

Confirmation of the Presence of the Flame Retardant Decabromobiphenyl Ether in River Sediment from Osaka, Japan

Isao Watanabe, ¹ Takashi Kashimoto, ² and Ryo Tatsukawa³

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

This paper describes the detection of decabromobiphenyl ether (DBBE), a flame retardant, in river sediment collected at Osaka, Japan. To our knowledge, this is the first report confirming the presence of this compound in the environment.

Halogenated flame retardants may be regarded as potential environmental pollutants in that their chemical structures resemble those of PCB compounds present throughout the environment. Several reports have already appeared on environmental pollution due to compounds such as pentabromotoluene (Mattson et al. 1975), polybrominated biphenyl ether (Andersson et al. 1981), Tetrabromobisphenol-A (Watanabe et al. 1983) and hexabromobenzene (The Environmental Agency of Japan 1983; Watanabe et al. 1985).

DBBE is used to reduce the flammability of materials such as resins, textiles and paints. In Japan, the annual consumption of DBBE was reported to be about 1,000 tons in 1976 by the Ministry of International Trade and Industry of Japan. DBBE consumption was second to Tetrabromobisphenol-A, 1,500 tons, amoung brominated flame retardants in the same year. This is sufficient reason to suspect this compound as an environmental pollutant.

MATERIALS AND METHODS

A sediment sample was collected, using a dredger, from the upper sediment layer of the Second Neya River in Osaka, Japan, in 1983. DBBE for reference was purchased from Aldrich Chemical Co. Inc.

A Varian 1800 gas chromatograph connected to an electron capture detector ($^{63}\rm{Ni}$) was used to determine DBBE content in the sediment, under the following conditions: separation column, 2% OV-1 column (2mm x 1.0m); column temperature, 285°C; carrier gas (N $_2$) flow rate, 40ml/min. 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 identify the DBBE residue in the sample, using the following conditions: separation column,

2%0V-1 (2mm x 0.3m); column temperature, 250 to 310°C (8°C/min.); carrier gas (He) flow rate, 20ml/min.; ion source temperature, 250°C; electron impact ionization voltage, 70eV.

In the present study, the sediment extract cleaned for analysis of hexabromobenzene (HBB) was used for the DBBE detection. The procedures for the extraction and cleaning have already described in our previous report on HBB residue in sediments (Watanabe et al. 1985).

RESULTS AND DISCUSSION

Figure 1 shows the gas chromatograms for the PCTs, decabromobiphenyl (DBB) and DBBE standards and the river sediment extract collected at Osaka. The peak corresponding to the DBBE standard (peak **a** in Figure 1-B) is for the river sediment extract in which no DBB was found. Identification of this peak was made by comparing its mass spectrum with that of the DBBE standard. Figure 2 shows both mass spectra to agree well within mesurement error and confirms the presence of DBBE in the river sediment.

The DBBE residue level of the sample was about $0.2\,\mu\text{g/g}$ (ppm) on a dry weight basis. The residue levels of the other halogenated pollutants in the same sample were as follows: PCBs, 1.5 ppm; PCTs, 0.25 ppm; HBB, 0.017 ppm; hexachlorobenzene (HCB), 0.004 ppm; DDT compounds, 0.030 ppm. The DBBE residue level was by far higher than those of HCB and DDT compounds and essentially the same as those of PCTs, though only one-tenth of those of PCBs. River sediment pollution by DBBE may thus constitute a serious environmental problem in Osaka.

DBBE may possibly decompose into lower brominated compounds by natural debromination, as is the case for HBB (Yamaguchi 1984). In a preliminary test of the photolysis of DBBE in a hexane solution using sun light, DBBE quickly decomposed into nona-, octa-, hepta- and hexabrominated compounds. In Figure 1-B, the retention times of unknown peaks 2 and 3 agree with those of octabromobiphenyl ethers produced by photolysis. These peaks may possibly correspond to the decomposition products of DBBE in the environment, though identification of these products has yet to be made. Tetra-, penta- and hexabromobiphenyl ethers has been reported to be present in fish in Sweden (Andersson et al. 1981).

Additional investigation on environmental pollution by DBBE and debrominated compounds resulting from its decomposition should be carried out immediately.

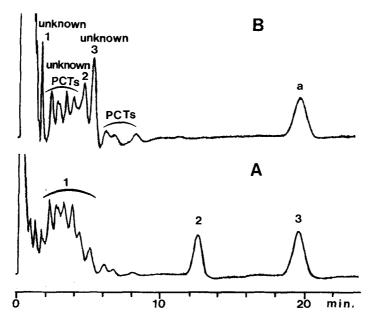


Figure 1. Gas chromatograms of A. PCTs, DBB and DBBE standards and B. an extract of river sediment collected at Osaka (1: PCTs, 2: DBB, 3: DBBE). GC conditions are described in the text.

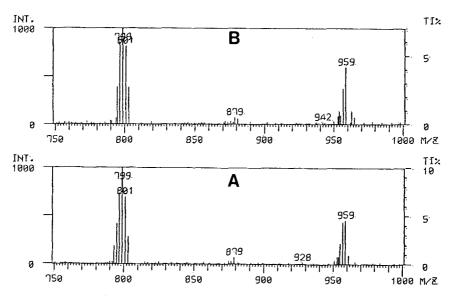


Figure 2. Mass spectra of A. the DBBE standard and B. the corresponding to peak a in the river sediment extract (Figure 1-B).

REFERENCES

- Andersson O, Blomkvist G (1981) Polybrominated aromatic pollutants found in fish in Sweden. Chemosphere 10: 1051-1060
- Mattson PE, Norstrom A, Rappe C (1975) Identification of the flame retardant pentabromotoluene in sewage sludge. J Chromatography 111: 209-213
- The Environmental Agency of Japan (1983) Chemicals in the environment. E.A., Off Health Studies Report Series No 9
- Watanabe I, Kashimoto T, Tatsukawa R (1983) The flame retardant Tetrabromobisphenol-A and its metabolite found in river and marine sediments in Japan. Chemosphere 12: 1533-1539
- Watanabe I, Kashimoto T, Tatsukawa R (1985) Hexabromobenzene and its debrominated compounds in river and estuary sediments in Japan. Bull Environ Contam Toxicol, submitted for publication
- Yamaguchi Y (1984) Basic researches on environmental behavior of organobrominated flame retardants. Master's Thesis, Ehime University, Japan (Japanese)
- Received June 20, 1985; accepted October 20, 1985