AN INDICATION OF TEMPORAL TRENDS IN ENVIRONMENTAL PBDE LEVELS IN EUROPE

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Introduction

Polybrominated diphenyl oxides or ethers (PBDEs) have been detected in the environment since the 1980s[1-6]. However, only in the last three years have substantial data sets on environmental levels of PBDEs been built up. Similar information from earlier years is scarce, which hinders the assessment of temporal trends. In this study, PBDEs were determined in sediment and fish samples from locations which had been previously sampled in 1995, 1992, or in the 1980s. In this way, an initial assessment of possible temporal trends of tetra, penta and decaBDE at some locations in The Netherlands, the UK and Ireland could be attempted.

Methods and materials

This study consists of three parts. In part one, European river sediments (Clyde, Humber, Tyne, Mersey, Scheldt) collected and analysed in 1995 under the DIFFCHEM program[2], were re-sampled and analysed in the period 1999-2001. The 1999 sampling locations were those of the DIFFCHEM samples[2]. In part two, Dutch river sediments (Rhine and Meuse delta, and river Roer) collected and analysed in 1992, were resampled and analysed in 1999. In part three, eels from rivers in The Netherlands (Rhine and Meuse delta, and river Roer) and cod (liver) from the southern and central North Sea were collected and analysed in 1999, and the results compared to samples from similar locations collected annually since the 1980s. The eels were sampled in May of each year, and were between 30 and 40 cm length. The cods were between 40 and 50 cm and samples were from different parts of the years, avoided the spawning period. Sediment samples were all surface sediments taken by a Van Veen grab or a modified Day grab.
The following PBDE congeners were analysed: 28, 47, 66, 71, 77,5, 77, 85, 99, 100, 119, 138, 153, 154, 190, and 209. The methods used for the determination of PBDEs included a Soxhlet extraction with hexane/acetone (1:1, v/v for the UK samples and 3:1, v/v, for the Dutch and Irish samples), a clean-up using GPC with PL gel columns, silica gel clean-up and sulphuric acid treatment (Dutch and Irish samples), and using alumina and silica column clean-up for the UK samples, and finally, for all samples, a GC/NCI-MS determination, using 15m DB5 or HP1 columns for the BDE209 determination and 50m CP Sil 8 or DB5 columns for the determination of all other BDE congeners[7]. The chlorobiphenyls 112 and 198 were used as internal standards. Both laboratories involved obtained good results during the BSEF interlaboratory study[8]. The method was different from the method used for the analysis of the DIFFCHEM study, as those samples were analysed at the ITM, Stockholm University, Sweden. The older data from Ducth eels and sediments are based on GC/ECD analyses.

Results and discussion

The results of this study and those of the DIFFCHEM study are compared in Table 1. In the Western Scheldt between the years 1995 and 1999, BDE47 and 99 concentrations decreased by 50% and 30%, repectively, whereas BDE 209 concentrations increased 50%. Apart from this single location, 18 other locations were sampled in the Western Scheldt. The other locations BDE concentrations (630-12,000 ng/g org. C) showed a slight decreasing trend from Antwerp harbour (DIFFCHEM location) towards sea. The Liffey (Ireland) shows a similar trend between 1995 and 1999, with a decrease in BDE47 and 99 concentrations (ca. 50%), and an increase for BDE 209 (>100%).

The situation in the Clyde (UK) is completely different from that of the Western Scheldt and the Liffey. All BDE concentrations have increased, BDE47 ca. 20-fold, BDE99 ca. 10-fold, BDE209 ca. 5-fold. Also in the Mersey, all BDE concentrations (tetra, penta, deca) have increased between 1995 and 2001. Relatively large uncertainties should be taken into account here, as the data showed a patchy pattern within the four replicate samples taken at these locations. In the Humber all BDE concentrations have ca. 10-fold decreased, which is deiating from most other samples. Although five replicates were sampled and analysed, the patchy pattern observed at several locations may have played a role here.

Table 1. Concentrations of BDEs sediments (in ng/g org. C), comparison with DIFFCHEM study.

River	BDE47		BDE99		BDE209	
	1999-2001	1995	1999-2001	1995	1999-2001	1995
Liffey	22	30	20	36	4457	2010
Clyde	410	23	300	32	1260	259
Mersey	140	90	190	93	104700	69700
Tyne		37		52		230
Humber	22	240	16	290	160	1630
Western Scheldt	6.5	12	6.0	9.1	7716	5670

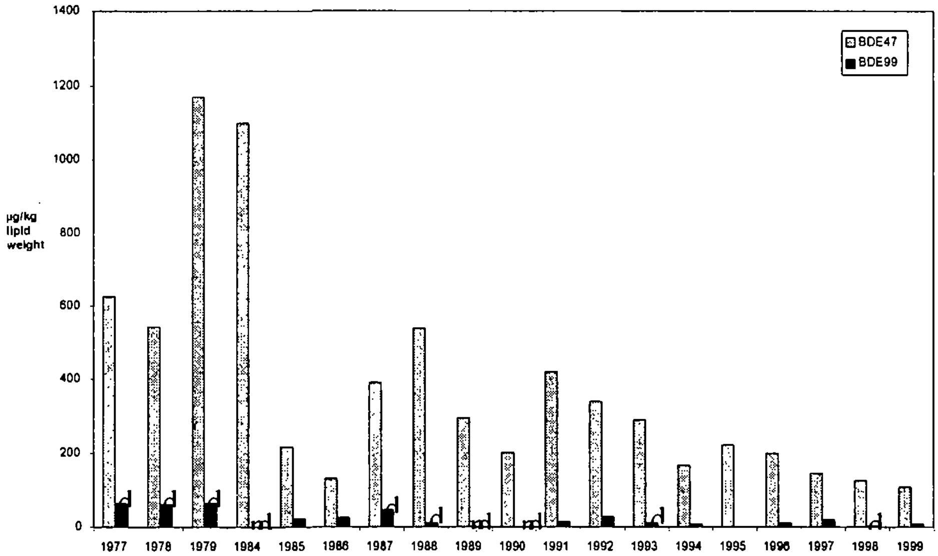
On a dry weight basis the BDE209 concentration in the river Tyne (UK) (1999) is 95 ng/g, which is much higher than the 3.3 ng/g (<63 μm fraction) which was found in the DIFFCHEM sample from 1995. Also, BDE47 and 99 levels have increased in this river since 1995. A reversed situation is found in the Humber (UK), in which all BDE levels have decreased (on a dry weight basis). In the Mersey (UK) 1999 BDE47, 99 and 209 concentrations were comparable (on a dry weight basis) with the 1995 concentrations.

In the second part of this study a few sediment samples from Dutch rivers were analysed and compared with 1992 samples from the same locations (Table 2). The BDE47 concentrations in the Rhine delta (Haringvliet, Waal and Nieuwe Merwede) have decreased ca. 5-30-fold, and ca. 10-fold in the river Meuse.

Table 2. Concentrations of BDEs in sediments from Dutch rivers (in ng/g org. C).

River	BDE47 (1999)	BDE47 (*1992*)	BDE99 (1999)	BDE99 (*1992*)	BDE209 (1999)	HBCD (1999)
Haringvliet-east	54	410	51	450	470	1510
Nieuwe Merwede	170	900	80	n.a.	910	8040
Waal (Tiel)	29	990	30	900	760	2310
Meuse (Keizersveer)	22	250	26	300	990	110

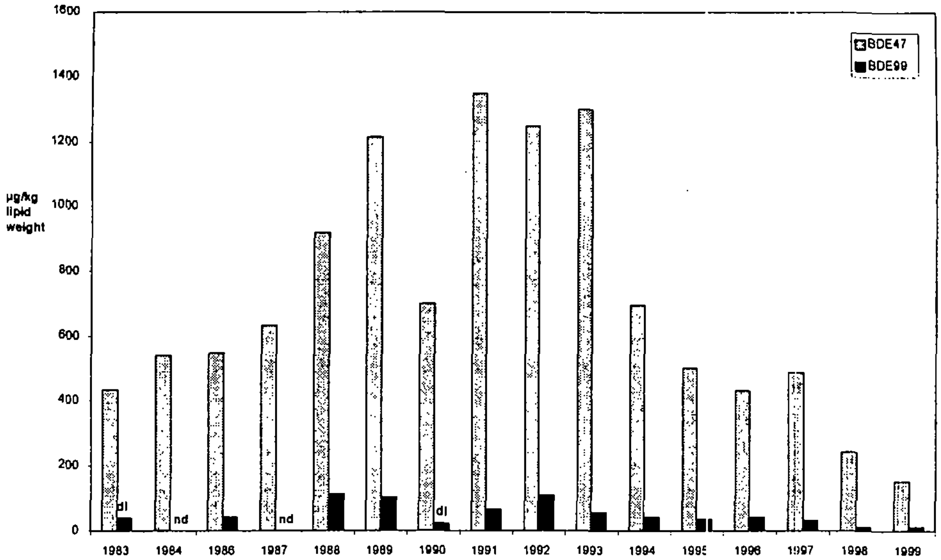
Fig. 1. Temporal trends of BDE47 and BDE99 in yellow eel from Haringvliet-east.



A similar decrease was found for BDE99 in the Rhine and Meuse delta. BDE209 was not analysed before in biota from these locations. The BDE209 concentrations in the Rhine and Meuse delta are considerably higher than the current BDE47 and 99 concentrations; in the Rhine delta they are similar to the 1992 BDE47 concentrations and in the Meuse 5-fold higher than in 1992.

PBDE concentrations in eel collected in The Netherlands from 1980-1999 were compared (Figures 1 and 2). Clearly, there was a decrease of the BDE47 and 99 concentrations over the last years, as was also shown in the sediment (Table 2). Also, the increase of BDE47 and BDE99 concentrations in eel from the river Roer in the period 1987-1993 thought due to use of the pentabromodiphenylether product in German coal mining is clearly visible, as well as the decrease of these levels after the termination of its use in these mining activities[3].

Figure 2. Temporal trends of BDE47 and BDE99 in yellow eel from the Roer (Vlodrop).



Finally, in the southern North Sea, BDE47 concentrations in cod liver decreased from 1000 ng/g (1983) to 240 ng/g lipid weight in 1999 and BDE99 concentrations from 22 (1983) to 7 ng/g ng/g lipid weight. In the central North Sea, BDE47 and 99 concentrations were generally stable at a level of ca. 180 and 6 ng/g lipid weight, respectively, but in 1994 and in 1998 BDE47 concentrations up to 500 ng/g lipid weight have been found. Although the number of samples was very limited, these trends are consistent with the decreasing BDE47 and BDE99 levels in Dutch rivers which flow into the southern North Sea, and the increasing BDE47 and BDE99 levels in some UK rivers which may influence the central North Sea..

Conclusions

It should be taken into account that the data presented are subject to a relatively large variation because, i) the DIFFCHEM study was only meant as a survey to map geographical differences in contaminant loads in Europe, ii) different laboratories have been involved in the analysis, applying different methods in different periods, and iii) sediments may show patchy patterns, which can influence the data markedly in case of limited sample numbers. Therefore, temporal trends in a strict statistical sense cannot be demonstrated. However, in spite of these limitations, some indications of temporal trends may be visible. A decrease of BDE47 and 99 (eel, cod liver and sediment) concentrations and an increase of BDE209 (sediment) can be observed in the Dutch rivers Rhine, Meuse and Scheldt, the southern North Sea, and in the Liffey (Ireland). Sediments from UK rivers show deviating trends: the Clyde and Tyne with an increase of tetra, penta and decaBDE since 1995 and the Humber with a decrease of tetra, penta and decaBDE. A sediment core study, which was another part of this project[9], indicates a leveling-off of the tetra and pentaBDE over the last ten years in cores from the Dutch Wadden Sea and an east-German Lake, while decaBDE concentrations had increased markedly in the late 1970s. A sediment core from

the Oslofjord (Norway) showed increasing tetra and pentaBDE levels until 1999. It appears that regional differences in tetra and pentaBDE trends occur in Europe.
DecaBDE concentrations have reached relatively high levels in some sediments. DecaBDE was not found in eel and cod liver samples, showing its very limited bioaccumulative properties.

Acknowledgement
This study was funded by the Bromine Science and Environmental Forum (BSEF), Brussels, Belgium. The authors thank Mr. Evin McGovern of the Marine Institute, Dublin, Ireland for making the Liffey sediment sample availble.

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