in the Asia-Pacific region including Japan were collected and their dioxin amounts were measured. Their total amounts, Toxicity Equivalent Quantity (TEQ) and homologue components as well as congener ones were evaluated.

Method and Materials

Seventeen samples of waste incinerators ashes were collected in 2000 from nine countries.

Table 1. The description of ashes analyzed

Name	Nation	Sampling Prefecture	Sampling site	Comments
Niigata	Japan	Niigata	Incineration plant	Industrial wastes, bottom ash
Shiga		Shiga	truck	Municipal wastes
Gifu		Gifu	Incineration site	Municipal wastes
Wakayama		Wakayama	Road construction site	Dumped illegally
Ibaragi		Ibaragi	Landfill site	Industrial wastes
Taiwan A	Taiwan			White color
Taiwan B				Black color
Korea	Korea			
Cambodia	Cambodia	Phnom Penh	Landfill site	Domestic wastes, incinerated open-doors in the landfill site
Malaysia	Malaysia	Pinan	Public Incinerator	Medical Wastes, animal bodies and business documents
Australia	Australia			
Mexico	Mexico			
Peru A	Peru	North of Lima	Landfill site	Glass, syringe needles, small timbers and soil in-mixed.
Peru B		West of Lima	Landfill site	Fine particles, brown color like soil
Peru C		Lima	Public Incinerator	10 km from Lima air port, largest in Lima
Bolivia A	Bolivia		Public Incinerator	So many burned residues of bones
Bolivia B			Public Incinerator	So many vials, ampules and syringe needles

Among the 17 samples, five were collected in Japan. Detailed information on the samples is shown in Table 1.

The extraction and cleanup of PCDD/Fs were carried out as described in the standard manual for dioxin analysis of solid wastes published by the Japanese Ministry of Welfare (1997)[2]. Each sample was air-dried and sieved through a 2mm mesh. Twenty grams of each dried sample was weighed and 13C-labeled internal standards were added. More than 200mL of 2M HCl was added, left until foaming stopped, and filtered. The filtrate was extracted with dichloromethane by shaking and the residue was Soxlet-extracted with acetone for 6 hours and then with toluene for 16 hours. Both extracts were combined and internal standards (cleanup spike) were added. After oxidation by sulfuric acid, cleanup was carried out first by chromatography on silica gel and next by chromatography on activated-carbon-impregnated silica gel.

Identification and quantification of PCDDs/DFs isomers were performed by HR-GC/MS (JMS-700, @10,000 RP), where the separation of PCDD/Fs was achieved by GC (HP 6890) equipped with CP-Sil88 and HP-5 columns. Using the GC/MS, among the 136 isomers

Table 2. The Quantity of PCDDs and PCDFs in the ashes (ng/g)

	T4CDDs	P5CDDs	H6CDDs	H7CDDs	O8CDD	P4CDFs	P5CDFs	H6CDFs	H7CDFs	O8CDF	PCDDs	PCDFs	Total
Niigata	3.4	9.0	17	23	25	63	71	75	34	17	78	260	338
Shiga	2.6	4.1	3.8	2.5	1.3	5.2	5.9	4.5	1.1	0.28	14	17	31
Gifu	23	47	52	49	39	12	22	40	24	9.3	211	107	317
Wakayama	0.13	0.15	0.13	0.059	0.11	0.57	0.32	0.21	0.059	0.012	0.59	1.2	1.8
Ibaragi	0.90	2.3	3.8	4.6	4.7	4.1	6.6	8.0	8.2	7.1	16	34	50
Taiwan A	1.0	4.8	20	58	122	5.5	11	27	34	27	205	105	310
Taiwan B	0.019	0.011	0.049	0.069	0.11	0.19	0.12	0.17	0.19	0.19	0.26	0.85	1.1
Korea	0.13	0.19	0.61	0.17	0.34	0.30	0.28	0.35	0.065	0.048	1.4	1.1	2.5
Cambodia	0.44	0.28	0.41	0.46	1.5	0.74	0.44	0.28	0.13	0.051	3.1	1.6	4.7
Malaysia	2.5	2.2	3.7	1.1	0.49	3.1	2.4	1.5	0.56	0.12	10.0	7.8	18
Australia	0.066	0.036	0.014	0.037	0.20	0.078	0.056	0.045	0.011	0.009	0.35	0.20	0.55
Mexico	0.081	0.033	0.042	0.074	0.29	0.065	0.065	0.062	0.018	0.012	0.52	0.22	0.74
Peru A	53	96	126	84	62	156	186	205	86	32	421	666	1087
Peru B	2.5	3.8	5.3	2.1	1.7	3.6	2.3	1.7	0.75	0.12	15	8.4	24
Peru C	0.68	0.57	0.49	0.32	0.21	11	4.0	2.4	1.0	0.26	2.3	19	21
Bolivia A	0.014	0.025	0.055	0.031	0.033	0.063	0.070	0.088	0.040	0.016	0.16	0.28	0.44
Bolivia B	1.9	1.9	1.8	0.85	0.34	8.7	5.3	4.2	1.5	0.16	6.8	20	27

Table 3. The TEQs of the ashes (WHO-TEQ pg/g)

	TCDDs							TCDFs										Total		
	2378	12378	123478	123678	123789	1234678	1-8	2378	12378	23478	123478	123678	123789	234678	1234678	1234789	1-8	PCDDs	PCDFs	PCDD/Fs
Niigata	127	858	112	133	124	127	2 5	111	204	2275	585	473	69	851	197	27	1.7	1483	4794	6277
Shiga	83	307	16	31	25	14	0 13	21	20	188	36	47	3 6	38	6 8	0.82	0 028	476	361	837
Gifu	139	1320	120	252	171	248	3.9	27	61	760	280	310	21	385	146	18	0 93	2254	2009	4263
Wakayama	1.3	4	0.30	0.50	0.40	0 27	0.011	2 2	0.91	10	1 8	1.7	0.31	2.1	0.45	0.028	0.0012	6 8	20	27
Ibaragi	17	63	13	27	14	23	0.47	11	23	203	82	75	3 6	88	46	7.0	0 71	157	540	697
Taiwan A	51	289	82	177	122	313	12	7 3	24	421	161	188	44	497	184	31	2.7	1046	1560	2605
Taiwan B	2.2	1.5	0 15	0.70	0.80	0.32	0.011	0.65	0.55	5 5	1 2	0.90	0.13	3 4	1.3	0 088	0 019	5.7	14	19
Korea	2.4	2.6	0.93	1.7	0 92	0.82	0 034	0.61	1.1	8.2	1.70	2 2	4 5	3.3	0.36	0.064	0.0048	9 3	22	31
Cambodia	0.72	4.0	0.90	0.70	1.8	2.4	0.15	3.4	2.1	14	2.1	3 4	0.078	2 1	0.92	0.061	0 0051	11	28	39
Malaysia	30	73	5.9	5.1	8.4	4.6	0.049	7 7	8.5	78	12	10	0.18	19	4.1	0 23	0.012	127	139	266
Australia	1.6	3.0	0.066	0.097	0 15	0.21	0.020	0 42	0 090	2.5	0.41	0.37	1.3	0.086	0 055	0 014	0.00091	5 2	5.3	10
Mexico	2.1	2.4	0.26	0.32	0.090	0.33	0 029	0 61	0.26	3.0	0.33	0.45	0.025	0 83	0 052	0 028	0 0012	5 5	5.6	11
Peru A	282	1660	201	577	369	400	6.2	159	603	4300	1329	1232	97	2242	407	88	3.2	3494	10460	13955
Peru B	17	40	5.0	8 0	8 0	11	0 17	5 1	6 9	47	12	6.5	3.2	13	4.6	0 31	0 012	89	98	187
Peru C	19	16	1.2	1.2	1.2	1 5	0 021	69	16	152	20	17	0 34	36	7.4	0 52	0 026	39	318	357
Bolivia A	0 82	0 0040	0.20	0 20	0 074	0.15	0.0033	0 22	0.25	2 0	0.80	0 50	0.14	1 5	0 28	0.030	0.0016	1 5	5.7	7.2
Bolivia B	40	54	4.0	6.0	5.0	3.8	0.034	27	18	163	34	31	1.9	40	8.4	0 74	0.016	113	325	437

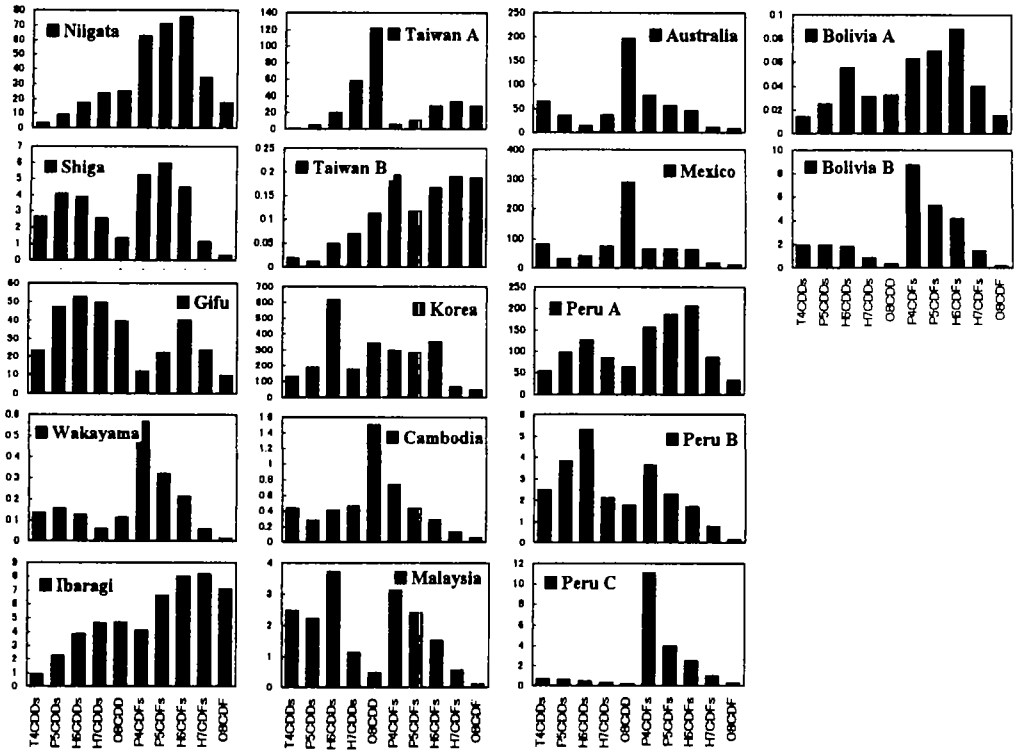

Fig. 1 The homologue profiles of the samples (y axis: ng/g)

of TCDD/Fs, 108 peaks in a chromatograph were identified as isomers or isomer groups and each of the peaks was quantitatively determined using the internal standards.

Results and Discussion

Total Quantity and TEQ

TCDD/Fs were found in all samples tested (Table 2). Their amounts ranged from 1.8 to 340 ng/g for Japanese samples and 0.44 to 1,100 ng/g for other samples. The TEQ of each sample is shown in Table 3. It ranged from 0.027 to 6.3 ngTEQ/g for Japanese samples and 0.0072 to 14ngTEQ/g for other samples. The TEQs of Niigata, Gifu, Taiwan A and Peru A were very high, among which those of Niigata, Gifu and Peru A were higher than the Japanese criteria, 3 ngTEQ/g; use of ash with a TEQ higher than this level is prohibited for landfills.

Homologue and Congener Profiles

Homologue profiles are shown in Fig.1. Niigata, Shiga, Gifu, Ibaragi, Peru A and Bolivia A had similar figures, but in only the case of Gifu, the contribution of TCDDs to the total quantity was higher than that of TCDFs. Taiwan A, Cambodia, Australia and Mexico were categorized into a group according to their figures and in recognition of the point that for these samples the contribution of 8D to the total quantity is the highest. Malaysia and Peru B had similar figures. Peru C and Bolivia B also had similar figures. Each of Wakayama, Taiwan B and Korea has its own profile.

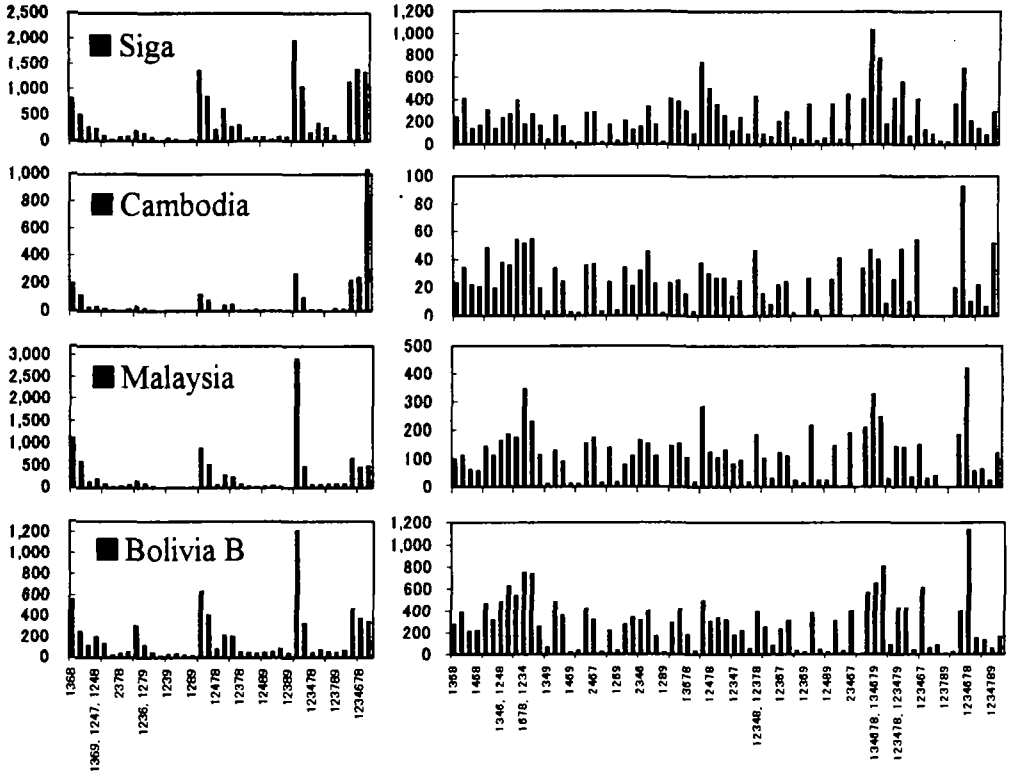

Fig. 2 The congener profiles of the samples (y axis: pg/g)

Congener profiles are shown in Fig.2. The profiles are similar to each other. The main isomers found in PCDDs were 12468/12479, 123468/124679/124689, 7D and 8D. The profiles of PCDFs were much more similar to each other than those of PCDDs.

Contribution to TEQ

In the case of homologue profiles, the contribution of 5D, 5F and 6F to the TEQ accounted for a significant percentage of the TEQ. In the case of isomers, 12378-PeCDD, 23478-PeCDF and 234678-HeCDF accounted for a significant percentage of the TEQ. These results were in agreement with those of ash, exhaust gas and living organisms. Sibayama reported that 23478-PeCDF always contributed significantly to TEQ (about 25%)[2]. The same result was obtained in this study.

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References

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