PBDEs LEVELS IN PINE NEEDLES AFFECTED BY MUNICIPAL SOLID WASTE MELTING FURNACES IN JAPAN

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Abstract
ERI has continued to conduct research on PCDD/PCDF concentrations in ambient air by using pine needles as bio-monitors with citizen participation for 8 years (1999-2006). In addition to PCDD/PCDF, we have initiated a pilot research for the study of PBDEs in ambient air using pine needles as bio-monitors as well. The target emission sources of this pilot study were the Municipal Solid Waste Incinerators (Gasification melting furnaces). Thus, the pine needles were sampled both in the vicinity of wastes disposal facilities and in the background areas across Japan. Through this research it was suggested that the total PBDEs levels tend to increase in ambient air in the vicinity of waste disposal facility installing highly advanced technologies such as pyrolysis or gasification furnaces. Further, despite ban to use PBDEs, with the exception of Deca-BDE, by voluntary regulation of the manufacturing industry, Penta-BDEs and Tetra-BDEs are detected in most of the pine needle samples as well as Deca-BDE. It is not evident but it can be assumed that lower brominated BDEs are produced by decomposition of Deca-BDE in the waste melting furnaces. It is also found that there are no correlation between PBDEs and PCDD/PCDF concentrations.

Introduction
PBDEs (Polybrominated Diphenyl Ethers) are one of the most commonly applied of the brominated fire retardants. Huge amounts of these compounds have been consumed until now. Meanwhile, impacts from these compounds have not been well surveyed by Governments in Japan. These compounds are used especially for products made of polymer plastics, for instance, fabric products, electric appliances and foam products (e.g. fire extinguishant). In a preceding research[1] PBDEs concentration accumulated in pine needles are measured and it has been found that PBDEs in pine needles picked at the central Tokyo area where there are many wastes incinerators) is 6 times higher than that picked at the rural area in Chiba Pref. Located at the entrance of Tokyo Bay.

Among PBDEs, only Deca-BDE, Octa-BDEs and Penta-BDEs are in the market as products. However, in Japan it has been banned to use PBDEs for flame-retardants except Deca-BDE since 1991 by voluntary regulation ruled by industry organization[2]. The lower brominated compounds have higher toxicity. Meanwhile, these lower brominated compounds (Tetra-BDE, Penta-BDE, etc.) have been detected in ambient air. Nevertheless, since the Governments have not paid much attention to the risk of PBDEs, the monitoring of PBDEs in the ambient air has been very limited in Japan.

On the other hand, ERI has accumulated more than 800 data of PCDD/PCDF by using pine needles as bio-monitor for 8 years with citizen participation[3-5]. It has been found that monitoring using pine needles is essentially effective to measure PCDD/PCDF concentration of both area-wide average and annual average with reasonable cost; therefore, we have started research about PBDEs using pine needles as bio-monitors in the same way as dioxins. This research is a pilot study focusing on the influence from most advanced waste disposal facilities (pylorysis or gasification melting furnaces), through the concentration of PBDEs within the pine needles reflecting ambient air pollution.

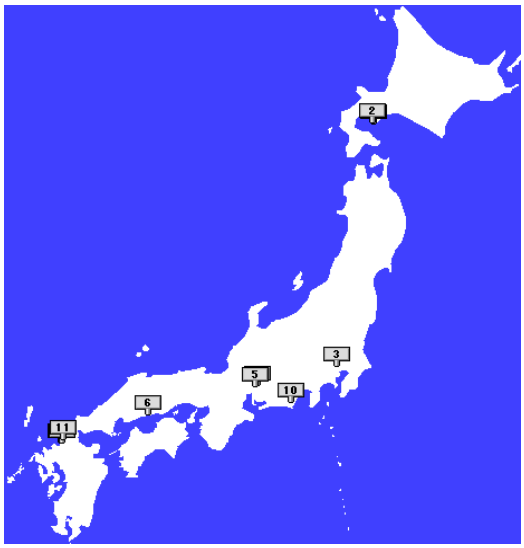

Fig. 1 Pine needles sampled

Materials and Methods

(1) Sampling

In this research, the pine needles, which were collected by citizens participating in the research for PCDD/PCDF, were diverted to analyze PBDEs. Target areas are shown in Table 1 and Fig.1. Each "plant" shown in Table 1 is a municipal solid waste facility, which includes melting furnaces.

Table 1 Pine needles sampling areas

Area, City	Pref.	About Plant	Area, City	Pref.	About Plant
1. Muroran City	Hokkaido	**Downwind icinity**	7. Koga City	Fukuoka	**Vicinity**
2. Date City		**Upwind vicinity**	8.Mushirouchi, Koga City		**Vicinity**
3. Kawaguchi City	Saitama	**Vicinity**	9. Entire Koga City		Background
4. East Kasugai City	Aichi	Background	10.Ita-tashiro, Shimada City	Shizuoka	Background
5. West Kasugai City			11. Munakata City	Fukuoka	**Vicinity**
6. Fukuyama City	Hiroshima	Background			

* Area 10 and 11 are red pine needles, others are black pine needles.

Table 2 shows relevant waste disposal facilities and its dioxin data. Dioxin concentration levels of the flue gas are measured only once a year, so it should be noted that it does not reflect annual average condition of each plant.

Table 2 Dioxin concentrations in exhaust gas of garbage disposal facilities[6]

Facility (garbage melting furnace)	Capacity (t/day)	Dust Collector	Installation Day	Dioxin conc. (ng-TEQ/m^3N)	Measuring Day
Nishi-iburi Regional Garbage Disposal Organization Facility No.1	105	BF	04/01/2003	0.00092	2004/11/12
Nishi-iburi Regional Garbage Disposal Organization Facility No.2	105	BF	04/01/2003	0.0036	2004/08/06
Asahi Environmental Center Furnace No.1	140	BF	12/01/2002	0.00012	2004/11/02
Asahi Environmental Center Furnace No.2	140	BF	12/01/2002	0.000081	2004/08/19
Asahi Environmental Center Furnace No.3	140	BF	12/01/2002	0.0000046	2004/11/04
Munakata Clean Center Furnace No.1	80	BF	06/10/2003	0.0032	2004/10/22
Munakata Clean Center Furnace No.2	80	BF	06/10/2003	0.000021	2004/10/22
Koga Clean Center Furnace No.1	130	BF	04/01/2003	0.0012	2004/07/14
Koga Clean Center Furnace No.2	130	BF	04/01/2003	0.0012	2004/07/14

BF: Bag Filter

(2) Analysis Method

Maxxam Analytics Inc. (Ontario Canada) conducted PBDEs concentration analysis by "BRL SOP-00413, 00414" which is based on the following two methods: "DBE-E-3430 and UEPA draft method 1614".

Results and Discussion

The analytical results for PBDEs for each number of brominated compounds are shown in Table 3 and Fig.2.

(1) Total PBDEs

The highest PBDE concentrations in pine needles are "3.Kawaguchi City, within the vicinity of the plant" and "7.Koga City, within the vicinity of the plant". 3rd highest is "8.Mushirouchi Koga City, including area vicinity of the plant". For all of these 3 areas, the pine needle samples were collected in the vicinities of the waste melting furnaces. On the other hand the lowest is "10. Ita-tashiro Shimada City, background area". As for the Fukuyama City of Hiroshima Pref., the 4th highest area, it should be noted that there are different emission sources other than the municipal solid waste melting furnace, such as a huge industrial wastes disposal facility.

Therefore it is necessary to survey all the related stationary emission sources especially for the background areas. However, it is assumed that the vicinities of the waste disposal facility, the level of PBDEs concentration in ambient air tend to be higher than the background areas.

(2) Compounds and Characteristics

Despite ban to use PBDEs except Deca-BDE by voluntary regulation, the detected compounds of PBDEs in the pine needles are not just Deca-BDE, but Penta-BDE, Tetra-BDE and others . Most of the cases, Penta-BDE and Tetra-BDE are higher than Deca-BDE. Since Penta and Tetra-BDEs are much more toxic and accumulative than Deca, only Deca-BDE is used as product in Japan.

Table 3 PBDEs concentrations in pine needles (unit: ng/g)

PBDEs		1.Muroran downwind vicinity	2.Date upwind vicinity	3.Kawaguchi vicinity	4.east Kasugai B.G.	5.west Kasugai B.G.	6.Fukuyama B.G.	7.Koga vicinity	8.Mushirouchi, Koga includes vicinity	9.entire Koga B.G.	10.Shimada B.G.	11.Munakata vicinity
Decabromodiphenyl ether		1.0	1.4	0.87	0.86	1.6	2.0	0.34	0.31	0.63	2.2	0.58
Tri	2,2',4	0.0054	ND	0.026	0.011	0.012	0.0068	0.012	0.015	0.0090	0.0070	0.0076
	244'+2'34	0.018	0.019	0.063	0.052	0.040	0.026	0.066	0.065	0.046	0.028	0.031
Tetra	2,2'4,4'	1.1	1.1	2.6	1.1	1.2	1.3	2.8	2.1	1.1	0.48	0.71
	2,3',4,4'	0.033	0.036	0.086	0.041	0.020	0.016	0.085	ND	0.042	0.023	0.024
	22'45' +23'4'6	0.034	0.037	0.096	0.041	0.050	0.043	0.081	0.083	0.039	0.023	0.028
Penta	2,2',3,4,4'	0.11	0.14	0.30	0.11	0.13	0.14	0.34	0.24	0.13	0.038	0.040
	2,2',4,4',5	1.6	2.0	4.6	1.6	1.8	2.0	4.9	3.2	1.8	0.58	0.66
	2,2',4,4',6	0.34	0.38	0.94	0.37	0.38	0.39	1.1	0.62	0.39	0.12	0.14
Hexa	22'344'5' +2344'56	0.030	0.038	0.093	0.014	0.032	0.030	0.069	0.054	0.028	ND	0.0067
	2,2',4,4',5,5'	0.16	0.23	0.44	0.031	0.17	0.21	0.44	0.31	0.15	0.060	0.060
	2,2',4,4',5,6'	0.16	0.21	0.41	0.14	0.17	0.19	0.45	0.31	0.15	0.056	0.058
Hepta	2,2',3,4,4',5',6	0.0060	0.0096	0.025	ND	0.013	0.0097	0.022	0.022	0.017	0.0062	ND
	2,3,3',4,4',5,6	ND	ND	ND	ND	0.0021	ND	ND	ND	ND	ND	ND
Total		**4.6**	**5.6**	**11**	**4.4**	**5.6**	**6.4**	**11**	**7.3**	**4.5**	**3.6**	**2.3**
Tri-BDEs		0.023	0.019	0.089	0.063	0.052	.033	0.078	0.080	0.055	0.035	0.039
Tetra-BDEs		1.2	1.2	2.8	1.2	1.3	1.4	3.0	2.2	1.2	0.53	0.76
Penta-BDEs		2.1	2.5	5.8	2.1	2.3	2.5	6.3	4.1	2.3	0.74	0.84
Hexa-BDEs		0.35	0.48	0.94	0.19	0.37	0.43	0.96	0.67	0.33	0.12	0.12
Hepta-BDEs		0.0060	0.010	0.025	0	0.015	0.010	0.022	0.022	0.017	0.0062	0
Deca-BDE		1.0	1.4	0.87	0.86	1.6	2.0	0.34	0.31	0.63	2.2	0.58

Note) Essential figure: 2digits

It can be assumed that lower brominated BDEs are generated by decomposition of Deca-BDE. Focusing on the percentage of Deca-BDE, the Deca-BDE conc. Levels of the 3 highest areas are lower than the other areas. However, at the same time, the Deca-BDE conc. levels were higher for the other areas except Munakata City (Vicinity of Waste Disposal facility), which is the 2nd lowest area among 11 target areas.

Although there are still very few data analyzed in this Pilot study, it is assumed that in the areas of lower concentration of Total

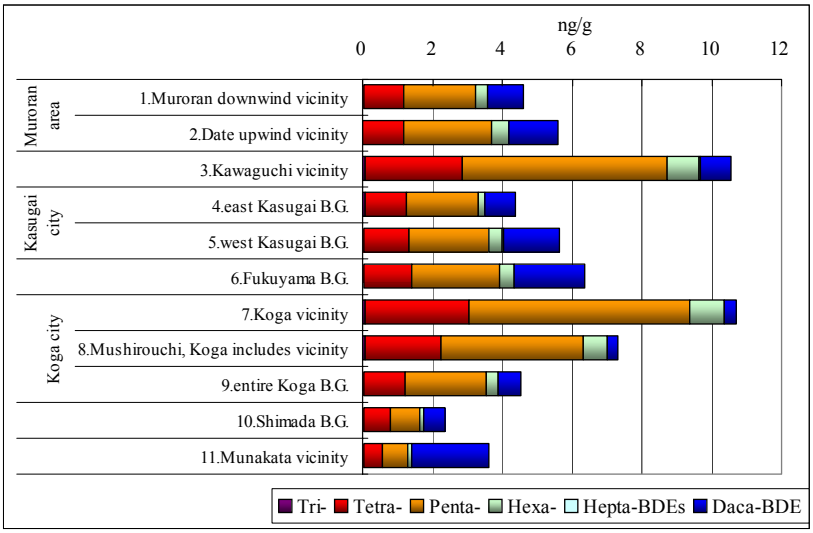

Fig.2 PBDEs concentrations in pine needles

PBDEs, Deca-BDE is not yet degraded into lower brominated BDEs in waste melting furnaces. And on the contrary, the areas of higher concentration of Total PBDEs, Deca-BDE is degraded into lower brominated BDEs then the concentrations of Tetra-BDEs and Penta-BDEs are increased.

Table 4 shows both PBDEs and Dioxin (PCDD/PCDF) concentration in identical pine needle samples. There are no correlation between PBDEs and PCDD/PCDF concentrations.

Table 4 PBDE and PCDD/PCDF conc. in identical pine needles (descending order of PBDEs conc.)

Area	Total PBDEs (ng/g)	Dioxin(PCDD/PCDF) (pg-TEQ/g)
7.Koga vicinity	11	0.41
3.Kawaguchi vicinity	11	-
8.Mushirouchi, Koga includes vicinity	7.3	0.36
6.Fukuyama B.G.	6.4	0.44
5.west Kasugai B.G.	5.6	1.3
2.Date upwind vicinity	5.6	0.32
1.Muroran downwind vicinity	4.6	0.32
9.entire Koga B.G.	4.5	0.44
4.east Kasugai B.G.	4.4	1.2
11.Munakata vicinity(red pine needles)	3.6	0.22
10.Shimada B.G. (red pine needles)	2.3	0.32

Note) Effective figures: 2digits

In this research only a limited number of pine needles served as samples for PBDE analysis, so PBDE sample analysis in pine needles from various areas and conditions should be continued. Hopefully, a correlation can be found between ambient air concentrations and pine needle sample concentrations. This will help in order to monitor the environmental pollution caused by PBDEs with reasonable cost by the same citizen participation as we experienced in the case of PCDD/PCDFs.

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