BROMINATED DIPHENYL ETHERS IN DUTCH FRESHWATER AND MARINE FISH.

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ABSTRACT

Since 1983 concentrations of tetra and penta brominated diphenyl ethers have been measured in eel from Dutch rivers and lakes and in cod liver and herring from the North Sea.
Concentrations upto 1.5 mg/kg on a fat base are found. Decreasing trends are identified in eel from the Rhine and the Meuse. An upward trend is found in eel from the river Roer.

INTRODUCTION

Polybrominated diphenyl ethers (BDEs) are widely used as flame retardants in textiles, paints and plastics in Japan, Western Europe and Japan (Watanabe et al., 1987). At the moment the annual production in the Netherlands is 2500 metric tons. In 1982 we were able to identify the presence of BDEs in a cormorant from the Rhine delta (Biesbosch) in the Netherlands. In the liver of this cormorant a total BDE concentration of 28 mg/kg on a product base was found. It appeared that in eel samples from several locations in the Netherlands BDEs were present. Since that time the analysis of BDEs was included in monitor programes for chlorinated pesticides and PCBs in Dutch fishery products. In some older samples the presence of BDEs could be shown already since 1977 (de Boer, 1989).

MATERIALS AND METHODS

A technical mixture Bromkal 70-5DE, consisting of 41.7% 2,4,2',4'-tetrabromodiphenyl ether (TBDE), 44.4% 2,4,5,2',4'-pentabromodiphenyl ether (PBDE), 7.6% pentabromo-diphenyl ether with an unknown structure (mentioned in this paper as x,y-PBDE) and 6% hexabromodiphenyl ethers (HBDEs), was used as a standard.
Eel samples were collected in Dutch rivers and lakes (fig.1). Cod liver and herring samples were obtained from different parts of the North Sea.
All fish samples consisted in principle of 25 fishes. Weights and lengths were determined. Equal weights of fillets were pooled and stored at -20°C. The method used for the analysis of PCBs and pesticides - soxhlet extraction, clean-up over alumina columns, fractionation over silica columns, GC-ECD analysis - was also used for the analysis of the BDEs. Full details of this method have been given before (de Boer, 1988). The bromodiphenylethers are found in the second fraction after silica gel elution.

RESULTS AND DISCUSSION

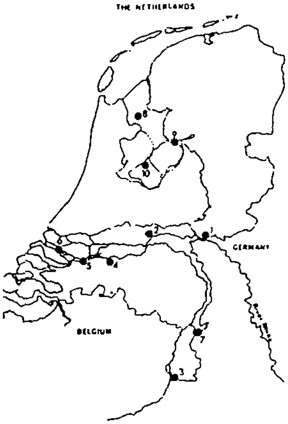

Fig.1 Locations of eel samples

An overview of the results is given in table 1. The concentration of 2,4,2',4'-TBDE and the sum of 2,4,2',4'-TBDE, 2,4,5,2',4'-PBDE and x,y,-PBDE are given. 2,4,2',4'-TBDE is always found as the main component, circa 70% of the total BDE with x,y,-PBDE at about 25% and 2,4,5,2',4'-PBDE at 5% of the total BDE concentration. HBDEs were always below detection limits.

These patterns are in accordance with the results of Andersson and Blomkwist (1981), Jansson et al. (1987) and Watanabe et al. (1987). Zitko and Hutsinger (1976) reported a lower membrane permeability for polybromobiphenyls with increasing bromine substition. This may explain the selective accumulation of TBDE and PBDEs. TBDE levels upto 1500 µg/kg on a fat base are found in Dutch eel samples (table 1, fig.2).

The main BDE contamination in the Netherlands is apparently caused by the flux of the Rhine and the Meuse. At the reach between the German and Belgian border and the North Sea no increase of BDE concentrations is found, despite the continuing BDE production in the Netherlands. In the Oostvaardersplassen, a closed lake system, no detectable amounts of BDEs were found. This points to a restricted aerial transport.

Decreasing trends are identified for TBDE concentrations in eel from the Rhine and the Meuse (fig.2). More than a factor 10 reduction in TBDE concentration occurred in both rivers since 1983. On the contrary an increase of TBDE concentration is found in eel from the river Roer. This relatively small stream with a flux of about 6% of the Meuse, flushes through a German mining area, across the Dutch border into the Meuse. The TBDE concentrations in eel from this river show an increase from 470 µg/kg on a fat base in 1983 upto 1400 µg/kg in 1989. This increase in BDE concentrations may be caused by the replacement of PCBs in the hydraulic systems, used in the German mining industry, by BDEs.

BDE concentrations in cod liver from the North Sea show a clear spatial trend decreasing from the southern to the northern part of the North Sea (de Boer, 1989).

In comparison with cod liver BDE concentrations in herring are a factor 3-8 lower on a fat base. Highest BDE concentrations in herring are also found in the southern North Sea, but spatial trends are less clear due to the migration patterns of herring.

Andersson and Blomkwist (1981) reported BDE concentrations between 1000 and 16,000 µg/kg on a fat base in eel from the Viskan river, south Sweden. These concentrations are upto a factor 10 above the BDE concentrations in Dutch eel, but were not confirmed for other Swedish waters. Watanabe et al. (1987) reported TBDE concentrations in mussels from the Osaka bay upto 14.6 µg/kg wet weight, which is, on a fat base, higher than the TBDE level in herring and cod liver in the southern North Sea.

Table 1: Concentrations of brominated diphenyl ethers in Dutch freshwater and marine fish (expressed in µg/kg on a fat base).

Sample/location**	concentrations of 2,4,2',4'-TBDE and total BDE year 1983	1984	1985	1986	1987	1988	1989
eel (Anguilla anguilla)							
Rhine, Lobith(1)	nm	1400/nm	590/830	360/490	770/nm	450/690	190/310
Waal, Tiel (2)	970/nm	1700/nm	500/790	560/870	670/nm	490/720	360/540
Meuse, Eijsden (3)	680/nm	50/nm	nm	420/760	400/nm	<30/<70	<20/<50
Meuse, Heusden (4)	nm	nm	nm	79/99	420/nm	150/230	69/90
Holland Diep (5)	810/nm	1100/nm	310/460	290/370	540/nm	450/590	200/310
Haringvliet (6)	nm	1200/nm	240/380	150/240	450/nm	500/730	320/470
Roer, Vlodrop (7)	470/nm	610/nm	nm	620/830	700/1300	1000/1300	1400/1700
IJsselmeer (8)	nm	210/nm	nm	61/95	85/120	nm	41/64
Ketelmeer (9)	nm	420/nm	290/490	nm	280/330	220/300	97/150
Oostvaardersplassen (10)	nm	<20/<50	nm	nm	nm	nm	nm
cod liver (Gadus morhua)							
Northern Noth Sea	68/nm	nm	nm	39/nm	39/47	nm	31/38
Central North sea	99/nm	150/nm	64/nm	nm	110/130	130/190	63/nm
Southern North Sea	nm	360/nm	280/330	nm	310/360	120/nm	110/130
herring (Clupea harengus)							
Northern North Sea	nm	nm	29/nm	nm	nm	nm	nm
Central North Sea	nm	nm	8.4/nm	nm	nm	nm	nm
Southern North Sea	nm	nm	100/nm	nm	nm	nm	nm
Straits of Dover	nm	nm	45/nm	nm	nm	nm	nm

* fat contents: eel 90-340 g/kg, cod liver 390-660 g/kg, herring 20-130 g/kg.
** locations: numbers refer to locations shown in fig.1.
nm: not measured.

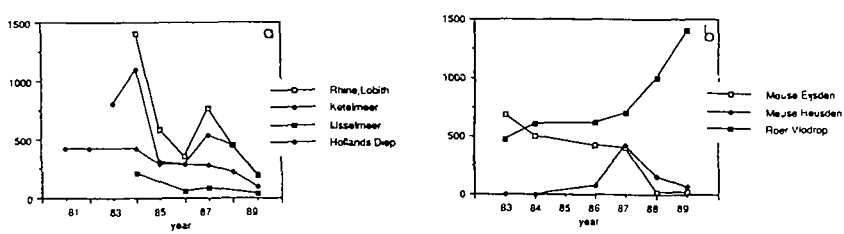

Fig.2. Trends of 2,4,2',4'-TBDE concentrations in eel from the Rhine-delta (a) and the rivers Meuse and Roer (b)

Although decreasing trends in BDE concentrations are found in eel samples from locations at the Dutch borders, the level of BDE contamination is still a concern in relation to the quality of fishery products in the Netherlands. The increased cytochrome P-450 induction by BDEs in rats, demonstrated by Carlson (1980) suggests possible long-lasting toxicological effects of these compounds.

From the analytical viewpoint there is a need for pure analytical standards of individual brominated diphenyl ethers.

REFERENCES

Andersson, Ö., G. Blomkwist (1981). Polybrominated aromatic pollutants found in fish in Sweden. Chemosphere, 10 (9), 1051-1060.

Boer, J. de (1988). Chlorobiphenyls in bound and non-bound lipids of fishes; comparison of different extraction methods. Chemosphere, 17 (9), 1803-1810.

Boer, J. de (1989). Organochlorine compounds and bromodiphenylethers in livers of Atlantic cod (Gadus morhua) from the North Sea, 1977-1987. Chemosphere, 18 (11/12), 2131-2140.

Carlson, G.P. (1980). Induction of xenobiotic metabolism in rats by brominated diphenyl ethers administered for 90 days. Toxicology Letters, 6, 207-212.

Jansson, B., L. Asplund, M. Olsson (1987). Brominated flame retardants - ubiquitous environmental pollutants? Chemosphere, 16 (10-12), 2343-2349.

Watanabe, I., T. Kashimoto, R. Tatsukawa (1987). Polybrominated diphenylethers in marine fish, shellfish and river and marine sediments in Japan. Chemosphere, 16(10-12), 2389-2396.

Zitko, V., O. Hutzinger (1976). Uptake of chloro- and bromobiphenyls, hexachloro- and hexabromobenzene by fish. Bull. Environm. Contam. Toxicol., 16 (6), 665-673.