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Hexabromobenzene and Its Debrominated Compounds in River and Estuary Sediments in Japan

Isao Watanabe,[1] Takashi Kashimoto,[2] and Ryo Tatsukawa[3]

[1]Osaka Prefectural Institute of Public Health, Nakamichi 1-3-69, Higashinari-ku, Osaka 537, [2]Department of Hygiene and Pharmacology, Setsunan University, Nagaotouge-cho 45-1, Hirakata 573, and [3]Department of Environment Conservation, Ehime University, Tarumi 3-5-7, Matsuyama 790, Japan

Hexabromobenzene (HBB) is used as a flame retardant in items such as plastics, paper and electric manufactured goods. Aromatic bromine-containing flame retardants may possibly be a source of environmental pollutants since their chemical structures are similar to those of organochlorine pollutants such as polychlorinated biphenyls (PCBs) and DDT compounds. Several reports on environmental pollution by brominated retardants (Mattsson et al. 1975; Andersson et al. 1981; Stafford 1983; Watanabe et al. 1983) have been published.

HBB has been found in estuary sediments collected at Tokyo, Japan, though at extremely low levels, i.e., 0.003 - 0.004 µg/g dry weight (The Environmental Agency of Japan 1983). It has been not found in any river, estuary or marine sediments collected outside the Tokyo area, as far as we know.

We found a peak having the same retention time as HBB in the gas chromatogram of an extract of the river sediment collected at Osaka, Japan, as shown in Figure 1 (peak **A** in Fig. 1-B). One of the PCB peaks, peak 19, interfered with this peak but the estimated HBB residue level in the sediment was above 0.01 µg/g dry weight. This residue level was higher than those of the sediments collected at Tokyo.

The shake extraction method for HBB in sediment using organic solvents such as acetone and benzene was also found less efficient. This paper describes a method for the extraction of HBB from sediment, and an attempt has been made to determine more accurately HBB in sediments in Japan. Also an examination has been made of the decomposition products of HBB in the environment.

MATERIALS AND METHODS

Sediment materials were taken from 17 sites from 1981 through 1983. They were collected with a dredger from upper sediment layers in rivers and estuaries. And stored frozen until use. The sampling sites are shown in Figure 2.

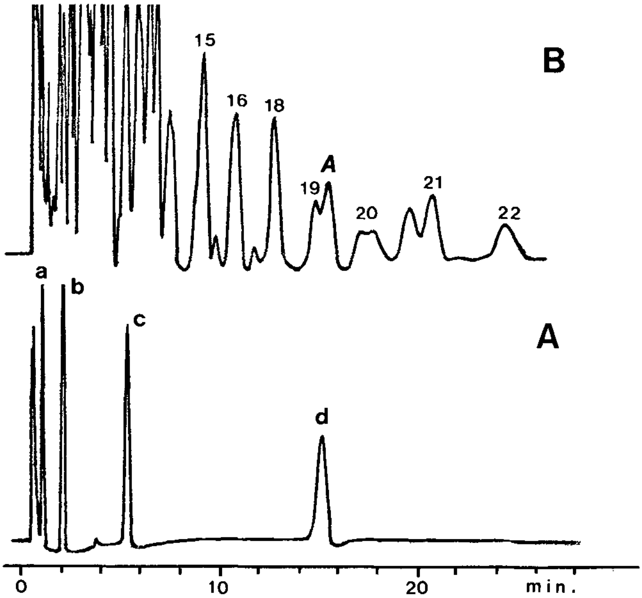

Figure 1. Gas chromatograms of A. brominated benzene standards and B. an extract of river sediment (a: 1,3,5-TrBB, b: 1,2,4,5-TeBB, c: PeBB, d: HBB, 15 - 22: PCBs). A 2%OV-1 column was used.

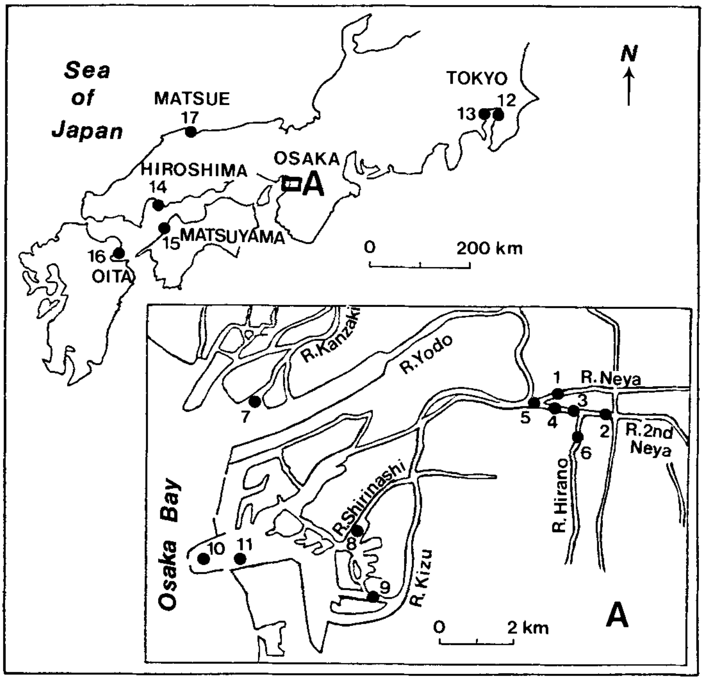

Figure 2. Location map of sediment samples.

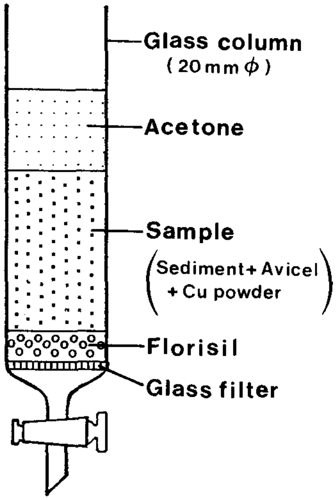

Figure 3. Column used for extraction of HBB from sediment.

1,3,5-Tribromobenzene (1,3,5-TrBB), 1,2,4,5-tetrabromobenzene (1,2,4,5-TeBB) and HBB for reference were purchased from Wako Pure Chemical Co. Ltd. (Japan). Pentabromobenzene (PeBB) was prepared by photolysis of HBB dissolved in hexane and its purity was about 50% as determined by a gas chromatograph-mass spectrometer (GC-MS).

A JEOL JMS DX-300 mass spectrometer connected to a Hewlett Packard 5710A gas chromatograph and a JEOL JMS 3500 data system was used to determine HBB and its debrominated compounds by mass fragmentographic analysis under the following conditions: separation column, a capillary column (0.28 mm x 25 m) of OV-1; column temperature, 75 to 250°C (8°C/min); carrier gas (He) flow rate, 1.0 ml/min.; electron impact ionization voltage, 70 eV.

A new extraction method for HBB and debrominated compounds in the sediment was devised in the present study. One gram of copper powder and 10 g of Avicel® (microcrystalline cellulose for column chromatography, Asahi Kasei Co. Ltd., Japan) were added to 10 g of wet sediment. These constituents were thoroughly mixed and packed into a glass column (20 mm x 25 cm), in which Florisil® (60 - 100 mesh) had previously been placed to a height of 3 cm (see Figure 3). The sediment column was then washed with 50 ml of acetone. HBB and debrominated compounds were eluted completely from the sediment column. The acetone extract was added to 300 ml of 2% NaCl solution. The HBB and debrominated compounds in this solution were extracted with 30 ml of hexane. The hexane extract was washed with 50 ml of 2% NaCl solution twice, and dehydrated with anhydrous Na_2SO_4. Twenty ml of the hexane extract were recovered and concentrated to about 1 ml.

The concentrated extract was cleaned with a miniature Florisil® column (glass column: 5 mm x 80 mm, Florisil®: 1.0 g, 60 - 100 mesh, activated at 130°C overnight). The HBB and debrominated compounds were eluted with 10 ml of hexane from this column. After treating the eluate with concentrated sulfuric acid, the HBB and debrominated benzenes were determined by mass fragmentography using a GC-MS. The monitored diagnostic fragment ions were as follows: M/Z= 314 and 316 for TrBB, M/Z= 392 and 394 for TeBB, M/Z= 472 and 474 for PeBB and M/Z= 550, 552 and 554 for HBB.

RESULTS AND DISCUSSION

For extraction of environmental pollutants such as organochlorine pesticides from the soil, the shake extraction procedure with organic solvent such as acetone, hexane and benzene has commonly been employed (Chiba 1969). Such a extraction method is adequate for the debrominated compounds of HBB from the sediment. However, the efficiency of the shake method for the extraction of HBB from the sediment is not satisfactory, being only about 60%. Consequently, the improved method of the present study was usedfor its extraction. This method is an improvement of the column extraction procedure described by Nash et al. (1972). Although column extraction has been reported less efficient than shake and Soxhlet extractions (Nash et al. 1973), its improved extraction efficiency was adequate through the addition of Avicel® to the sediment. Recovery of HBB in the sediment by the method of this study was 91 ± 2% (the average of five times). Recovery of TrBB, TeBB and PeBB was also good, being above 85%.

Figure 4 shows the mass fragmentograms of HBB and other brominated benzene standards and the extract of the river sediment collected from Osaka. A comparison of the retention times and ratios of the fragment ion peak intensities of the sample extract with standard values demonstrated the presence of HBB and the other brominated benzenes in the sample. That is, peaks **a**,**b**,**c** and **d** were determined as 1,3,5-TrBB, 1,2,4,5-TeBB, PeBB and HBB, repectively. Peaks **a**'and **b**' also appeared to be TrBB and TeBB, respectively. Yamaguchi (1984) reported HBB to decompose into lower brominated benzenes by light and in soils and rat. TrBBs, TeBBs and PeBB found in the sediment in the present study were confirmed to be the decomposition products of HBB in the environment. The decomposition products of HBB were also confirmed to be pollutants in the sediment.

The residue levels of HBB and its decomposition products along with the PCBs and hexachlorobenzene (HCB) levels in the sediment are given in Table 1, on a dry weight basis. HBB was found in all river sediments collected from Osaka and to range from 5.6 to 60 µg/kg. The HBB residue levels in the samples were significantly higher than those of HCB but about one-hundredth of those of PCBs.

Table 1. HBB, its debrominated compounds and organochlorine compounds levels in the sediment samples (μg/kg, on dry weight basis).

Sampling site[1]	Compound					
	Brominated Benzene				HCB	PCBs
	HBB	PeBB	TeBB	TrBB		
River						
1	60.1	2.8	nd	nd	1.8	1,000
2	16.9	7.8	1.7	nd	3.5	1,500
3	40.2	15.9	2.9	0.5	5.8	1,800
4	7.2	3.3	2.2	1.0	8.1	7,700
5	14.3	2.4	0.5	nd	3.7	2,500
6	5.6	1.1	nd	nd	3.5	1,900
Estuary(Osaka)						
7	4.9	nd	nd	nd	2.6	410
8	nd	nd	nd	nd	7.4	4,400
9	6.2	nd	nd	nd	100	3,100
10	nd	nd	nd	nd	2.1	600
11	0.8	nd	nd	nd	0.8	420
Estuary(except Osaka)						
12	0.6	nd	nd	nd	4.2	560
13	3.4	nd	nd	nd	1.7	180
14	0.5	nd	nd	nd	0.5	53
15	nd	nd	nd	nd	0.5	12
16	nd	nd	nd	nd	5.6	14
17	nd	nd	nd	nd	nd	7

[1] See Fig. 2., nd: <0.5 μg/kg.

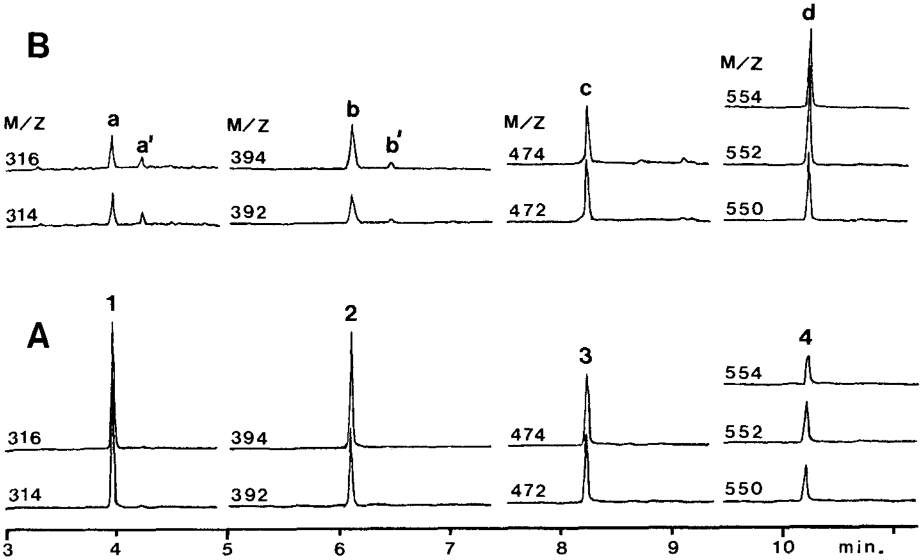

Figure 4. Mass fragmentograms of A. brominated benzene standards and B. an extract of river sediment (1: 1,3,5-TrBB, 2: 1,2,4,5-TeBB, 3: PeBB, 4: HBB).

HBB was also found in the estuary sediments. However, its occurrence and residue levels were much lower than those in river sediments. In the study of the Environmental Agency of Japan (1983), nearly all sediment samples for HBB analysis were from estuaries and marine sources in Japan. HBB was found only in samples collected from the estuaries in Tokyo. Thus, sediment pollution by HBB in Japan may be serious in river but not at estuary and marine sites.

TrBB, TeBB and PeBB were also found in river sediments collected from Osaka, as shown in Table 1. Although, the TrBB and TeBB residue levels were very low, that of PeBB was essentially the same as HCB but lower than that of HBB. Therefore, the decomposition products of HBB in the environment, particularly PeBB, should also be examined in studying environmental pollution by HBB.

HCB is a ubiquitous environmental pollutant though its residue levels are low compared to those of PCBs. The data of the present study demonstrate ubiquitous sediment pollution by HCB. However, sediment pollution by HBB was found to be confined to rivers. The extremely low solubility of HBB may be one of reasons for this. The water solubility of HBB, 0.1 µg/l, is very low compared to that of HCB, i.e., 5.0 µg/l (Geyer et al. 1980). Diffusion of HBB by water in the environment is thus only slight.

Few reports are available on the levels of HBB in the environmental samples. For an accurate determination of environmental pollution by HBB, further investigation on HBB residues in other environmental samples should be carried out. The authors found HBB in household dust collected by an electric vacuum cleaner (unpublished data). Indoor samples such as air and dust should be also investigated for determination of the presence of HBB and its debrominated compounds.

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