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Polybrominated diphenyl ethers (PBDEs), polybrominated dibenzo-*p*-dioxins/dibenzofurans (PBDD/Fs) and monobromo-polychlorinated dibenzo-*p*-dioxins/dibenzofurans (MoBPXDD/Fs) in the atmosphere and bulk deposition in Kyoto, Japan

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Abstract

Polybrominated diphenyl ethers (PBDEs), polybrominated dibenzo-*p*-dioxins/dibenzofurans (PBDD/Fs) and monobromo-polychlorinated dibenzo-*p*-dioxins/dibenzofurans (MoBPXDD/Fs) in atmosphere, bulk atmospheric deposition and soil in Kyoto, which is an urban city in Japan, were measured. Decabromodiphenyl ether (D₁₀BDE, BDE-209) was detected in relatively high concentrations compared to other PBDE congeners in most samples. Similar results, in which D₁₀BDE was predominantly detected, were reported in other studies in Japan. However, these homologue profiles differ from those of studies conducted in North America. The partitioning of semivolatile organic compounds between atmospheric gas phase and particulate-associated phase is an important factor in their environmental behavior. In this study, atmospheric particulate phase fraction (f_p) of the brominated compounds increased with increasing bromine number, and f_p was higher in samples collected in winter than in those collected in summer. Moreover, f_p of PBDFs and MoBPXDFs was higher than that of PCDFs with the same halogen number. These results agree well with expectations from the vapor pressure of the brominated compounds and PCDD/Fs. Among the brominated compounds in the atmosphere, the level of MoBPXDD/Fs correlates positively with that of PCDD/Fs. This relationship has been previously observed in waste incineration samples. These results suggest that one of the sources of MoBPXDD/Fs in the atmosphere is incineration byproduct. The level of PBDD/Fs seems to correlate positively with that of PBDEs. This relationship suggest that the PBDD/Fs in the atmosphere relate to PBDEs, which is an impurity of PBDE products, or formed by the manufacture or combustion of plastics containing PBDEs.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are flame retardants added to plastics to prevent fires. The estimated demand for decabromodiphenyl ether products in Japan was 4500 tons in 1986, and this amount increased every year until it reached 12000 tons in 1990. At that point the trend reversed and in 2000 the demand was 2800 tons (Watanabe and Kawano, 1997; Kagaku Kogyo Nippo Co. Ltd., 2001). Since the 1980s it has been known that PBDEs cause environmental pollution; PBDEs in fish (Andersson and Blomkvist, 1981; Watanabe et al., 1987), sediment (Watanabe et al., 1986, 1987) and birds (Jansson et al., 1987) have been reported. In 1998, Norén and Meironyté reported that the concentrations of PBDEs in human breast milk of Swedish women had increased exponentially from 1972 to 1997, whereas other organochlorine compounds had decreased to various extents (Norén and Meironyté, 1998, 2000; Meironyté and Norén, 2001). Their reports attracted much attention to PBDEs environmental pollution. Recently, numerous studies on environmental pollution and toxicity on PBDEs have been published (WHO, 1994; Pijnenburg et al., 1995; Watanabe and Kawano, 1997; Darnerud et al., 2001; Rahman et al., 2001; de Wit, 2002). Much research has been reported on the pollution in sediment, fish, birds, marine mammals and humans. However, there is relatively little information on PBDEs in the atmospheric environment.

Polybrominated dibenzo-*p*-dioxins/dibenzofurans (PBDD/Fs) are PCDD/F analogues in which all of the chlorine atoms are substituted with bromine atoms. PBDD/Fs are known to form by thermolysis of brominated flame retardants through the manufacture and combustion of plastics containing brominated flame retardants (WHO, 1994, 1998). Polybromo-polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PXDD/Fs) are also PCDD/F analogues in which some of the chlorine atoms of PCDD/Fs are substituted with bromine atoms. Monobromo-polychlorinated dibenzo-*p*-dioxins/dibenzofurans (MoBPXDD/Fs), in which one chlorine atom is substituted with bromine, are found in residues and gases (Schäfer and Ballschmiter, 1986; Schwind et al., 1988; Sovocool et al., 1989; Chatkittikunwong and Creaser, 1994; Vehlow et al., 2000; Sakai et al., 2001). As with PBDEs, there is little information on these brominated dioxins in the atmospheric environment.

The purpose of this study was to determine the levels of PBDEs, PBDD/Fs and MoBPXDD/Fs in the atmospheric environment.

2. Materials and methods

2.1. Sampling

Samples were collected at Kyoto University, which is located in the urban and north-eastern area of Kyoto City in Japan. Atmospheric samples were collected using a high-volume air sampler equipped with a glass fiber filter (GFF) and three polyurethane foam plugs (PUF) at a flow rate of $0.7 \text{ m}^3 \text{ min}^{-1}$. Sampling periods were one week (in Aug. 2000 and Jan. 2001) and three days (in Sept. 2001). The GFF and PUF were exchanged every day to prevent breakthrough of the analyte. Due to an experimental complication, only atmospheric samples of Aug. 2000 for PBDEs analysis were collected with a low-volume air sampler. Bulk deposition samples were collected using a glass funnel with a cross section of 0.069 m^2 connected to a glass bottle covered with aluminum foil. Rain samples were collected using a stainless steel funnel with a cross section of 0.10 m^2 connected to an amber-colored glass bottle and an automatic rain sampler (a device that detects rainfall and then opens the lid of the funnel, MODEL W-2B, SHIBATA, Tokyo, Japan). Sampling periods for bulk deposition and rain were two weeks. Surface soil (0–5 cm depth) samples were collected at the same sampling point as the atmospheric samples.

2.2. Chemicals

Standard compounds used in this study are shown in Table 1. Solutions of standard compounds were purchased from Cambridge Isotope Laboratories (Andover, USA) and Wellington Laboratories (Guelph, Canada). Unlabeled standard solutions of PBDEs, PBDD/Fs and MoBPXDD/Fs were used as calibration standards. $^{13}\text{C}_{12}$ -labeled standard solutions of PBDEs and PBDD/Fs were used as internal standards. $^{13}\text{C}_{12}$ -labeled PCDD/Fs were used as internal standards for MoBPXDD/Fs analysis due to the lack of $^{13}\text{C}_{12}$ -labeled MoBPXDD/Fs standards.

2.3. Extraction and cleanup

An apparatus made of amber-colored glass or covered with aluminum foil to prevent photolysis of the brominated compounds was used for the analysis. The soil samples and GFF samples were Soxhlet-extracted with toluene. PUF samples were Soxhlet-extracted with acetone. Bulk deposition samples, which consisted of

Table 1
Standard compounds used in this study

Analyte	Unlabeled standards	Internal standards
<i>PBDEs</i>		
244'-(BDE-28)	244'-(BDE-28)	¹³ C ₁₂ -244'-(BDE-28)
22'45'-(BDE-49)	22'45'-(BDE-49)	¹³ C ₁₂ -22'44'-(BDE-47)
22'44'-(BDE-47)	22'44'-(BDE-47)	¹³ C ₁₂ -22'44'-(BDE-47)
23'44'-(BDE-66)	23'44'-(BDE-66)	¹³ C ₁₂ -22'44'-(BDE-47)
33'44'-(BDE-77)	33'44'-(BDE-77)	¹³ C ₁₂ -22'44'-(BDE-47)
22'44'6'-(BDE-100)	22'44'6'-(BDE-100)	¹³ C ₁₂ -22'44'5'-(BDE-99)
22'44'5'-(BDE-99)	22'44'5'-(BDE-99)	¹³ C ₁₂ -22'44'5'-(BDE-99)
22'44'56'-(BDE-154)	22'44'56'-(BDE-154)	¹³ C ₁₂ -22'44'56'-(BDE-154)
22'44'55'-(BDE-153)	22'44'55'-(BDE-153)	¹³ C ₁₂ -22'44'55'-(BDE-153)
22'344'5'6'-(BDE-183)	22'344'5'6'-(BDE-183)	¹³ C ₁₂ -22'344'5'6'-(BDE-183)
<i>M₁BDEs</i>		
M ₁ BDEs	4-(BDE-3)	¹³ C ₁₂ -4-(BDE-3)
D ₂ BDEs	44'-(BDE-15)	¹³ C ₁₂ -44'-(BDE-15)
T ₃ BDEs	244'-(BDE-28)	¹³ C ₁₂ -244'-(BDE-28)
T ₄ BDEs	22'44'-(BDE-47)	¹³ C ₁₂ -22'44'-(BDE-47)
P ₅ BDEs	22'44'5'-(BDE-99), 22'44'6'-(BDE-100)	¹³ C ₁₂ -22'44'5'-(BDE-99)
H ₆ BDEs	22'44'56'-(BDE-154), 22'44'55'-(BDE-153)	¹³ C ₁₂ -22'44'56'-(BDE-154)
H ₇ BDEs	22'344'5'6'-(BDE-183)	¹³ C ₁₂ -22'344'5'6'-(BDE-183)
O ₈ BDEs	22'344'5'6'-(BDE-183)	¹³ C ₁₂ -22'344'5'6'-(BDE-183)
N ₉ BDEs	22'344'5'6'-(BDE-183)	¹³ C ₁₂ -22'344'5'6'-(BDE-183)
D ₁₀ BDE (BDE-209)	D ₁₀ BDE (BDE-209)	¹³ C ₁₂ -D ₁₀ BDE (BDE-209)
<i>PBDDs</i>		
M ₁ BDDs	1-M ₁ BDD	¹³ C ₁₂ -2378-T ₄ BDD
D ₂ BDDs	27/28-D ₂ BDD	¹³ C ₁₂ -2378-T ₄ BDD
T ₃ BDDs	237-T ₃ BDD	¹³ C ₁₂ -2378-T ₄ BDD
T ₄ BDDs	2378-T ₄ BDD	¹³ C ₁₂ -2378-T ₄ BDD
P ₅ BDDs	12378-P ₅ BDD	¹³ C ₁₂ -12378-P ₅ BDD
H ₆ BDDs	123478-H ₆ BDD, 123678-H ₆ BDD, 123789-H ₆ BDD	¹³ C ₁₂ -123478-H ₆ BDD
H ₇ BDDs	1234678-H ₇ BDF	¹³ C ₁₂ -123478-H ₆ BDD
O ₈ BDD	O ₈ BDD	¹³ C ₁₂ -123478-H ₆ BDD
<i>PBDFs</i>		
M ₁ BDFs	1-M ₁ BDD	¹³ C ₁₂ -2378-T ₄ BDF
D ₂ BDFs	27-D ₂ BDF	¹³ C ₁₂ -2378-T ₄ BDF
T ₃ BDFs	238-T ₃ BDF	¹³ C ₁₂ -2378-T ₄ BDF
T ₄ BDFs	2378-T ₄ BDF	¹³ C ₁₂ -2378-T ₄ BDF
P ₅ BDFs	12378-P ₅ BDF, 23478-P ₅ BDF	¹³ C ₁₂ -23478-P ₅ BDF
H ₆ BDFs	123478-H ₆ BDF	¹³ C ₁₂ -123478-H ₆ BDD
H ₇ BDFs	1234678-H ₇ BDF	¹³ C ₁₂ -123478-H ₆ BDD
O ₈ BDF	O ₈ BDD	¹³ C ₁₂ -123478-H ₆ BDD
<i>MoBPXDDs</i>		
Br ₁ Cl ₃ DDs	2-Br-378-T ₃ CDD	¹³ C ₁₂ -2378-T ₄ CDD
Br ₁ Cl ₄ DDs	1-Br-2378-T ₄ CDD	¹³ C ₁₂ -12378-P ₅ CDD
Br ₁ Cl ₅ DDs	2-Br-36789-P ₅ CDD	¹³ C ₁₂ -123478-H ₆ CDD
Br ₁ Cl ₆ DDs	1-Br-236789-H ₆ CDD	¹³ C ₁₂ -1234678-H ₇ CDD
Br ₁ Cl ₇ DDs	1-Br-2346789-H ₇ CDD	¹³ C ₁₂ -O ₈ CDD
<i>MoBPXDFs</i>		
Br ₁ Cl ₃ DFs	3-Br-278-T ₃ CDF	¹³ C ₁₂ -2378-T ₄ CDF
Br ₁ Cl ₄ DFs	1-Br-2378-T ₄ CDF	¹³ C ₁₂ -12378-P ₅ CDF
Br ₁ Cl ₅ DFs	2-Br-36789-P ₅ CDD	¹³ C ₁₂ -123478-H ₆ CDF
Br ₁ Cl ₆ DFs	1-Br-236789-H ₆ CDD	¹³ C ₁₂ -1234678-H ₇ CDF
Br ₁ Cl ₇ DFs	1-Br-2346789-H ₇ CDD	¹³ C ₁₂ -O ₈ CDF

rainwater and a small amount of solid material, and rain samples were filtered, the residue was Soxhlet-extracted with toluene, and the filtrate was liquid/liquid-extracted with dichloromethane.

The cleanup procedure was conducted as specified for PCDD/Fs (JIS, 1999). The extracts were concentrated and cleaned up by using multilayer silica gel column chromatography (AgNO₃-silica/H₂SO₄-silica/KOH-silica). For samples for PBDD/Fs and MoBPXDD/Fs analysis, fractionation was conducted using activated-carbon-impregnated silica gel column chromatography. The final extracts were concentrated for analysis.

2.4. Quantification

The final extracts were quantified by a gas chromatograph (GC) equipped with a high-resolution mass spectrometer (HRMS). The GC column was a DB-5ms capillary column (JW Scientific, Folsom, USA). MS was operated in the electron impact (EI) mode with selected-ion monitoring (SIM). The GC/MS chromatograms those isotope ratios of the two ions monitored for each compounds were within $\pm 15\%$ of the theoretical value were identified and quantified by internal standard method.

3. Results and discussion

3.1. Concentrations of PBDEs

Concentrations are shown in Table 2. Atmospheric concentrations of the sum of mono- to nona-BDEs were 4.5–65 pgm⁻³ and that of D₁₀BDE were ND–48 pgm⁻³. In earlier Japanese studies of atmospheric PBDEs, Watanabe et al. (1995) reported PBDE levels in airborne dust collected between 1993 and 1994 from Osaka (urban site). They showed that levels of tetra- to hexa-BDE congeners ranged from a few to several tens of pgm⁻³-air and those of D₁₀BDE were 83–3060 pgm⁻³-air. Ohta et al. (2002) analyzed PBDEs in the atmosphere from samples collected in 2001 from the Osaka district. They reported that the sum of tri- to hepta-BDEs was 2.0–6.6 pgm⁻³ and D₁₀BDE was 100–340 pgm⁻³.

For data on North America, Strandberg et al. (2001) analyzed PBDEs in the atmosphere from samples collected between 1997 and 1999 from urban, rural and remote sites in the Great Lakes region. They reported only on samples taken when the atmospheric temperature was 20 \pm 3 °C. PBDEs levels (sum of seven congeners) were 4.4–21 pgm⁻³ at rural and remote sites, and 33–77 pgm⁻³ at urban site. Alae et al. (2001) reported that PBDEs in the atmosphere from samples collected in 1994 from Alert (the Arctic) ranged between 10 and

700 pgm⁻³. Gouin et al. (2002) reported that PBDEs in the atmosphere from samples collected in 2000 from a rural site in southern Ontario, Canada ranged between 88 and 1250 pgm⁻³. For data on the UK, Lee et al. (2002) reported that PBDEs (sum of 21 congeners) in the atmosphere from samples collected in Hazelrigg and Chilton in 2001 ranged between 2.8 and 37 pgm⁻³, and that from remote site ranged between 0.2 and 11 pgm⁻³.

Greenpeace Netherlands (Greenpeace Netherlands, 2003; Peters, 2003) reported PBDE congeners in rainwater collected in the Netherlands. They collected precipitation samples (using a bulk deposition sampler) and analyzed brominated flame retardants and other compounds (alkylphenol, phthalates, etc.). They reported that BDE-47, -99, -154 were detected in about 10% of the 50 samples and their levels were a few ng l⁻¹. Concentrations in rainwater in our study agree with the results of their study.

3.2. Homologue profiles of PBDEs

In general, D₁₀BDE (BDE-209) was detected in relatively high concentrations compared to other PBDE congeners in most samples. D₁₀BDE was predominant in bulk deposition and soil samples, where it accounted for more than 75% of total PBDEs. In atmosphere, D₁₀BDE was detected in three of five samples, and the ratio of D₁₀BDE to total PBDEs was smaller than that in the bulk deposition and soil samples. Similar results, in which D₁₀BDE was predominantly detected, were reported in other studies in Japan (Watanabe et al., 1995; Ohta et al., 2002).

However, these homologue profiles differ from those of studies conducted in North America. Strandberg et al. (2001) measured PBDE congeners in the atmosphere at sites near the Great Lakes and reported that BDE-47 and -99 were predominantly detected but D₁₀BDE was scarcely detected (only detected at trace levels (sub-pgm⁻³) in the filter samples from Chicago). They pointed out that this congener composition resembles the penta-BDE commercial product. Alae et al. (2001) measured PBDEs in the atmosphere in Arctic and Great Lakes air. They reported that P₅BDEs had the highest concentration followed by T₄BDEs; H₆BDEs had the third highest concentration; and O₈BDEs, N₉BDEs and D₁₀BDE were not detected. In European studies, Greenpeace Netherlands (Greenpeace Netherlands, 2003; Peters, 2003) measured PBDEs in rainwater collected in the Netherlands and reported that D₁₀BDE was not detected.

It is not well known why D₁₀BDE was detected only in Japanese samples. However, these differences in atmospheric PBDE profiles between Japan and North America may reflect differences in the demand for PBDE products in the respective regions. For example,

Table 2
Concentration of PBDEs, PBDD/Fs and MoBPXDD/Fs

Atmosphere [pgm ⁻³]		Aug. 17–24, 2000		Aug. 24–31, 2000		Jan. 22–29, 2001		Jan. 29–Feb. 5, 2001		Sept. 4–7, 2001		
	Part.	Gas	Part.	Gas	Part.	Gas	Part.	Gas	Part.	Gas	Part.	Gas
PBDEs												
244'-(BDE-28)	<0.2	2.2	<0.2	1.1	<0.01	0.25	0.023	0.33	<0.03	0.73	<0.03	0.73
22'45'-(BDE-49)	<0.2	1.9	<0.2	0.50	0.047	0.14	0.13	0.14	<0.03	0.38	<0.03	0.38
22'44'-(BDE-47)	<0.2	23	<0.2	1.3	0.21	0.38	0.44	0.34	<0.03	1.1	<0.03	1.1
23'44'-(BDE-66)	<0.2	1.2	<0.2	0.52	0.050	0.064	0.11	0.059	<0.03	0.22	<0.03	0.22
33'44'-(BDE-77)	<0.2	<0.4	<0.2	0.26	0.014	<0.02	0.026	<0.02	<0.03	<0.06	<0.03	<0.06
22'44'6'-(BDE-100)	<0.2	3.6	<0.2	0.27	0.073	0.017	0.11	0.013	<0.03	0.052	<0.03	0.052
22'44'5'-(BDE-99)	0.9	19	<0.2	1.2	0.38	0.056	0.59	0.048	0.048	0.33	<0.1	0.33
22'44'56'-(BDE-154)	<0.6	1.2	<0.6	0.87	0.055	<0.06	0.098	<0.06	<0.1	<0.2	<0.1	<0.2
22'44'55'-(BDE-153)	0.76	1.1	<0.6	0.97	0.071	<0.06	0.13	<0.06	<0.1	<0.2	<0.1	<0.2
22'344'5'6'-(BDE-183)	2.4	<1.2	0.94	4.0	0.14	<0.06	0.19	<0.06	<0.1	<0.2	<0.1	<0.2
M₁BDEs												
M ₁ BDEs	<2	<4	<2	<4	<0.1	0.63	<0.1	0.55	<0.3	0.36	<0.3	0.36
D₂BDEs												
D ₂ BDEs	<0.2	2.4	<0.2	1.0	<0.01	0.85	0.012	1.3	<0.03	3.1	<0.03	3.1
T₃BDEs												
T ₃ BDEs	<0.2	4.0	<0.2	2.2	0.023	0.75	0.064	1.2	<0.03	2.0	<0.03	2.0
T₄BDEs												
T ₄ BDEs	<0.2	26	<0.2	2.5	0.31	0.60	0.72	0.59	0.032	1.7	0.032	1.7
P₃BDEs												
P ₃ BDEs	0.90	23	<0.2	2.5	0.59	0.093	0.94	0.081	0.070	0.51	0.070	0.51
H₆BDEs												
H ₆ BDEs	0.76	2.2	<0.6	3.1	0.21	<0.06	0.40	<0.06	<0.1	<0.2	<0.1	<0.2
H₇BDEs												
H ₇ BDEs	2.4	<1.2	0.94	4.0	0.23	<0.06	0.37	<0.06	0.10	<0.2	0.10	<0.2
O₈BDEs												
O ₈ BDEs	1.8	<1.2	<0.6	0.67	0.15	<0.06	0.26	<0.06	0.16	<0.2	0.16	<0.2
N₉BDEs												
N ₉ BDEs	1.6	<1.2	<0.6	<1.2	0.033	<0.06	0.053	<0.06	0.26	<0.2	0.26	<0.2
D₁₀BDE (BDE-209)												
D ₁₀ BDE (BDE-209)	15	<20	48	<20	<0.5	<1	<0.5	<1	3.7	<4	3.7	<4
Total PBDEs ^a	22	58	49	16	1.5	2.9	2.8	3.7	4.3	7.7	4.3	7.7
PBDDs												
M ₁ BDDs	<0.002	0.0082	<0.002	0.0026	<0.002	0.0034	<0.002	0.0025	<0.01	<0.02	<0.01	<0.02
D ₂ BDDs	<0.002	0.0076	<0.002	0.0045	<0.002	<0.004	<0.002	0.0038	<0.01	<0.02	<0.01	<0.02
T ₃ BDDs	0.0021	0.017	<0.002	0.0036	<0.002	0.0035	0.0040	0.0067	<0.01	<0.02	<0.01	<0.02
T ₄ BDDs	0.026	0.054	0.0040	0.0059	0.044	0.0031	0.094	0.0040	<0.01	<0.02	<0.01	<0.02
P ₃ BDDs	<0.02	<0.04	<0.02	<0.04	<0.02	<0.04	<0.02	<0.04	<0.1	<0.2	<0.1	<0.2
H ₆ BDDs	<0.04	<0.08	<0.04	<0.08	<0.04	<0.08	<0.04	<0.08	<0.2	<0.4	<0.2	<0.4
H ₇ BDDs	<0.1	<0.2	<0.1	<0.2	<0.1	<0.2	<0.1	<0.2	<0.5	<1	<0.5	<1
O ₈ BDD	<1	<2	<1	<2	<1	<2	<1	<2	<5	<10	<5	<10
PBDFs												
M ₁ BDFs	0.011	1.2	0.0055	0.63	0.0029	0.38	0.0042	0.26	<0.01	0.51	<0.01	0.51

22'44'-(BDE-47)	9700	1000	560	2700	8200	320	220	1200	790	21
23'44'-(BDE-66)	3200	320	180	1100	2900	200	<100	340	<300	4.9
33'44'-(BDE-77)	460	29	<20	270	510	<100	<100	<300	<300	0.65
22'44'6-(BDE-100)	600	84	54	270	850	<100	<100	<300	<300	2.5
22'44'5-(BDE-99)	12000	920	520	4500	13000	280	<100	2000	510	22
22'44'56'-(BDE-154)	480	<60	<60	350	820	<300	<100	<800	<800	13
22'44'55'-(BDE-153)	2400	150	100	1100	2900	800	<300	<800	<800	25
22'344'5'6-(BDE-183)	4500	150	<60	430	900	5300	<300	<800	<800	120
M ₁ BDEs	<200	<200	<200	<500	<500	<1000	<1000	<3000	<3000	<20
D ₂ BDEs	30	69	28	<50	<50	120	250	<300	<300	11
T ₃ BDEs	340	300	130	<50	320	300	430	430	<300	2.0
T ₄ BDEs	17000	1500	850	4500	14000	740	310	1600	970	40
F ₅ BDEs	17000	1200	700	6900	19000	340	<100	2500	610	24
H ₆ BDEs	3200	210	180	1900	4300	1100	<300	840	<800	50
H ₇ BDEs	5200	170	220	430	900	6400	<300	1100	<800	150
O ₈ BDEs	3600	280	390	<200	<200	2800	<300	2400	<800	95
N ₉ BDEs	16000	430	420	<200	<200	400	<300	5300	<800	80
D ₁₀ BDE (BDE-209)	1500000	24000	8300	13000	4500	8000	<5000	120000	140000	9100
Total PBDEs ^a	1600000	28000	11000	27000	43000	20000	990	130000	140000	9600
PBDDs										
M ₁ BDDs	<2	<2	<2	<5	<5	<10	<10	<30	<30	<1
D ₂ BDDs	<2	<2	<2	<5	<5	<10	<10	<30	<30	<1
T ₃ BDDs	<2	<2	<2	<5	<5	<10	<10	<30	<30	1.1
T ₄ BDDs	9.0	3.9	<2	<5	7.4	<10	<10	<30	<30	1.3
P ₃ BDDs	<20	<20	<20	<50	<50	<100	<100	<300	<300	<10
H ₆ BDDs	<40	<40	<40	<100	<100	<200	<200	<500	<500	<20
H ₇ BDDs	<100	<100	<100	<300	<300	<500	<500	<1000	<1000	<50
O ₈ BDD	<1000	<1000	<1000	<3000	<3000	<5000	<5000	<10000	<10000	<500
PBDFs										
M ₁ BDFs	11	7.9	6.5	10	7.2	18	16	61	33	2.4
D ₂ BDFs	110	19	83	29	29	<10	110	<30	140	23
T ₃ BDFs	770	63	36	230	430	27	<10	<30	<30	54
T ₄ BDFs	820	73	13	290	610	150	<10	<30	<30	70
P ₃ BDFs	140	<20	<20	120	180	<100	<100	<300	<300	71
H ₆ BDFs	150	<40	<40	<100	<100	<200	<200	790	<500	61
H ₇ BDFs	190	<100	<100	<300	<300	<500	<500	<1000	<1000	<50
O ₈ BDF	<1000	<1000	<1000	<3000	<3000	<5000	<5000	<10000	<10000	<500
Total PBDD/Fs ^a	2200	170	140	680	1300	200	130	850	170	280

Table 2 (continued)

	Bulk deposition [$\mu\text{g m}^{-2} \text{d}^{-1}$]			Rain [$\mu\text{g l}^{-1}$]			Soil [$\mu\text{g g}^{-1}$]	
	Aug. 17–31, 2000	Jan. 22–Feb. 5, 2001	Sept. 4–18, 2001	Aug. 17–31, 2000, 1.9 l ^b	Jan. 26–Feb. 5 ^c , 2001, 5.3 l ^b	Sept. 4–18, 2001, 9.4 l ^b	Sept. 4–18, 2001, 9.4 l ^b	Aug. 17, 2000
	Part.	Dissol.	Part.	Part.	Dissol.	Part.	Dissol.	Part.
<i>MoBPeXDDs</i>								
Br ₁ Cl ₃ DDs	<2	<2	<10	<5	<10	<100	<100	<4
Br ₁ Cl ₄ DDs	<2	<2	<10	<5	<10	<100	<100	<4
Br ₁ Cl ₅ DDs	<4	32	27	<10	<20	<300	<300	<8
Br ₁ Cl ₆ DDs	<4	<4	<50	<10	<20	<700	<700	<8
Br ₁ Cl ₇ DDs	<10	<10	<100	<30	<50	<1000	<1300	<10
<i>MoBPeXDFs</i>								
Br ₁ Cl ₃ DFs	<2	<2	<10	<5	<10	<100	<100	24
Br ₁ Cl ₄ DFs	<2	<2	<10	<5	<10	<100	<100	17
Br ₁ Cl ₅ DFs	<4	<4	<20	<10	<20	<300	<300	11
Br ₁ Cl ₆ DFs	<4	<4	<50	<10	<20	<700	<700	<8
Br ₁ Cl ₇ DFs	<10	<10	<100	<30	<50	<1000	<1000	<10
Total MoBPeXDD/Fs ^a	ND	32	27	ND	ND	ND	360	52
<i>PCDD/Fs</i>								
Total (sum of 4–8 Cl)	1600	880	NA ^d	1300	1000	1900	NA	540
TEQ	22	13	NA	13	11	20	NA	11
Rain [$\mu\text{g m}^{-2} \text{d}^{-1}$] ^e								
Aug. 17–31, 2000, 1.9 l ^b			Jan. 26–Feb. 5 ^c , 2001, 5.3 l ^b			Sept. 4–18, 2001, 9.4 l ^b		
Part.	Dissol.	Part.	Dissol.	Part.	Dissol.	Part.	Dissol.	Part.
<20	120	<20	27	<20	<20	<20	<20	<20
190	640	39	<20	39	<20	89	60	60
1000	3100	60	42	60	89	26	<20	<20
410	1100	38	<20	38	<20	<20	<20	<20
100	190	<20	<20	<20	<20	<20	<20	<20
100	320	<20	<20	<20	<20	150	39	<60
1700	4900	52	<60	<60	<60	<60	<60	<60
130	310	150	<60	<60	<60	<60	<60	<60
430	1100	1000	<60	<60	<60	<60	<60	<60
160	340	1000	<60	<60	<60	<60	<60	<60
<i>PBDEs</i>								
244'-(BDE-28)	<20	120	<20	27	<20	<20	<20	<20
22'45'-(BDE-49)	190	640	39	<20	<20	89	60	60
22'44'-(BDE-47)	1000	3100	60	42	60	26	<20	<20
23'44'-(BDE-66)	410	1100	38	<20	<20	<20	<20	<20
33'44'-(BDE-77)	100	190	<20	<20	<20	<20	<20	<20
22'44'6'-(BDE-100)	100	320	<20	<20	<20	150	39	<60
22'44'5'-(BDE-99)	1700	4900	52	<60	<60	<60	<60	<60
22'44'56'-(BDE-154)	130	310	150	<60	<60	<60	<60	<60
22'44'55'-(BDE-153)	430	1100	1000	<60	<60	<60	<60	<60
22'344'5'6'-(BDE-183)	160	340	1000	<60	<60	<60	<60	<60

M ₁ BDEs	<200	<200	<200	<200	<200	<200	<200	<200	<200
D ₂ BDEs	<20	22	47	81	120	140	160	170	<200
T ₃ BDEs	<20	57	81	59	20	65	210	340	<20
T ₄ BDEs	1700	5400	7000	1600	340	160	340	160	74
P ₅ BDEs	2600	7000	1600	700	160	340	160	340	46
H ₆ BDEs	700	1600	340	160	340	160	340	160	<60
H ₇ BDEs	160	340	160	340	160	340	160	340	<60
O ₈ BDEs	<60	530	<60	180	<60	180	<60	400	<60
N ₉ BDEs	<60	76	<60	400	11000	11000	11000	11000	<60
D ₁₀ BDE (BDE-209)	4800	1700	1500	9400	11000	11000	11000	11000	11000
Total PBDEs ^a	10000	16000	3800	190	10000	11000	11000	11000	11000

<i>PBDDs</i>									
M ₁ BDDs	<2	<2	<2	<2	<2	<2	<2	<2	<2
D ₂ BDDs	<2	<2	<2	<2	<2	<2	<2	<2	<2
T ₃ BDDs	<2	<2	<2	<2	<2	<2	<2	<2	<2
T ₄ BDDs	<2	2.8	<2	<2	<2	<2	<2	<2	<2
P ₅ BDDs	<20	<20	<20	<20	<20	<20	<20	<20	<20
H ₆ BDDs	<40	<40	<40	<40	<40	<40	<40	<40	<40
H ₇ BDDs	<100	<100	<100	<100	<100	<100	<100	<100	<100
O ₈ BDD	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000

<i>PBDFs</i>									
M ₁ BDFs	3.9	2.7	3.4	3.1	4.6	2.5	2.5	2.5	2.5
D ₂ BDFs	11	11	<2	21	<2	<2	<2	<2	11
T ₃ BDFs	87	160	5.1	<2	<2	<2	<2	<2	<2
T ₄ BDFs	110	230	29	<2	<2	<2	<2	<2	<2
P ₅ BDFs	45	66	<20	<20	<20	<20	<20	<20	<20
H ₆ BDFs	<40	<40	<40	<40	60	<40	<40	<40	<40
H ₇ BDFs	<100	<100	<100	<100	<100	<100	<100	<100	<100
O ₈ BDF	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000
Total PBDD/Fs ^a	260	470	38	24	64	14	14	14	14

<i>MoBPXDDs</i>									
Br ₁ Cl ₃ DDs	<2	<2	<2	<2	<10	<10	<10	<10	<10
Br ₁ Cl ₄ DDs	<2	<2	<2	<2	<10	<10	<10	<10	<10
Br ₁ Cl ₅ DDs	<4	<4	<4	<4	<20	<20	<20	<20	27
Br ₁ Cl ₆ DDs	<4	<4	<4	<4	<50	<50	<50	<50	<50
Br ₁ Cl ₇ DDs	<10	<10	<10	<10	<100	<100	<100	<100	<100

<i>MoBPXDFs</i>									
Br ₁ Cl ₃ DFs	<2	<2	<2	<2	<10	<10	<10	<10	<10
Br ₁ Cl ₄ DFs	<2	<2	<2	<2	<10	<10	<10	<10	<10

Table 2 (continued)

	Rain [$\text{pgm}^{-2}\text{d}^{-1}$] ^a					
	Aug. 17–31, 2000, 1.9 l ^b		Jan. 26–Feb. 5, 2001, 5.3 l ^b		Sept. 4–18, 2001, 9.4 l ^b	
	Part.	Dissol.	Part.	Dissol.	Part.	Dissol.
Br ₁ Cl ₃ DFs	<4	<4	<4	<4	<20	<20
Br ₁ Cl ₄ DFs	<4	<4	<4	<4	<50	<50
Br ₁ Cl ₇ DFs	<10	<10	<10	<10	<100	<100
Total MoBPXDD/Fs ^a	ND	ND	ND	ND	ND	27
PCDD/Fs						
Total (sum of 4–8 Cl)	470	380	350	63	NA ^d	NA
TEQ	5.0	4.1	3.8	ND	NA	NA

^a The value that homologue concentration was below the quantification limit was regarded as 0.

^b Rainwater volume.

^c Sampling period was 10 days, because of experimental problem.

^d Not analysed.

^e Converted unit from [pgl^{-1}] to [$\text{pgm}^{-2}\text{d}^{-1}$] with values of rainwater volume and cross section of rain sampler.

penta-BDE products are more in demand in North America than in Asia (BSEF, 2000).

3.3. Concentrations and homologue profiles of PBDD/Fs and MoBPXDD/Fs

In all samples, PBDFs were predominant and PBDDs were detected only at trace levels. Hepta- and octa-BDD/Fs were not detected in almost all samples. MoBPXDDs and MoBPXDFs were present at the same levels in the atmosphere. Watanabe et al. (1995) measured PBDD/Fs and MoBPXDD/Fs in airborne dust in Osaka, Japan. They reported that the concentrations of PBDFs (sum of tetra- to hexa-BDFs) were 4.2–17 pgm^{-3} -air and that PBDDs were not detected. They also reported that semiquantitative values (due to the lack of standards) of MoBPXDDs and MoBPXDFs (sum of tetra- to octa-halogenated homologues) were 4–22 pgm^{-3} -air and 2–23 pgm^{-3} -air, respectively. Homologue profiles in the present study were similar to those found by Watanabe et al. (1995). Ohta et al. (2002) reported that PBDD/Fs (sum of 11 congeners) and MoBPXDD/Fs (sum of eight congeners) in the atmosphere from the Osaka district were 0.036 and 0.0023 pgm^{-3} , respectively.

3.4. Atmospheric gas-particle partitioning

Semivolatile organic compounds in the atmosphere exist in the gas phase or particulate-associated phase. The partitioning of compounds between these atmospheric phases is an important factor in their subsequent fate, transport and degradation. Gas-to-particulate partitioning is controlled by vapor pressure (VP) of the compounds (Bidleman, 1988). VP depends on temperature; VP increases with increasing temperature. It is also known that VP of PCDD/Fs decreases with increasing chlorine number (Shiu and Ma, 2000). From observing the gas-to-particulate partitioning of atmospheric PCDD/Fs, it is known that particulate phase fraction (f_p) of PCDD/Fs increases with increasing chlorine number and with decreasing temperature (Lohmann and Jones, 1998).

For the physico-chemical properties of the brominated compounds, VP of PBDEs (Tittlemier and Tomy, 2000; Wong et al., 2001) and PBDD/Fs (Rordorf et al., 1990) are known to decrease with increasing bromine number. For the relationship of VP among these brominated compounds, Rordorf et al. (1990) reported that VP of PBDD/Fs was lower than that of PCDD/Fs with the same halogen number. Subcooled liquid vapor pressure of PBDEs (Tittlemier and Tomy, 2000; Wong et al., 2001) seems to be lower than that of PCDD/Fs (Shiu and Ma, 2000) with the same halogen number. From the physical-chemical properties of these brominated compounds, f_p of PBDEs, PBDD/Fs and MoBPXDD/Fs is expected to increase with increasing halogen

number and with decreasing temperature. It is also expected that f_p of these brominated compounds is higher than that of PCDD/Fs.

The f_p of the brominated compounds measured in this study is shown in Table 3. As expected, f_p of

PBDEs, PBDFs and MoBPXDD/Fs increased with increasing halogen number, and was higher in samples collected in winter than in those collected in summer. Moreover, f_p of PBDFs and MoBPXDFs was higher than that of PCDFs with the same halogen number,

Table 3
Fraction of particulate phase in the atmosphere (f_p)

	Aug. 17–24, 2000	Aug. 24–31, 2000	Jan. 22–29, 2001	Jan. 29–Feb. 5, 2001	Sept. 4–7, 2001
BDE-28	< ^a	<	<	6.5	<
BDE-49	<	<	25	48	<
BDE-47	<	<	36	56	<
BDE-66	<	<	44	65	<
BDE-77	^b	<	>	>	<
BDE-100	<	<	81	89	<
BDE-99	4.5	<	87	92	13
BDE-154	<	<	>	>	<
BDE-153	41	<	>	>	<
BDE-183	> ^c	19	>	>	<
T ₃ BDEs	<	<	3.0	5.1	<
T ₄ BDEs	<	<	34	55	1.8
P ₃ BDEs	3.8	<	86	92	12
H ₆ BDEs	26	<	>	>	<
H ₇ BDEs	>	19	>	>	>
M ₁ BDFs	0.91	0.87	0.76	1.6	<
D ₂ BDFs	1.3	1.4	1.9	2.1	<
T ₃ BDFs	5.3	5.9	32	42	<
T ₄ BDFs	25	34	95	96	27
P ₅ BDFs	70	83	>	>	>
H ₆ BDFs	72	>	>	>	>
Br ₁ Cl ₃ DDs	<	<	16	44	<
Br ₁ Cl ₄ DDs	<	<	>	>	<
Br ₁ Cl ₅ DDs	63	52	>	>	>
Br ₁ Cl ₆ DDs	>	>	>	>	>
Br ₁ Cl ₇ DDs	>	>	>	>	>
Br ₁ Cl ₃ DFs	<	<	29	44	<
Br ₁ Cl ₄ DFs	23	<	92	93	<
Br ₁ Cl ₅ DFs	63	>	>	>	>
Br ₁ Cl ₆ DFs	>	>	>	>	>
Br ₁ Cl ₇ DFs	>	>	>	>	>
T ₄ CDDs	5.5	5.2	15	12	7.1
P ₅ CDDs	23	22	78	72	25
H ₆ CDDs	47	43	98	98	68
H ₇ CDDs	85	80	>	>	94
O ₈ CDD	96	95	>	>	>
T ₄ CDFs	6.2	4.8	14	15	6.3
P ₅ CDFs	20	14	68	70	22
H ₆ CDFs	43	38	96	97	60
H ₇ CDFs	76	73	99.2	99.6	91
O ₈ CDF	92	95	>	>	>

^a <: Particulate phase concentration was below the quantification limit.

^b blank: Concentrations of both phase were below the quantification limit.

^c >: Gaseous phase concentration was below the quantification limit.

and f_p of PBDEs was lower than that of PBDFs with the same bromine number.

The same results were observed in the study of Strandberg et al. (2001); they reported that the percentages of the gas phase were about 80% for BDE-47, about 55–65% for BDE-100 and -99, and about 30% for BDE-154 and -153. Similar results were also observed in the study of Harless et al. (1992). They conducted experiments for evaluating air samplers and an analytical method for PBDD/Fs, MoBPXDD/Fs and PCDD/Fs in the atmosphere. In their study, air samplers equipped with quartz fiber filter (QFF) and polyurethane foam (PUF) were operated to load atmospheric particulate matter to the QFF. Then, the QFF containing particulate matter loadings was spiked with a solution of PBDD/Fs, monobromo-trichloro DD/Fs and PCDD/Fs, and the air samplers were operated for another 24 h. QFF and PUF were then analyzed and the fraction of spiked compounds retained by the QFF was determined. In the results, the fraction retained by the QFF was higher for PBDD/Fs than that of PCDD/Fs with the same halogen number.

3.5. Correlation between bulk depositions and atmospheric concentrations

Deposition of PCDD/Fs can occur in dry gaseous form (gas phase PCDD/Fs adsorption at the air–surface interface), dry particulate form (sedimentation of particles that associate with PCDD/Fs) and wet form (scavenging of particles and gas phase PCDD/Fs by raindrops). Horstmann and McLachlan (1997) showed experimentally that the bulk deposition sampler of a glass funnel collected almost exclusively PCDD/Fs associated with sedimenting particles and wet deposition, with little contribution from dry gaseous deposition or impacting/diffusing particles. From this, it is expected that values of bulk deposition of brominated compounds also correlate positively with atmospheric particulate phase concentrations.

Atmospheric particulate phase concentration and bulk deposition of each homologue of the brominated compounds measured in this study are plotted in Fig. 1. As seen in the figure, bulk depositions correlate positively with atmospheric particulate phase concentrations.

On the other hand, there was very weak correlation between atmospheric gaseous phase concentration and bulk deposition (Fig. 2).

3.6. Correlations among brominated compounds in the atmosphere

In this section the relationships among atmospheric concentrations of PBDEs, PBDD/Fs, MoBPXDD/Fs, and PCDD/Fs are discussed.

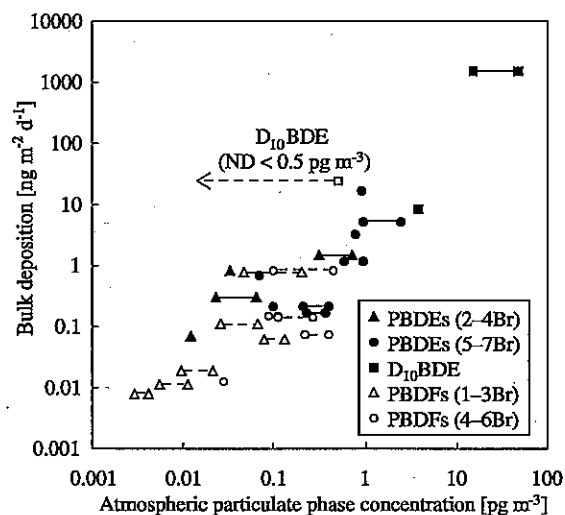


Fig. 1. Plot of bulk deposition and atmospheric particulate concentration of PBDEs and PBDFs. An open square means the value that atmospheric particulate phase concentration was ND (0.5 pg m^{-3}) and bulk deposition was $24 \text{ ng m}^{-2} \text{ d}^{-1}$.

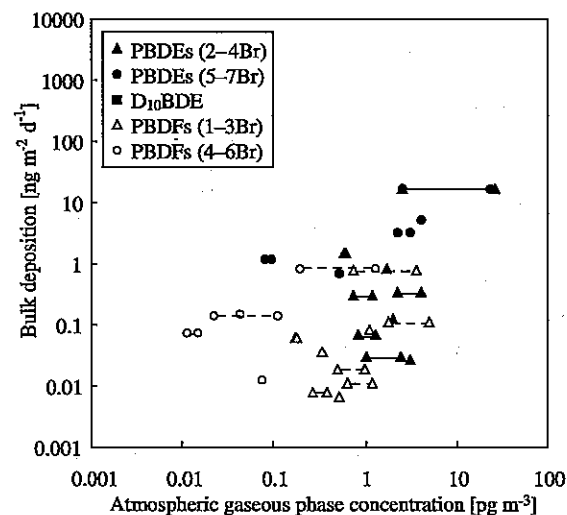


Fig. 2. Plot of bulk deposition and atmospheric gaseous concentration of PBDEs and PBDFs.

The atmospheric concentrations of PBDEs, PBDD/Fs, MoBPXDD/Fs, and PCDD/Fs are plotted in Fig. 3. In Fig. 3 the levels of MoBPXDD/Fs increases with increasing PCDD/Fs levels. From this tendency, it seems to be that the level of MoBPXDD/Fs correlates positively with that of PCDD/Fs. There would be a large degree of uncertainty because of the very limited data however, this relationship has been previously observed in waste incineration samples. Yoneda et al. (2001) investigated the emission of brominated dioxins during

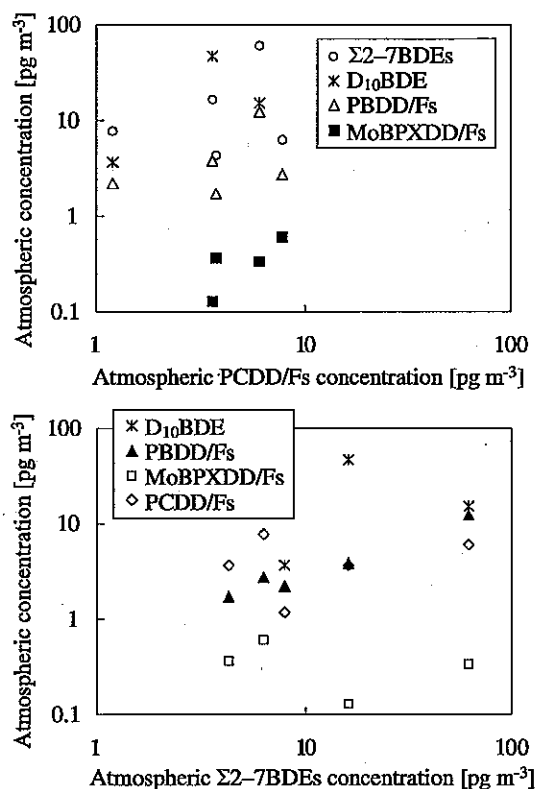


Fig. 3. Relationship between PBDEs, PBDD/Fs, MoBPXDD/Fs and PCDD/Fs in the atmosphere. $\Sigma 2-7$ PBDEs: the sum of di- to hepta-brominated homologues. PBDD/Fs: the sum of mono- to hexa-brominated homologues. MoBPXDD/Fs and PCDD/Fs: the sum of tetra- to octa-halogenated homologues.

municipal and industrial solid waste incineration in Japan and reported that MoBPXDD/F levels correlated with PCDD/F levels in emission gas and that MoBPXDD/F levels were about 10–20% of PCDD/F levels. Watanabe and Kawano (1997) reported that the level of MoBPXDDs in airborne dust correlates positively with that of PCDDs. In addition, we (Sakai et al., 2001) previously combusted waste television casings and resin pellets containing brominated flame retardants in a rotary kiln furnace and found a correlation between the level of MoBPXDD/Fs and PCDD/Fs in the waste gas before gas treatment. These results suggest that one of the sources of MoBPXDD/Fs in the atmosphere is the same as that of PCDD/Fs, which is incineration byproduct.

Fig. 3 also shows that the PBDD/Fs level seems to correlate positively with the sum of D₂BDEs to H₇BDEs level. As mentioned before, PBDFs were predominant in PBDD/Fs in the atmosphere. For homologue profiles of PBDD/Fs, it is known that PBDFs are predominant in incineration byproducts of polymeric matrices containing D₁₀BDE (Lenoir et al., 1994). Similar profiles are

known for PBDD/Fs in PBDE products (as an impurity) and in PBDD/Fs formed during the production processes of plastics containing PBDEs (WHO, 1998). These relationships suggest that the PBDD/Fs in the atmosphere relate to PBDEs, which is an impurity of PBDE products, or formed by the manufacture or combustion of plastics containing PBDEs. Fig. 3 also shows that the level of PBDFs does not correlate with that of PCDD/Fs. This suggests that the contribution of waste incineration emission gas to atmospheric PBDD/Fs is small.

Concentrations of atmospheric PBDEs were higher in the samples collected in summer than those collected in winter. This suggests that the level of atmospheric PBDEs is controlled by partitioning of PBDEs between the air and environmental surface (e.g. soil). This agrees well with the study of Gouin et al. (2002). They suggest that at warmer temperatures PBDEs are driven from the surface to the air due to the temperature dependence of physico-chemical properties, as determined from the result of Clausius–Clapeyron plots.

There is no known plant that manufactures BFRs near the sampling site of the present study. Details of the source of atmospheric PBDEs are still unknown and further investigation is necessary.

References

- Alaee, M., Cannon, C., Muir, D., Blanchard, P., Brice, K., Fellin, P., 2001. Spatial distribution and seasonal variation of PBDEs in Arctic and Great Lakes air. *Organohalogen Compd.* 52, 26–29.
- Andersson, O., Blomkvist, G., 1981. Polybrominated aromatic pollutants in fish in Sweden. *Chemosphere* 10, 1051–1060.
- Bidleman, T.F., 1988. Atmospheric processes. *Environ. Sci. Technol.* 22, 361–367.
- BSEF (Bromine Science and Environmental Forum), 2000. An introduction to brominated flame retardants. October 19, 2000. Downloaded from website <http://www.bscef.com/> in July 2002.
- Chatkittikunwong, W., Creaser, C.S., 1994. Bromo-, bromo-chloro- and chloro-dibenzo-*p*-dioxins and dibenzofurans in incinerator fly ash. *Chemosphere* 29, 559–566.
- Darnerud, P.O., Eriksen, G.S., Jóhannesson, T., Larsen, P.B., Viluksela, M., 2001. Polybrominated diphenyl ethers: occurrence, dietary exposure, and toxicology. *Environ. Health Perspect.* 109 (Suppl. 1), 49–68.
- de Wit, C.A., 2002. An overview of brominated flame retardants in the environment. *Chemosphere* 46, 583–624.
- Gouin, T., Thomas, O., Cousins, I., Barber, J., Mackay, D., Jones, K.C., 2002. Air–surface exchange of polybrominated diphenyl ethers and polychlorinated biphenyls. *Environ. Sci. Technol.* 36, 1426–1434.
- Greenpeace Netherlands, 2003. Onzichtbare chemie. Downloaded from website http://www.greenpeace.nl/news/details?item_id=126608 in July 2003 (in Dutch).
- Harless, R.L., Lewis, R.G., McDaniel, D.D., Gibson, J.F., Dupuy Jr., A.E., 1992. Evaluation of a sampling and

- analysis method for determination of polyhalogenated dibenzo-*p*-dioxins and dibenzofurans in ambient air. *Chemosphere* 25, 1317–1322.
- Horstmann, M., McLachlan, M.S., 1997. Sampling bulk deposition of polychlorinated dibenzo-*p*-dioxins and dibenzofurans. *Atmos. Environ.* 31, 2977–2982.
- Jansson, B., Asplund, L., Olsson, M., 1987. Brominated flame retardants—ubiquitous environmental pollutants. *Chemosphere* 16, 2343–2349.
- JIS (Japan Industrial Standards), 1999. JIS K0312: Method for determination of tetra- through octa-chlorodibenzo-*p*-dioxins, tetra- through octa-chlorodibenzofurans and coplanar polychlorobiphenyls in industrial water and wastewater.
- Kagaku Kogyo Nippo Co. Ltd., 2001. Kagaku Kogyo Nenkan 2001 (in Japanese).
- Lee, R.G.M., Thomas, G.O., Jones, K.C., 2002. Atmospheric concentrations of PBDEs in western Europe. *Organohalogen Compd.* 58, 193–196.
- Lenoir, D., Zier, B., Bieniek, D., Kettrup, A., 1994. The influence of water and metals on PBDD/F concentration in incineration of decabromobiphenyl ether in polymeric matrices. *Chemosphere* 28, 1921–1928.
- Lohmann, R., Jones, K.C., 1998. Dioxins and furans in air and deposition: a review of levels, behaviour and processes. *Sci. Total Environ.* 219, 53–81.
- Meironyté, D., Norén, K., 2001. Polybrominated diphenyl ethers in Swedish human milk. The follow-up study. In: Proceedings of the 2nd International Workshop on Brominated Flame Retardants. May 14–16, 2001, Stockholm, pp. 303–305.
- Norén, K., Meironyté, D., 1998. Contaminants in Swedish human milk. Decreasing levels of organochlorine and increasing levels of organobromine compounds. *Organohalogen Compd.* 38, 1–4.
- Norén, K., Meironyté, D., 2000. Certain organochlorine and organobromine contaminants in Swedish human milk in perspective of past 20–30 years. *Chemosphere* 40, 1111–1123.
- Ohta, S., Nakao, T., Nishimura, H., Okumura, T., Aozasa, O., Miyata, H., 2002. Contamination levels of PBDEs, TBBPA, PCDDs/DFs, PBDDs/DFs and PXDDs/DFs in the environment of Japan. *Organohalogen Compd.* 57, 57–60.
- Peters, R.J.B., 2003. Hazardous Chemicals in Precipitation. TNO-report R2003/198. Downloaded from website http://www.greenpeace.nl/news/details?item_id=126608 in September 2003.
- Pijnenburg, A.M.C.M., Everts, J.W., de Boer, J., Boon, J.P., 1995. Polybrominated biphenyl and diphenylether flame retardants: analysis, toxicity, and environmental occurrence. *Rev. Environ. Contam. Toxicol.* 141, 1–26.
- Rahman, F., Langford, K.H., Scrimshaw, M.D., Lester, J.N., 2001. Polybrominated diphenyl ether (PBDE) flame retardants. *Sci. Total Environ.* 275, 1–17.
- Rordorf, B.F., Sarna, L.P., Webster, G.R.B., Safe, S.H., Safe, L.M., Lenoir, D., Schwind, K.H., Hutzinger, O., 1990. Vapor pressure measurements on halogenated dibenzo-*p*-dioxins and dibenzofurans. An extended data set for a correlation method. *Chemosphere* 20, 1603–1609.
- Sakai, S., Watanabe, J., Honda, Y., Takatsuki, H., Aoki, I., Futamatsu, M., Shiozaki, K., 2001. Combustion of brominated flame retardants and behavior of its byproduct. *Chemosphere* 42, 519–531.
- Schäfer, W., Ballschmiter, K., 1986. Monobromo-polychloro-derivatives of benzene, biphenyl, dibenzofurans and dibenzodioxins formed in chemical-waste burning. *Chemosphere* 15, 755–763.
- Schwind, K.H., Hosseinpour, J., Thoma, H., 1988. Brominated/chlorinated dibenzo-*p*-dioxins and dibenzofurans. *Chemosphere* 17, 1875–1884.
- Shiu, W.-Y., Ma, K.-C., 2000. Temperature dependence of physical-chemical properties of selected chemicals of environmental interest. II. Chlorobenzenes, polychlorinated biphenyls, polychlorinated dibenzo-*p*-dioxins, and dibenzofurans. *J. Phys. Chem. Ref. Data* 29, 387–462.
- Sovocool, G.W., Donnelly, J.R., Munslow, W.D., Vonnahme, T.L., Nunn, N.J., Tondeur, Y., Mitchim, R.K., 1989. Analysis of municipal incinerator fly ash for bromo- and bromochloro-dioxins, dibenzofurans, and related compounds. *Chemosphere* 18, 193–200.
- Strandberg, B., Dodder, N.G., Basu, I., Hites, R.A., 2001. Concentrations and spatial variations of polybrominated diphenyl ethers and other organohalogen compounds in Great Lakes air. *Environ. Sci. Technol.* 35, 1078–1083.
- Tittlemier, S.A., Tomy, G.T., 2000. Vapor pressures of six brominated diphenyl ether congeners. *Organohalogen Compd.* 47, 206–209.
- Vehlow, J., Bergfeldt, B., Jay, K., Seifert, H., Wanke, T., Mark, F.E., 2000. Thermal treatment of electrical and electronic waste plastics. *Waste Manage. Res.* 18, 131–140.
- Watanabe, I., Kawano, M., 1997. Brominated flame retardants and their environmental behavior. In: Proceedings of IEA-ISWGM/JWRF Seminar on Integrated Solid-Waste Management. September 24–25, 1997, Kyoto, pp. 11-1–11-12.
- Watanabe, I., Kashimoto, T., Tatsukawa, R., 1986. Confirmation of the presence of the flame retardant decabromobiphenyl ether in river sediment from Osaka, Japan. *Bull. Environ. Contam. Toxicol.* 36, 839–842.
- Watanabe, I., Kashimoto, T., Tatsukawa, R., 1987. Polybrominated biphenyl ethers in marine fish, shellfish and river and marine sediments in Japan. *Chemosphere* 16, 2389–2396.
- Watanabe, I., Kawano, M., Tatsukawa, R., 1995. Polybrominated and mixed polybromo/chlorinated dibenzo-*p*-dioxins and -dibenzofurans in the Japanese environment. *Organohalogen Compd.* 24, 337–340.
- WHO, 1994. Environmental Health Criteria 162: brominated diphenyl ethers. WHO, International Programme on Chemical Safety, Geneva.
- WHO, 1998. Environmental Health Criteria 205: polybrominated dibenzo-*p*-dioxins and dibenzofurans. WHO, International Programme on Chemical Safety, Geneva.
- Wong, A., Lei, Y.D., Alace, M., Wania, F., 2001. Vapor pressures of the polybrominated diphenyl ethers. *J. Chem. Eng. Data* 46, 239–242.
- Yoneda, K., Tani, A., Morita, M., Sakai, S., 2001. Emissions of polybrominated dioxins and related compounds from incineration plants and final disposal sites. In: Proceedings of the 10th Conference of Environmental Chemistry. May 23–25, Matsuyama, pp. 106–107 (in Japanese).