

INVESTIGATION OF SIMPLE EVALUATION METHOD OF AIR POLLUTION BY BROMINATED ENVIRONMENTAL POLLUTANTS USING JAPANESE BLACK PINE NEEDLE AS AN INDICATOR (THE FIRST REPORT)

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Abstract

Seven ambient air samples and nine Japanese black pine needle leaf samples from on the campus of Setsunan University of Hirakata City, Osaka, Japan, were investigated on the actual pollution situation of PBDEs, one of representative brominated fire retarding agents, for the purpose of development of the air pollution appraisal method of the brominated environmental pollutants using Japanese black pine needle leaf as an index. The pollution level of PBDEs in the atmosphere was changed considerably during experimental period of ca. 2 months. The congener ratio pattern of PBDEs completely differed by the particle phase and vapor phase. The average concentration of PBDEs in the black pine needle samples was 447 pg/g-wet weight with the range of 176 pg/g on October 24 to 766 pg/g. It became clear that the accumulative amount of PBDEs in 1 g of black pine needle was equivalent to the existence amount of PBDEs in ca. 22 m³ of the ambient air.

Introduction

We have already shown clearly that the concentration in the atmosphere of various environmental pollutants including dioxin, HCH, and DDT is changed sharply temporally. For example, in the case of dioxin analogues, the pollution level was in a great time alteration with a several tens times within a year¹⁾. Therefore, many tens of measurement is needed for grasp of exact concentration of contaminant at every year. However, the analysis cost of the commercial base for the high toxicity halogenated pollutants with a super-low concentration including dioxin analogues is very big-ticket. Therefore, a huge amount of costs are required for grasp of reliable air pollution, and it is actually next to impossible. Therefore, development of the economical and reliable pollution appraisal method replaced with the existing direct air measuring method was an indispensable subject. From such a reason, development of the economical and reliable pollution appraisal method replaced with the existing direct air measuring method was an indispensable subject. We found that the Japanese black pine of the evergreens, which widely distributed over our country, could accumulate efficiently the dioxin analogues in the atmosphere, and developed the air pollution appraisal method of the dioxin using a black pine²⁾. The basic knowledge about dioxin accumulation was as follows.: (1) the cumulative dosage per 1g of needle leaves was equal to ca. a ten m³-atmosphere content, (2) there is very little temporal change of needle leaf accumulation concentration compared with air pollution concentration, (3) accumulation concentration correlated with the age of the moon of a needle leaf, (4) the dioxin analogues of a gas state accumulated in a needle leaf, and (5) their rate of a gas state correlated with monthly average temperature.

In recent years, rapid increase of the amount used was being enhanced globally, and brominated flame retardants have caused the environmental pollution of the earth scale. Since rapid contamination was advancing, especially polybrominated diphenylether (PBDEs) was specified as the environmental pollutant which needs the measure against control of an earth scale³⁾. Moreover, in 2003 and afterwards, centering on Europe, the high concentration environmental pollution of hexabromocyclododecane (HBCD) was clarified, and many specialist were anxious about the pollution influence. Since HBCD has living thing accumulative comparable as dioxin, PCB, etc., it has been a pressing subject with a global elucidation of an environmental dynamic state. In our country, if HBCD over 30,000t has been used by the present and taking into consideration the difficulty resolvability and the high accumulative one of HBCD, we will be anxious about the advanced environmental pollution by HBCD also in our country, but the actual condition has not yet clarified.

From such a viewpoint, this research tried construction of the simple air pollution appraisal method of brominated flame retardants using bio-monitoring.

Materials and Methods

1) Analysis sample

The sampling for ambient air was performed during a period of on August 23 to October 24 of 2007 on the campus of Setsunan University in Hirakata City, Osaka Prefecture, Japan. We got seven samples of continuous 7days collecting using a high-volume air sampler with the flow rate of 100 L/min. The samplers possessed a glass fiber filter (GFF) for collection of particle phase compounds and two polyurethane from plugs for vapor

phase compounds. On the other hand, nine Japanese black pine needle samples were obtained during a period of May 28 to October 24, of 2007 at the same sampling point to the case of ambient air sample.

2) Analytical method:

The outline of the analysis method of an air sample was essentially composed of an addition of $^{13}\text{C}_{12}$ -labeled internal standard of PBDEs and HBCD, extraction with toluene (for collection on GFF) and acetone (for collection on PUF) for 5hrs. under reflux. The two extracts were separately concentrated and cleaned up on a multi-layer silica gel column (from a top, 1 g of Na_2SO_4 , 1 g of $\text{AgNO}_3/\text{silica}$, 0.3g of silica, 2 g of 44%(w/w) $\text{H}_2\text{SO}_4/\text{silica}$, 1.5 g of 22%(w/w) $\text{H}_2\text{SO}_4/\text{silica}$, 0.3g of silica, 1 g of 2%(w/w) KOH/silica , 1g of Na_2SO_4 and adsorbent cotton), followed by an elution with 70 ml of 20% methylene chloride in n-hexane. The eluate was concentrated, dried, dissolved with 10 ml of n-hexane and cleaned up on an activated carbon-dispersed silica gel column (from a top, 1.5 g of Na_2SO_4 , 0.5 g of activated carbon-dispersed silica, and 1.5 g of Na_2SO_4) followed by an elution of 90 mL of 25% methylene chloride in n-hexane.

On the other hand, an addition of $^{13}\text{C}_{12}$ -labeled internal standard of PBDEs and HBCD, 50 g of pine needle sample was extracted with 300 mL of toluene for 5 hrs. under reflux. The extract was concentrated and cleaned up on a silica gel column (30 g) for removal of chlorophyll. The eluate was concentrated, dried, dissolved with 10 mL of n-hexane and cleaned up on a multi-layer silica gel column and an activated carbon-dispersed silica gel column.

The cleaned up extracts from air sample and pine needle sample were analyzed for PBDEs in EI-SIM mode at a resolution of 10,000 using a Hewlett Packard 5890J gas chromatograph-JEOL M700 mass spectrometer.

Results and Discussion

1) Time alteration of PBDEs pollution in the atmosphere

Seven ambient air samples of continuous 7 days collecting were obtained during a period of on August 23 to October 24 of 2007 on the campus of Setsunan University in Hirakata City, Osaka Prefecture, Japan. As shown in Table 1, the pollution level of PBDEs changed considerably during experimental period of ca. 2 months, showing the PBDEs concentrations to be 6.87 to 26.0 pg/m^3 in the particle phase, 3.50 to 10.4 pg/m^3 in the vapor phase and 16.3 to 34.0 pg/m^3 in the total, respectively. The average levels of the particle phase, the vapor phase and the total were respectively 14.1, 6.50 and 20.6 pg/m^3 . In 2001, we investigated the pollution level PBDEs

Table 1. Concentrations of PBDE congeners in the atmosphere at a sampling point in Hirakata City in Osaka Prefecture

Sampling period	Compound	Concentrations of PBDE congeners (pg/m^3)								Ratio (%)
		TrBDE	TeBDE	PeBDE	HpBDE	OBDE	NBDE	DeBDE	Total	
Aug. 23-29	Particle phase	0.0455	0.128	0.318	0.770	0.113	2.21	3.29	6.87	41.3
	Vapor phase	4.12	1.42	0.373	1.58	0.223	1.18	0.870	9.76	58.7
	Total	4.17	1.54	0.691	2.35	0.336	3.39	4.16	16.6	100.0
Sep. 6-12	Particle phase	0.125	0.0720	0.373	0.940	0.0660	2.76	4.93	9.27	72.6
	Vapor phase	1.16	0.306	0.116	1.05	0.172	0.430	0.270	3.50	27.4
	Total	1.28	0.378	0.489	1.99	0.238	3.19	5.20	12.8	100.0
Sep. 13-19	Particle phase	0.153	0.115	0.102	1.58	0.287	2.88	6.82	11.9	73.3
	Vapor phase	1.470	0.426	0.079	1.22	0.262	0.440	0.460	4.36	26.7
	Total	1.623	0.541	0.181	2.80	0.549	3.320	7.28	16.3	100.0
Sep. 27-30 Oct. 1-3	Particle phase	1.65	1.58	0.665	1.11	0.267	4.25	16.5	26.0	76.6
	Vapor phase	1.03	0.478	0.164	1.92	0.461	1.98	1.93	7.96	23.4
	Total	2.68	2.06	0.829	3.03	0.728	6.23	18.4	34.0	100.0
Oct. 3-10	Particle phase	0.0278	0.0680	0.0770	1.21	0.270	3.00	4.19	8.84	48.1
	Vapor phase	2.70	1.07	0.276	3.29	0.210	0.940	1.07	9.56	51.9
	Total	2.73	1.14	0.353	4.50	0.480	3.94	5.26	18.4	100.0
Oct. 11-17	Particle phase	0.101	0.135	0.184	2.23	0.437	6.07	7.74	16.9	62.0
	Vapor phase	4.85	1.81	0.452	1.22	0.184	0.920	0.920	10.4	38.0
	Total	4.95	1.95	0.636	3.45	0.621	6.99	8.66	27.3	100.0
Oct. 18-24	Particle phase	0.138	0.329	0.377	2.22	0.397	4.87	10.7	19.0	80.8
	Vapor phase	1.340	0.596	0.188	1.48	0.176	0.410	0.32	4.51	19.2
	Total	1.478	0.925	0.565	3.70	0.573	5.28	11.0	23.5	100.0
Average	Particle phase	0.319	0.347	0.299	1.44	0.262	3.72	7.73	14.1	68.5
	Vapor phase	2.190	0.787	0.209	1.47	0.216	0.841	0.789	6.50	31.5
	Total	2.490	1.087	0.454	2.59	0.422	3.87	7.00	20.6	100.0

at the same point of Setsunan University⁴). At those times, the average pollution level of PBDEs was 335 pg/m³ in the summer and 200 pg/m³ in the autumn. Therefore, it became clear that the pollution level of PBDEs in the atmosphere in 2007 was decreasing to about 1/10 - 1/16 in 2001.

PBDEs exist in the atmosphere with two forms, a particle state, which stuck to the air suspended particulate, and a gaseous phase state. As shown in Table 1, the average existence percentage was 68.5% in the state of a particle and 31.5% in the state of the vapor phase, and the existence-in particle state rate was overwhelmingly higher. However, in the period of August 23-29 and October 3-10, the existence-in vapor state was larger than the existence-in particle state rate. In addition, the existence-in particle state rate considerably changed with 41.3% of August 23-29 to 80.8% of October 18-24.

As shown in Fig. 1, the congener ratio pattern of PBDEs completely differed by the particle phase and vapor phase. In the particle phase, the highly brominated congener of DeBDE and NBDE occupied 53.0% and 28.3%. On the contrary to this, TrBDE and HpBDE were the major congeners with the congener ratio of 32.4% and 25.3%, respectively. In the total PBDEs, the main congeners were DeBDE with the congener ratio of 38.8%, NBDE with 21.9%, HpBDE with 15.5% and TrBDE with 13.2%. From this result, it became clear that the most of higher brominated diphenyl ethers with low vapor pressure exist with the particle phase combined with the air suspended particulate, and that the most of lower brominated diphenyl ethers with high vapor pressure exist as vapor phase.

2) Time alteration of PBDEs pollution in the black pine needle

Table 2 showed the analytical result of PBDEs in Japanese black pine needle samples collected during a period of May 28 to October 24, 2007 on the campus of Setsunan University in Hirakata City, Osaka Prefecture, Japan. The average concentration of PBDEs in the black pine needle samples was 447 pg/g-wet weight with the range of 176 pg/g on October 24 to 766 pg/g. From this result, it became clear that the accumulative amount of PBDEs in 1 g of black pine needle was equivalent to the existence amount of PBDEs in ca. 22 m³ of the ambient air.

As well as the case of ambient air, the pollution level of PBDEs in the black pine needle fairly changed with 176 to 766 pg/g-wet weight during the experimental period of ca. five months. The ratio of the maximum to minimum level was ca. 4 times. In the case of the ambient air sample, the ratio of the maximum to minimum level was ca. 3 times during the experimental period of ca. 2 months. Therefore, taking the length of the experimental period into the consideration, the magnitude of time alteration on PBDEs pollution level was presumed to be almost the same by the pine needle and the air sample.

Table 4 showed the congener ratios of PBDEs in black pine needle samples. In the case of the black pine needle, DeBDE occupied 50.4% of the total PBDEs. The semi main congeners were NBDE with the congener ratio of 16.4%, TeBDE with 10.5% and TrBDE with 8.7%. In addition, the time alteration of the congener ratio of PBDEs was confirmed to remarkably change with the C.V. of 57.3% of TrBDE, 63.4% of TeBDE, 52.9% of PeBDE, 70.7% of HpBDE and 140% of OBDE, respectively.

In the case of dioxin analogues including PCDDs, PCDFs and DL-PCBs, the congener ratios of these pollutants in the black pine needle were all similar to ones of the vapor phase in the ambient air samples. Namely, we had already revealed that the dioxin analogues in the vapor phase accumulated mainly in the pine needles⁵).

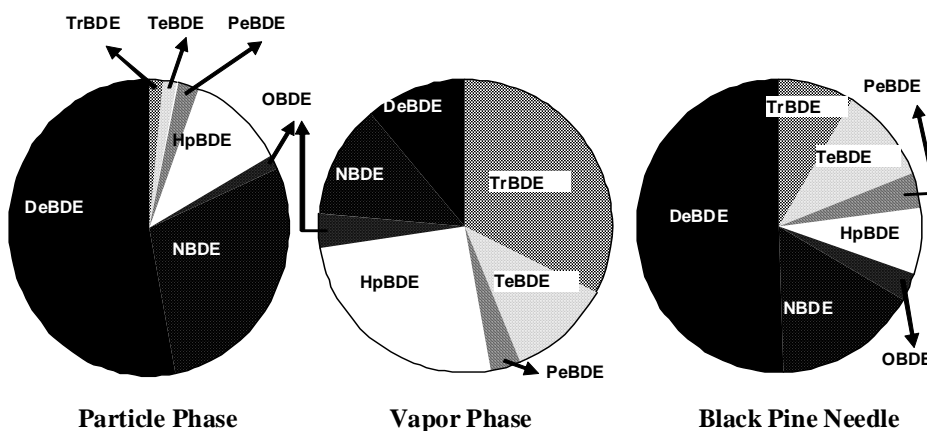


Fig. 1 Comparison of congener ratio of PBDEs in particle phase, gas phase and pine needle

Sampling date	Concentrations of PBDE congeners (pg/g-wet weight)							
	TrBDE	TeBDE	PeBDE	HpBDE	OBDE	NBDE	DeBDE	Total
May 28, 2007	24.6	27.3	10.4	95.2	24.1	160	267	609
June 9, 2007	15.8	15.8	6.86	32.7	32.9	52.3	99.1	255
Aug. 15, 2007	19.6	16.6	7.83	65.5	20.1	190	446	766
Aug. 22, 2007	12.7	16.6	7.71	30.5	3.75	45.9	211	328
Sep. 12, 2007	42.9	52.9	22.1	15.2	3.45	46.6	177	360
Sep. 19, 2007	42.1	63.9	24.1	9.26	5.06	63.1	321	528
Sep. 26, 2007	75.1	98.2	38.2	11.9	3.18	92.9	318	637
Oct. 17, 2007	62.1	82.8	24.2	6.17	1.76	29.4	155	361
Oct. 24, 2007	22.8	19.6	7.65	17.2	3.19	24.8	80.8	176
Average	35.3	43.7	16.6	31.5	10.8	78.3	231	447
S.D.	21.8	31.8	11.1	30.0	11.6	58.7	119	197
C.V. (%)	61.8	72.6	66.9	95.2	108	75.0	51.4	44.1

Sampling date	Congener ratio of PBDEs (%)							
	TrBDE	TeBDE	PeBDE	HpBDE	OBDE	NBDE	DeBDE	Total
May 28, 2007	4.0	4.5	1.7	15.6	4.0	26.3	43.9	100.0
June 9, 2007	6.2	6.2	2.7	12.8	12.9	20.5	38.8	100.0
Aug. 15, 2007	2.6	2.2	1.0	8.6	2.6	24.8	58.3	100.0
Aug. 22, 2007	3.9	5.1	2.3	9.3	1.1	14.0	64.3	100.0
Sep. 12, 2007	11.9	14.7	6.1	4.2	1.0	12.9	49.1	100.0
Sep. 19, 2007	8.0	12.1	4.6	1.8	1.0	11.9	60.7	100.0
Sep. 26, 2007	11.8	15.4	6.0	1.9	0.5	14.6	49.9	100.0
Oct. 17, 2007	17.2	22.9	6.7	1.7	0.5	8.1	42.9	100.0
Oct. 24, 2007	12.9	11.2	4.3	9.8	1.8	14.1	45.9	100.0
Average	8.7	10.5	3.9	7.3	2.8	16.4	50.4	100.0
S.D.	5.0	6.6	2.1	5.2	3.9	6.1	8.8	0.0
C.V. (%)	57.3	63.4	52.9	70.7	139.9	37.5	17.4	0.0

However, as illustrated in Fig. 1, the accumulative pattern of PBDEs in black pine needle resembled the existence pattern in the particle phase. Now, about this reason, it is unknown. From now on, the accumulation trend of PBDEs to a black pine needle leaf is due to be examined.

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References

1. Miyata, H., Iwata, N., Nakao, T., Aozasa, O., Shimamura, A., Ohta, S. (2001) *Organohalogen Compounds* 50, 213
2. Miyata, H., Iwata, N., Nakao, T., Aozasa, O., Shimamura, A., Ohta, S. (2002) *Organohalogen Compounds* 59, 103
3. Ohta, S., Nakao T, Aozasa O, Miyata H (2002) *Chemosphere*, 46, 689
4. Ohta, S., Nakao T, Nishimura, H., Okumura, T., Aozasa O, Miyata H (2002) : *Organohalogen Compounds* 57: 57