

**Polybrominated dibenzo-p-dioxins (PBDDs) and -dibenzofurans (PBDFs) in Atmospheric Air in Taiwan and Japan**

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In recent years, there have been reports stating that considerable amounts of brominated dibenzo-p-dioxins (PBDDs) and -dibenzofurans (PBDFs) are produced by the pyrolysis of brominated flame retardants, especially polybrominated biphenyl ethers (PBBEs)<sup>1</sup> or plastic matrix treated with PBBEs<sup>2</sup>. Although the biological effects of PBDDs and PBDFs have not yet been extensively studied, 2,3,7,8-tetrabromodibenzo-p-dioxin (2,3,7,8-T4BDD) was reported to elicit toxic effects on animals similar to that of the chlorinated analogue 2,3,7,8-T4CDD<sup>3,4</sup>.

Therefore, PBDDs/PBDFs have become a matter of great concern as potential environmental pollutants, in addition to PCDDs/PCDFs. These toxic contaminants can be formed through the presence of brominated flame retardants in a fire<sup>5</sup>, or by the incineration of products treated with PBBEs at the municipal waste incinerator (MWI)<sup>6</sup>. These contaminants can then possibly be spread into the environment.

Unfortunately, very little information exists on the environmental occurrences of PBDDs/PBDFs from which to assess their potential risk to the environment and to the public. Atmospheric air can be polluted directly by the incineration by-products from MWI and by smoke from combustion. This report presents the occurrence and the level of PBDDs/PBDFs and PBBEs in atmospheric air in Taiwan and Japan. Further, sources of PBDDs/PBDFs in the environment are also discussed.

**EXPERIMENTAL**

**Samples:** Sample collection was performed following the procedure of the Japanese Environmental Agency on PCDDs/PCDFs<sup>7</sup>. Air samples were collected for 24 hours at the flow rate of approximately 700L/min. A high volume sampler equipped with a quartz fiber filter (QFF) and polyurethane foam (PUF) was used. Total sample volume was about 1000m<sup>3</sup>. The atmospheric air samples were collected at two recycling resource areas in southern Taiwan and at an urban area in Osaka, Japan.

**Extraction and Cleanup:** QFF and PUF were individually Soxhlet extracted using acetone for over 20 hours. Each extract was combined and transferred to n-hexane. Internal standards such as <sup>13</sup>C-2,3,7,8-T4BDD together with <sup>13</sup>C-2,3,7,8-T4CDD/CDF were spiked to the hexane extract at this point. The sample extract was K-D concentrated and treated with concentrated sulfuric acid. The extract was cleaned up using a multilayer column (glass column: 20mm i.d. x 30cm). The column contained silica gel which was treated with silver nitrate, concentrated sulfuric acid and potassium hydroxide<sup>8</sup>. The column was eluted with 5% dichloromethane in n-hexane. This eluate was passed through a neutral alumina column and separated into two fractions. The first fraction eluted with 4% dichloromethane in n-hexane contained PBBEs and the second fraction eluted with 50% dichloromethane in n-hexane contained PBDDs/PBDFs and PCDDs/PCDFs. Each fraction was quantified using GC-HRMS. To avoid photodegradation of PBDDs/PBDFs<sup>9</sup>, amber color glassware were used.

**GC-HRMS Determination:** The Shimadzu-Kratos Concept 1 mass spectrometer interfaced with a Shimadzu GC-14A was used to perform the analysis. The mass spectrometer was operated in EI mode at a resolution of 10,000. The two most intensive ions per each congener group were monitored. A DB-5 capillary column (30m x 0.25mm i.d., 0.1um film thickness, J&W) was used. The column head pressure of helium gas was 0.63 kg/cm<sup>2</sup>. The oven temperature program was 140°C for 1 min., 15°C/min. to 230°C and then 4°C/min. to 290°C. The final hold time was 20 min.

### **RESULTS AND DISCUSSION**

The initial recovery test was performed using known spike concentrations of PBDDs/PBDFs and PBBEs to the new QFF prior to air sampling. The recoveries of the spiked compounds were >80%.

Figure 1 shows SIM chromatograms of tri- to hexa-BDDs/BDFs standard solution and the extract of the air sample collected in southern Taiwan. The SIM chromatograms of the sample extract obtained from the urban area in Japan showed a similar pattern to that in Taiwan.

Details of the results obtained are presented in Table 1. There exists no report on PBDDs/PBDFs in the atmospheric air in Japan. However, the Environmental Agency of Japan has studied PCDDs/PCDFs in atmospheric air samples from several sites in Japan. The present data is comparable to the urban area results reported by the environmental Agency<sup>10</sup>.

An earlier report by Harless et al.<sup>11</sup> showed that the ambient air collected in North Carolina, U.S.A. contained tetra- to hexa-BDFs with total residue levels of 0.13-0.71 pg/m<sup>3</sup>. The PBDFs levels found in Taiwan and Japan were about ten times higher than those found in the U.S.A. These higher levels may be attributable to the sampling sites in Taiwan, i.e. the two recycling resource centers, and in Japan, the urban area, Osaka. This may also be true since PCDDs/PCDFs levels in these two countries were also higher than the levels reported by Harless et al.<sup>11</sup>

PBDFs levels, especially tri- and tetra-BDF, in the air collected in Taiwan are generally higher than in Japan (Table 1). A similar trend was also found in PBBEs residue levels. On the other hand, PCDDs/PCDFs levels in air samples collected in Taiwan were almost the same or slightly lower than those in the air samples of Japan. It is discernible from the data that there exists some relationship between PBDFs levels and PBBEs levels in atmospheric air.

For the purpose of considering the source of PBDFs in air, one soil sample from an incineration field in Taiwan was analyzed. This sample included a large amount of ash from plastic materials. About 100 ng/g of total PBDFs were detected with PBBEs and PCDDs/PCDFs in this soil. The SIM chromatogram obtained in this sample extract was similar to those obtained in the atmospheric air collected in Taiwan. One of the major sources for PBDDs/PBDFs in the atmosphere has been identified as automobile exhaust<sup>12,13</sup>. It has been found in the present investigation that significant sources for PBDDs/PCDDs in the environment are the by-products of the pyrolysis of brominated flame retardants, especially PBBEs.

By mass chromatography of the soil extract described above, we detected a large number of mixed halogenated dibenzofurans (PHDFs) together with PBDFs and PCDDs/PCDFs. However, there were no mixed halogenated dibenzo-p-dioxins (PHDDs) in the same sample. PHDDs/PHDFs, especially monobromopolychlorinated congeners, have been recognized in the MWI fly ash<sup>14,15,16</sup>. In this case, the finding of many polybrominated mixed dibenzofurans as well as monobrominated congeners and no PHDDs, may give some information about the formation of PHDFs. That is, at first, PBDFs are produced and then PHDFs may be produced by substitution of chlorine, as described by Thoma et al.<sup>17</sup>

The stability of PBDDs/PBDFs in the particulate phase in atmosphere has been reported to be less degradable compared to solution phase<sup>18</sup>. Because of the rising annual consumption of brominated flame retardants in Japan, the emissions of PBDDs/PBDFs are expected to increase in the environment. Therefore, further investigation of the occurrence, distribution and behavior of PBDDs/PBDFs and mixed PHDDs/PHDFs as well as PCDDs/PCDFs are needed.

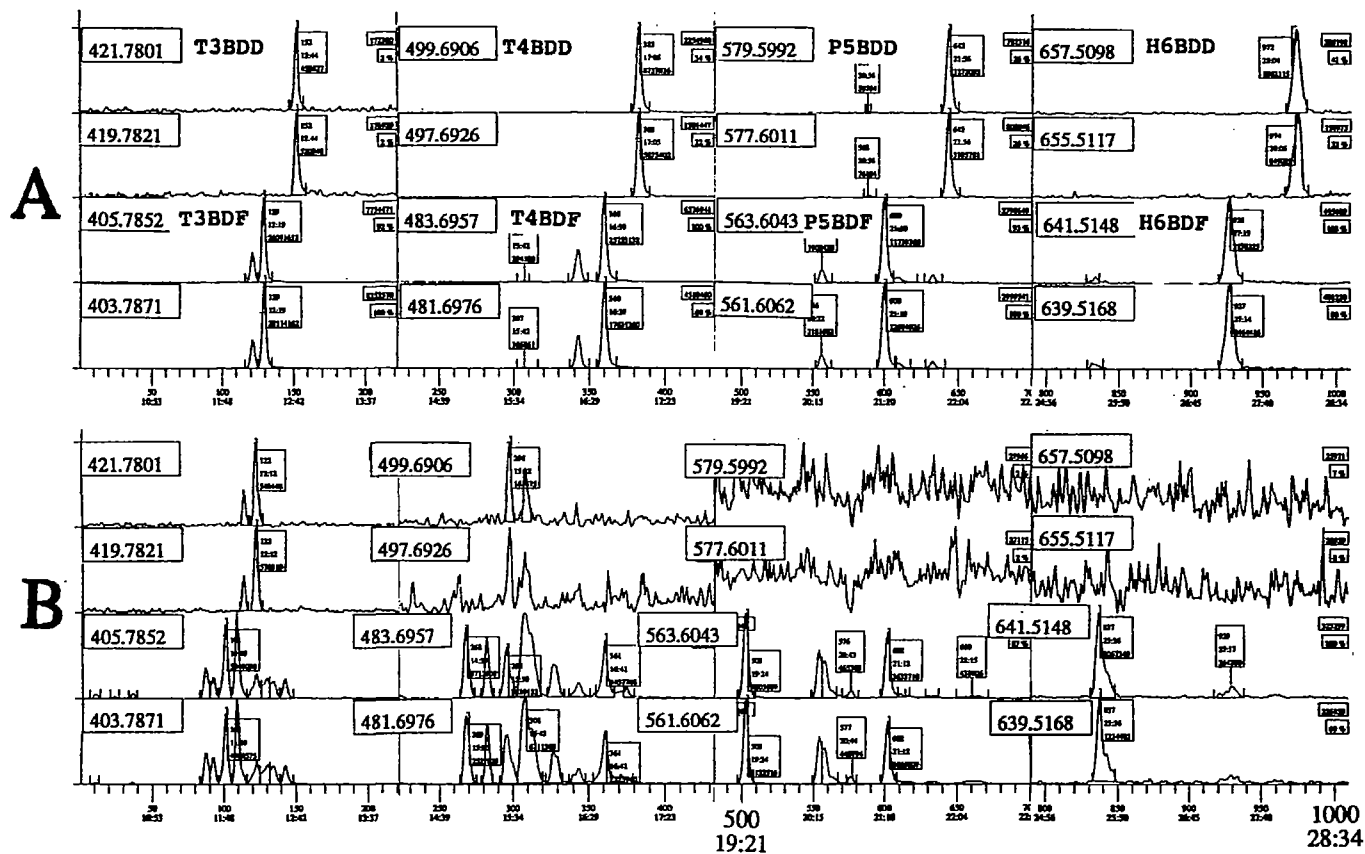


Figure 1. SIM chromatograms of PBBE standards (A) and the extract of air sample (B) collected in Taiwan.

Table 1. The PBDDs/PBDFs, PCDDs/PCDFs and PBBEs levels (pg/m<sup>3</sup>) in atmospheric air in Taiwan and Japan.

Sample	PBDDs				PBDFs			
	tri- <sup>a</sup>	tetra-	penta-	hexa-	tri-	tetra-	penta-	hexa-
Taiwan 1	0.4	0.2	nd	nd	4.4	6.6	7.7	3.4
2	0.5	nd	nd	nd	3.3	3.9	2.8	1.8
3	0.3	0.1	nd	nd	1.7	2.1	1.8	1.1
Japan 1	0.06	0.2	nd	nd	1.0	0.5	1.1	0.7
2	nd	nd	nd	nd	0.3	0.2	0.2	0.3
3	nd	nd	nd	nd	0.3	0.9	2.0	1.4
4	0.09	0.3	nd	nd	0.4	0.9	1.1	1.5
5	0.09	0.3	nd	nd	0.8	2.3	3.7	5.1

Sample	PBBEs				PCDDs	PCDFs
	tri-	tetra-	penta-	hexa-	total	total
Taiwan 1	30	54	13	6.1	16	23
2	34	55	23	81	19	25
3	33	48	34	5.6	7.6	12
Japan 1	7.7	39	18	33	24	46
2	4.7	16	4.7	12	12	19
3	6.1	10	5.2	17	19	29
4	10	20	6.9	26	27	45
5	6.9	22	9.7	18	51	73

<sup>a</sup> Estimated values using T4BDD as the standard, since there was no T3BDD standard available.  
nd: not detected

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