

POLYBROMINATED FLAME RETARDANTS - POSTERS

LEVELS OF SOME POLYBROMINATED DIPHENYL ETHER (PBDE) FLAME RETARDANTS IN DATED SEDIMENT CORES.

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Introduction

Brominated flame retardants are used in plastics, electrical equipment and textiles for safety reasons. The PBDEs are not chemically bound to the products and may therefore leach out into the environment¹. PBDEs have been mainly marketed in the form of three formulations: Pentabromo diphenyl ether (PeBDE; e.g. Bromkal 70-5 DE), Octabromo diphenyl ether (OcBDE), and Decabromo diphenyl ether (DeBDE). The PeBDE formulations contain mainly tetra-, penta- and hexa-BDEs. Since 1994 the use of the PeBDE formulation has been reduced in several countries because of its bioaccumulation potential and toxicity². Decabromo diphenyl ether, consists for more than 97% of the fully brominated BDE 209 with minor contributions of some octa- and nonabromo-BDEs.

Due to their hydrophobic character and their resistance to degradation certain, especially lower brominated, PBDEs are bioaccumulated³. Certain PBDE have been detected in biota and sediments⁴⁻⁷. In western European estuaries there is a relation between detection and BDE manufacturing sites and between detection and heavily industrialized and populated areas in general^{8,9}. In a sediment core from the Bornholm deep in the Baltic, PBDEs showed a continuous increase of the PBDEs 47, 99 and an unknown pentaBDE over the last 30 years until 1987¹⁰. PBDE concentrations in guillemot (*Uria algae*) eggs from the Baltic Sea over the same decades showed a maximum in the middle nineteen eighties with a subsequent decline in later years (BDE 209 was not determined in both studies)¹¹.

The present study focuses on the determination of individual PBDE-congeners in sediment cores from different locations in Europe. The main goal in this study is to investigate if there is a time-dependent pattern in the distribution of PBDEs. The results of the first three cores are discussed in this paper.

Methods and Materials

Sample collection and dating: The Drammenfjord is a branch of the Oslo fjord. The core was collected in October 1999 with a Rheineck boxcorer at the position 59°38'01"N and 10°25'38"E from the RV 'Pelagia'. A sub-core was taken with a liner of 70 mm diameter which was sliced in parts of 0.5 cm. The slices were dated by measuring the isotopes ²¹⁰Pb and ¹³⁷Cs. No BDE 209 could yet be determined in the core of the Drammenfjord due to contamination.

The core from the western Wadden Sea was taken in June 1997 in the area of the former gully 'De Vlieter' at 53°00',649N, 5°04',891E. This was the main gully entering the 'Zuiderzee' from the Wadden Sea before it was suddenly closed in 1932 by the closure of the 'Afsluitdijk' between the provinces of North-Holland and Friesland. This dike presently forms the northern border of the fresh water lake IJssel. The samples were taken with a gravity corer and the determination of the age of the different layers in the core was done by ²¹⁰Pb dating and the PCB and PAH-levels¹².

Lake Woserin is a small fresh water lake fed by a stream in Pommern (Germany) in a rural area.

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The samples were a kind gift of Professor J.F.W. Negendank of the Geological Research Center of the University of Potsdam (Germany), who also carried out the age determination by varve counting.

Extraction: About 10 gram of wet sediment was extracted overnight in an Erlenmeyer (>12 hrs) with 15 ml acetone on a Lab-line shaker (125 rpm), Decabromobiphenyl (BB 209) was added as internal standard. This compound could not be detected in a series of 150 samples from Dutch environments (Pers. comm. J. de Boer). After addition of 15 ml pentane the erlenmeyer was shaken for another 2 hrs. The contents of the erlenmeyer were transferred to a 75 ml centrifugation tube and 20 ml bi-distilled water was added. The tube was centrifuged for 15' at 2500 rpm and the organic layer was collected and treated with sulfuric acid (2* 2ml) to remove co-extractants. The extracts are then passed over a silica column (2 g, deactivated with 6% water, elution with 20 mL pentane) for the final clean-up.

Analysis: The levels of individual PBDEs were determined by gas chromatography, followed by mass selective detection. The GC was a Hewlett Packard 6890; specifications: split-splitless injection, split valve closed for 1.5 min. $T_{injector}$ 270°C. Column: stationary phase CP Sil-8, 25 m * 0.25 mm * 0.25 μ m (Chrompack, NL). Carrier gas He; linear gas velocity 74 cm s⁻¹, constant flow programmed. Oven temperature program: 90°C (1.5') / 20°C min⁻¹ / 190°C (0') / 4.5°C min⁻¹ / 270°C (5') / 10°C min⁻¹ / 320°C (10'). The MS was a Hewlett Packard 5973 mass selective detector; specifications: negative chemical ionization (NCI) in the SIM mode at the m/z ratios of both bromine isotopes (m/z 79 and 81 and for the detection of BDE 209 m/z = 487. Ionization gas CH₄. $T_{ion\ source}$ 210°C; $T_{transferline}$ 320°C; $T_{quadrupole}$ 160°C.

Results and Discussion

The results of all three cores show that the majority of the BDE congeners become present in the early nineteen sixties, BDE 209 emerges about a decade later (Figs 1-3). This is in agreement with the industrial production figures. BDEs 47, 99 and 209 are the most common congeners found, whereas BDEs 28, 66, 75, 85, 100, 153 and 154 are regularly found at lower concentrations. The BDEs 71, 77, 138 and 190 are not detected in the cores studied.

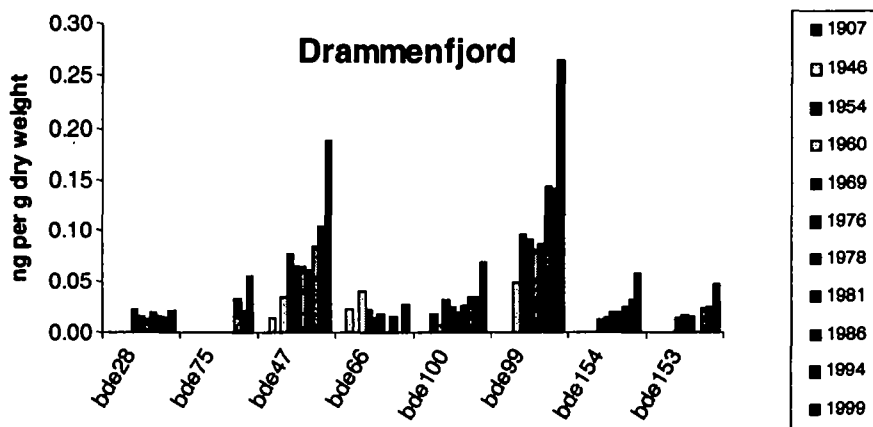


Fig. 1 Temporal trends of BDE-congeners found in a core from Drammenfjord.

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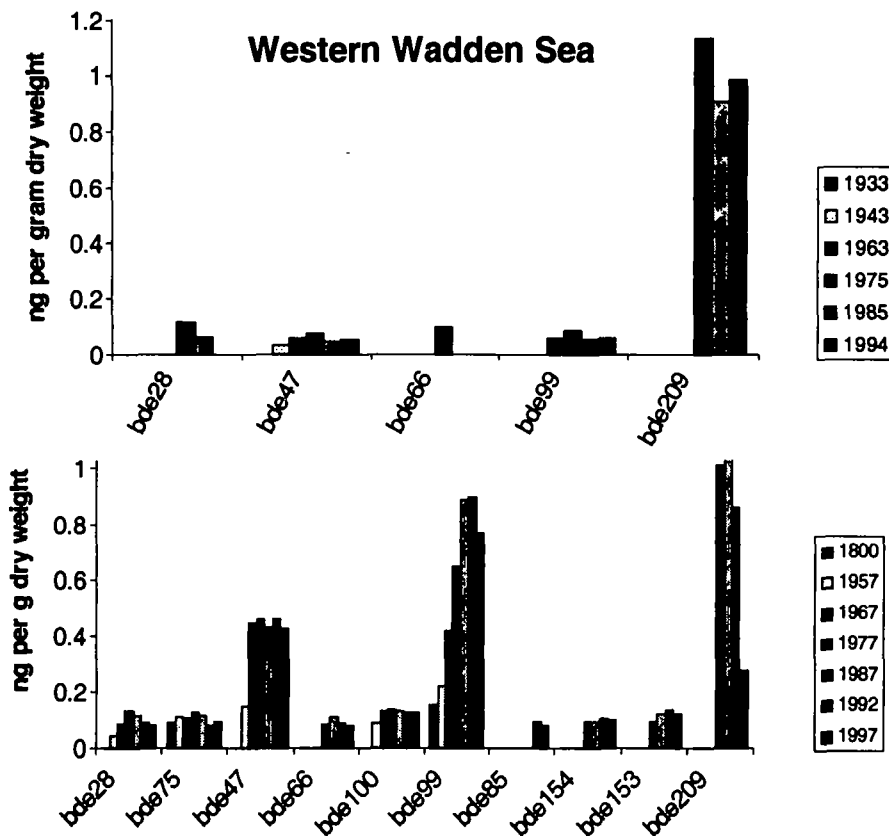


Fig. 2 and 3 Temporal trends of BDE-congeners found in a core from western Wadden Sea (top) and Lake Woserin (bottom).

In the core of the Drammenfjord the levels of all BDEs increase until 1999. Due to temporary contamination problems, BDE 209 was not yet analyzed in this core. The ratios between BDEs 47, 99, and 100 remain highly similar during the last 30 years. They are also similar to the ratios found in the Bromkal 70-5DE PeBDE formulation. When this, or a similar formulation, is a main source, it would imply a high degree of persistence of these compounds to degradation processes in the sediments.

In the core from the western Wadden Sea, the relative amounts of BDE 209 are much higher than in lake Woserin, indicating the possibility of a local source. Other work has identified the Scheldt estuary at the boarder between the Netherlands and Belgium as a possibility. The originally southbound current from the Western Scheldt turns clockwise by a gyre off Ostend and merges with North Sea coastal water which moves with a residual northeasterly current along the Dutch coast to the western Wadden Sea¹³. The other congeners in the core show very low levels, which obscures the calculation of their ratios.

In the core from Lake Woserin, the increase of all BDEs except BDE 209, starts already in 1957. The PBDE levels are much higher than in the Drammenfjord, but this might be due to higher TOC

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values. The concentrations of the congeners level off in the nineteen seventies, just when BDE 209 is appearing for the first time in the sediment. This is in agreement with the shift in production volume from PeBDEs towards the higher brominated formulations.

In summary, the preliminary results of this work show that PBDE levels have a time-dependent pattern in these cores, with BDE 209 arriving about one-two decades later than the congeners present in PeBDE mixtures such as Bromkal 70-5 DE. In the cores from the western Wadden Sea and Lake Woserin, the concentrations on a dry-weight basis are leveling off, whereas those in the Drammenfjord are still increasing. However, levels should be expressed on an organic carbon basis before any definite statements can be made in this respect.

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References

1. de Boer, J., de Boer, K., and Boon, J. P. (1999) in: *New types of persistent halogenated compounds* (Paasivirta, J.), Springer-Verlag.
2. Report WHO (1994): Polybrominated diphenyl Ethers. IPCS, Environmental Health Criteria.
3. Sellström, U., Kierkegaard, A., de Wit, C. and Jansson, B. (1998) *Environ.Toxicol.Chem.* 17, 1065.
4. Allchin, C. R., Law, R. J. and Morris, S. (1999) *Environ.Pollut.* 105, 197.
5. Jansson, B., Asplund, L. and Olsson, M. (1987) *Chemosphere* 16, 2343.
6. Sellström, U., Jansson, B., Kierkegaard, A., Wit, C. de, Odsjö, T. and Olsson, M. (1993) *Chemosphere* 26, 1703.
7. de Boer, J. (1989) *Chemosphere* 18, 2131.
8. Kierkegaard, A., Sellström, U., Wideqvist, U., Winberg, A., and Alsberg, T. (1997) in: *Oslo and Paris Commissions SIME 97/6/1-E* (van Zeijl, H).
9. Sellström, U., Kierkegaard, A., Alsberg, T., Jonsson, P., Wahlberg, C. and de Wit, C (1999) *Organohalogen Compsds.* 40, 383.
10. Nylund, K., Asplund, L., Jansson, B., Jonsson, P., Litzén, K. and Sellström, U. (1992) *Chemosphere* 24, 1721.
11. Sellström, U.(1999), *Determination of some polybrominated flame retardants in biota, sediment and sewage sludge* (*Ph.D. thesis*), University of Stockholm, ISBN 91-7265-023-0.
12. Beurskens, J. E. M.(1995), *Microbial transformation of chlorinated aromatics in sediments.* (*Ph.D. thesis*), Wageningen Agricultural University.
13. Nihoul, J. C. J. and Hecq, J. H. (1984) *Cont.Shelf Res.* 3, 167.