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# Levels of Polybrominated Diphenyl Ether Flame Retardants in Sediment Cores from Western Europe

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The levels of 14 brominated diphenyl ether (BDE)-congeners in sediment cores from three locations in Western Europe have been determined by GC/MS (negative chemical ionization mode). Sediments from the Drammenfjord (Norway), the western Wadden Sea (The Netherlands), and the freshwater Lake Woserin (Mecklenburg-Vorpommern, Germany) showed a time-dependent pattern in the distribution of BDEs since the beginning of the industrial production of polybrominated diphenyl ether (PBDE) formulations. Two out of three commercially available PBDE formulations could be distinguished. Starting from the beginning of the 1970s, the penta-mix formulation is clearly present, but the deca-mix formulation is only present since the late 1970s. The octa-mix formulation appeared to be still absent in these sediments, as its marker congener, BDE183, was never detected. In the cores from the western Wadden Sea and Lake Woserin, all TOC-normalized concentrations of the penta-BDE-derived congeners were leveling off in the most recent sediment layers representing 1995 and 1997, whereas those in the Drammenfjord were still increasing in 1999. The levels of BDE209, however, decreased in the most recent layer of all three cores. In Lake Woserin, the concentrations of BDE209 were much less elevated above those of the tri- to hexa-BDEs than in the other two areas. This might be due to the absence of a significant PBDE input from sources other than the atmosphere to this rural lake. The absence of all PBDE congeners in the older layers of the three sediment cores, as well as in several 100–150-My-old layers from an extremely organic-rich marine sediment from the Kimmeridge clay formation in Dorset (UK), indicated the absence of natural production of the BDE congeners analyzed.

## Introduction

Brominated flame retardants are added to many plastics and printed circuit boards used in electronic household equipment, and in textile and polyurethane foam in furniture and

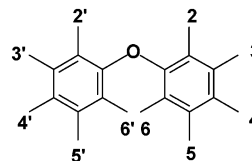


FIGURE 1. General structure of PBDEs;  $C_{12}OBr_xH_{(10-x)}$ . The positions 2–6 and 2'–6' may contain either bromine or hydrogen atoms. In theory, 209 different molecules are possible.

cars, for safety reasons. Among the brominated flame retardants (BFRs), there are three commercial formulations that contain the diphenyl ether skeleton. In order of increasing overall bromination, these formulations are named the penta-mix, octa-mix, and deca-mix. The global market demands in 1999 were 54 800 t for the deca-mix, 8500 t for the penta-mix, and 3825 t for octa-mix (1).

Polybrominated diphenyl ethers (PBDEs) are very hydrophobic ( $\log K_{ow}$  5–10) and resistant to environmental degradation processes. The congeners are numbered according to the IUPAC nomenclature used for PCBs (Figure 1). The aqueous solubility and vapor pressure of BDE congeners decreases with increasing degree of bromination, whereas hydrophobicity increases (2–4). The concentrations of the tetrabrominated BDE47, and the pentabrominated BDE99, and BDE 100 in guillemot (*Uria algae*) eggs from Stora Karlsö in the central part of the Baltic Proper were measured between 1969 and 1997: the levels of BDE47  $\gg$  BDE99 > BDE100. The lipid-normalized levels of all three congeners showed a sharp increase from 1973 to 1985 with an about equally rapid decrease from 1987 to 1997 (5).

The temporal trends of the occurrence of pollutants in the environment can also be derived from undisturbed and well-dated sediments in seas or lakes. The only example of this approach that is reported in the peer-reviewed literature refers to a sediment core from the Bornholm deep in the Baltic Sea (6). At that time, only the congeners BDE47, BDE99, and an unknown penta-BDE congener (probably BDE100) were reported, which showed continuous increases from 1972 to 1987.

This present study focused on the determination of a wider range of individual BDE-congeners in a number of sediment cores from three different locations in northwestern Europe. The main aim of this study was to investigate whether the distribution of PBDEs reflected the scale of their industrial production, or whether there were any indications of the occurrence of naturally produced BDE congeners, by investigating older layers of the same sediment cores as well as in ancient organic-rich sediments. The results of three cores with sediment deposited within the last 100 years and an ancient marine sediment core from the Kimmeridge clay formation on the south coast of England are discussed in this paper.

## Experimental Section

**Sample Collection. Drammenfjord Core.** The Drammenfjord is a branch of the Oslofjord in Norway. The sediment was collected in October 1999 with a Rheineck box corer at the position 59°38' N and 10°26' E from the R/V *Pelagia*, in a water depth of 100 m. A subcore was taken with a liner of 70-mm diameter which was sliced into sections of 0.5 cm.

**Wadden Sea Core.** The "Vlieter" was the main gully between the Wadden Sea and the former Zuiderzee before the latter was shut off from the Wadden Sea by the construction of a dike between the provinces of North Holland

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and Friesland in 1932, turning the Zuiderzee into the freshwater lake IJssel. The abrupt change in hydrodynamic conditions resulted in enhanced sedimentation both in the Wadden Sea and in Lake IJssel. The sediment was sampled with a gravity corer. The core consisted of a 160-cm-long segment of fine-grained sediment (alternating layers of fine sand and salty clay) overlying a coarse sandy section that was typical of the hydrodynamic conditions in the Vlieter prior to 1932. The alternating layers of clay and fine sand are indicative of intermittent sedimentation patterns. The core was taken in June 1997 at the position at 53°00' N, 5°04' E.

**Lake Woserin Core.** Lake Woserin, position 53°40' N, 12°01' E, is a small freshwater lake fed by a small stream in a rural area in the state of Mecklenburg-Vorpommern in Germany. The sediment samples were a kind gift of Professor J. F. W. Negendank of the Geological Research Center of Potsdam (Germany).

**Kimmeridge Clay Formation.** This is a marine formation from the Jurassic period (100–150 Ma), known for its high organic carbon content. For this study sediment from Swanworth Quarry 1 (Dorset, UK, 50°60' N, 2°05' W) was used, belonging to the Blackstone-Band (7).

**Dating of the Sediments.** Different methods were used to determine the ages of the sediment slices from different cores.

**Drammenfjord Core.** The ages of the different slices were determined by measurement of the specific activities of the isotopes  $^{137}\text{Cs}$  and  $^{210}\text{Pb}$ .

For analyses of  $^{210}\text{Pb}$  activity, the sediment samples were spiked with  $^{209}\text{Po}$  and digested with 5 mL of concentrated  $\text{HNO}_3$  and 5 mL of concentrated HF in a microwave oven for 3 h. Subsequently, 2 mL of 3.5%  $\text{HClO}_4$  was added and the acids were removed by evaporation. The resulting precipitate was redissolved in 40 mL of 0.5 M HCl, followed by spontaneous electrochemical deposition of the Po-isotopes onto silver in 0.5 M HCl at 80 °C for 4 h. The activity of  $^{210}\text{Pb}$  was measured via its  $\alpha$ -particle-emitting granddaughter isotope  $^{210}\text{Po}$  with a passivated implanted planar silicon detector (Canberra A-600-23-AM). Counting time was 48 h, and the counting error was 3–7%. The sedimentation rates were calculated according to the constant flux and constant sedimentation model with a correction being applied to allow for compaction (8).

The activity of  $^{137}\text{Cs}$  can be used to mark distinct years in the age of the sediment layers. Because the environmental occurrence of this compound is due to atmospheric nuclear fall-out, it cannot be present prior to the bombing of Hiroshima and Nagasaki at the end of World War II in 1945. However, the input from 1945 to 1951 has been negligible compared to the input from 1952 to 1963 (9). For instance, the input from 1945 to 1951 was only 11% of the input in 1952 alone (9). Therefore, we have interpreted the oldest sediment layer where  $^{137}\text{Cs}$  was detected as originating from 1952. Around 1963, the atmospheric levels of  $^{137}\text{Cs}$  produced globally as a result of the atmospheric testing of nuclear weapons reached a temporary maximum, after which the levels gradually decreased until the accident in the Chernobyl nuclear power plant in 1986. Especially in Scandinavia, this accident caused a sharp and unprecedented increase in atmospheric  $^{137}\text{Cs}$  concentrations.

The level of  $^{137}\text{Cs}$  was measured in 1 g of dry sediment from the different slices of the Drammenfjord core using a Canberra high-purity germanium  $\gamma$ -ray well-detector (Canberra GCW2522) with 25% relative efficiency. Counting time was 1 to 3 days, resulting in a counting error of 5–10%. The gamma detector was calibrated with a QCY48 standard mixed with sediment (10, 11).

**Vlieter Core (Western Wadden Sea).** Measurements of  $^{210}\text{Pb}$  were made, but the results were very difficult to interpret because of differences in grain size distribution, even after

correction for specific surface area. Therefore, this core was dated by comparing the concentration profiles of PCBs and PAHs to reported profiles from a sedimentation area in Lake IJssel (12). Similar contaminant distributions were identified in the Vlieter core, notably the 1940–1950 concentration minimum of PAHs, the 1960–1970 concentration maximum for PCBs and PAHs, and the sharp decrease in concentrations of both groups of contaminants after 1970.

**Lake Woserin Core.** The age of the different slices was determined by varve-counting at the Geological Research Institute in Potsdam, Germany.

**Kimmeridge Clay Core.** The two layers analyzed of the core from the Kimmeridge clay formation in southern England (Swanworth Quarry, Dorset, UK,) are from the Blackstone-Band, a stone formation out of the Kimmeridgian period (100–150 million years (My) old). At the time of deposition, this was a marine environment.

**Determination of the Total Organic Carbon Content.** Lipophilic compounds such as PBDEs have a high affinity for natural organic matter in sediments. To exclude concentration differences between sediment layers due to differences in their organic matter content, all measured BDE congener concentrations were normalized to the total organic carbon (TOC) contents of the respective layers. The TOC content of the slices was determined on a Carlo-Erba NA-11500 elemental analyzer (12) by combustion of the samples in tin cups after removal of all inorganic carbon with 10–50  $\mu\text{L}$  of sulfurous acid (J. T. Baker, Deventer, The Netherlands). The accuracy of the measurements, expressed as the coefficient of variation, was about 0.01 (13).

**Extraction Method for the Determination of PBDEs.** About 10 g of wet sediment was extracted overnight (> 12 h) in an Erlenmeyer flask with 15 mL of acetone on a Lab-line shaker (125 rpm); a spatula of sodium sulfite was added for sulfur removal. Decabromobiphenyl (BB209) was added as an internal standard. This compound was not detected in a series of 150 samples previously sampled from Dutch environments (14). After addition of 15 mL of pentane to the acetone–sediment slurry, the Erlenmeyer flask was shaken for another 2 h. The contents of the Erlenmeyer flask were subsequently transferred to a 75-mL centrifugation tube and 20 mL of bi-distilled water (pre-extracted with pentane) was added. The tube was centrifuged for 15 min at 2500 rpm, and the organic layer was collected and treated with sulfuric acid (2  $\times$  2 mL) to remove co-extractants. Subsequently, the extracts were passed over a silica column (2 g, deactivated with 6% water, elution with 20 mL of pentane) for the final cleanup. During this step the more polar hydroxylated and methoxylated BDEs are retained on the silica. The method has been described in more detail elsewhere as the “NIOZ” method (15).

**Analysis of PBDEs.** The concentrations of 14 individual BDE congeners (Cambridge Isotope Laboratories, Inc. Andover, MA) were determined by gas chromatography–mass spectrometry (GC/MS). The GC was a Hewlett-Packard 6890; the mass-selective detector was a Hewlett-Packard 5973. GC specifications: split-splitless injection; split valve closed for 1.5 min;  $T_{\text{injector}}$ , 270 °C; column, stationary phase CP Sil-8, 25 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$  (Chrompack, NL); carrier gas, He; linear gas velocity, 74  $\text{cm s}^{-1}$ ; constant flow programmed; oven temperature program, 90 °C (holding 1.5 min)/20 °C  $\text{min}^{-1}$ /190 °C (0 min)/4.5 °C  $\text{min}^{-1}$ /270 °C (5 min)/10 °C  $\text{min}^{-1}$ /320 °C (10 min). MSD specifications: negative chemical ionization (NCI) in the SIM mode at the  $m/z$  ratios of both bromine isotopes (79 and 81) and  $m/z = 487$  (for BDE 209 only); Ionization gas  $\text{CH}_4$ ;  $T_{\text{ion source}}$  210 °C;  $T_{\text{transferline}}$  320 °C;  $T_{\text{quadrupole}}$  160 °C.

The limit of detection (LOD), defined as a signal of 3 $\times$  the noise level, was established at 0.6 ng  $\text{g}^{-1}$  TOC for all BDE congeners, when an amount of 5 g of sediment with a TOC

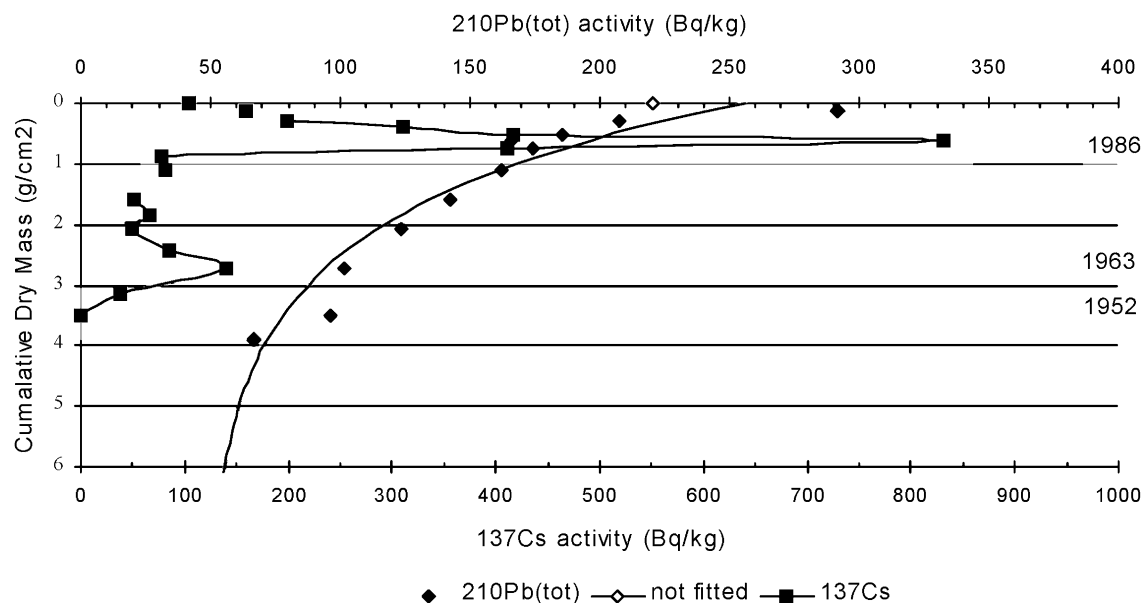


FIGURE 2. Age profile of the sediment core from the Drammenfjord (Norway) as established with the decay of  $^{210}\text{Pb}$  and absolute values of  $^{137}\text{Cs}$ .

of 1% was extracted. Only the fully brominated BDE 209 had a LOD of  $4.7 \text{ ng g}^{-1}$  TOC under the same circumstances. Other amounts of TOC affect these LOD values proportionally.

**Quality Assurance.** Before sample treatment, decabromobiphenyl (BB209) was added as an internal standard compound for the determination of recovery; a recovery within 70–120% was accepted. Although BB209 has been produced in France until recently, no indication of its occurrence has been found in the present set of samples, which were run simultaneously without the addition of this internal standard. Moreover, polybrominated biphenyls (PBBs) were also not detected in any sample from a large set of samples collected from Dutch coastal waters (14). Standard addition experiments showed good linearity for the compounds reported, and recoveries found after a second exhaustive extraction of the sediments were lower than 10%. At present, reference materials certified for BDE congeners are not available, but our participation in the first inter-laboratory study for PBDEs showed good performance for the sample matrixes sediment and biota (16).

## Results and Discussion

**Patterns of BDE Congeners.** In general, 3 out of 14 congeners analyzed were present as major compounds: BDE47 (2,2',4,4'-Br<sub>4</sub>), BDE99 (2,2',4,4',5-Br<sub>5</sub>), and, especially, the fully brominated BDE209 (2,2',3,3',4,4',5,5',6,6'-Br<sub>10</sub>). BDE28 (2,4,4'-Br<sub>3</sub>), BDE100 (2,2',4,4',6-Br<sub>5</sub>), BDE153 (2,2',4,4',5,5'-Br<sub>6</sub>), and BDE154 (2,2',4,4',5,6'-Br<sub>6</sub>) were regularly found at lower concentrations, while the BDE congeners BDE75 (2,4,4',6-Br<sub>4</sub>), and BDE85 (2,2',3,4,4'-Br<sub>5</sub>) were detected occasionally. The congeners BDE71 (2,3',4',6-Br<sub>4</sub>), BDE77 (3,3',4,4'-Br<sub>4</sub>), BDE138 (2,2',3,4,4',5'-Br<sub>6</sub>), BDE183 (2,2',3,4,4',5',6-Br<sub>7</sub>), and BDE190 (2,3,3',4,4',5,6-Br<sub>7</sub>) were never detected. The concentrations of the individual BDE congeners in the four sediment cores are listed in Tables SI-1–SI-4 in the Supporting Information.

**Temporal Trends.** The ages of the sections of the Drammenfjord core as determined by the  $^{210}\text{Pb}$  age model could be refined by calibration using the two distinct maxima of the  $^{137}\text{Cs}$  concentration, in 1963 and 1986, as well as the absence of  $^{137}\text{Cs}$  from sediment layers before 1952 (Figure 2).

In the Drammenfjord core, the three major BDE congeners of the industrial penta-mix PBDE formulation (the tetra-brominated congener BDE47 and the pentabrominated

BDE99 and BDE100) were first encountered in 1973 ( $\pm 1$ ), and the concentrations steadily increased until 1999 (Figure 3 and Table SI-1). The pattern of the major congeners remained very similar to that of the industrial formulation Bromkal 70-5DE throughout the entire core, indicating the absence of degradation processes affecting the different congeners in a selective manner. BDE209 appeared for the first time in 1975, and the concentration increased rapidly thereafter. Since 1978, BDE209 remains the dominant BDE congener in this core. In all subsequent years, its concentration is about an order of magnitude higher than those of the most prominent tetra- (BDE47) and penta-BDE (BDE99).

In the Vlieter core from the western (Dutch) Wadden Sea, the concentrations of all congeners were the highest compared to those of the other two cores (Figure 4 and Table SI-2). Moreover, the major individual compounds BDE47 and BDE99 were first found in  $1965 \pm 5$ , which seems somewhat earlier than in the Drammenfjord, although the dating of the Vlieter core was less precise. Just as in the Drammenfjord, however, BDE209 was detected for the first time in the late 1970s.

In Lake Woserin, the concentrations of the tri- to hexa-brominated congeners are similar to those in the Drammenfjord core, but the concentrations of BDE209 are about an order of magnitude lower (Figure 5 and Table SI-3). The increase in concentrations of the tri- to hexa-BDE congeners began in 1973 and the concentrations leveled off in the 1980s. In contrast to the other two cores, BDE209 cannot be detected before 1980, but appeared for the first time in 1985.

The most recent slice of all three cores showed a decrease in BDE209 levels compared to the levels found in the previous one. In Lake Woserin, this decreasing trend starts as early as 1991 and continues to the most recent layer of 1997. In the Vlieter core, the levels decreased from 1989 to the next layer representing 1995. In the Drammenfjord the BDE209 levels increased until 1998, but levels had decreased in 1999.

All PBDE signals were below the LOD in the 100–150-My-old sediments from the Kimmeridge clay formation at Swanworth Quarry, Dorset, UK, despite a very high organic carbon content of 15–25% (Table SI-4). Thus, this study provides no evidence for naturally produced BDEs in an ancient anoxic marine sediment where the environmental conditions have been favorable for the preservation of many natural organic compounds. This is in contrast to evidence



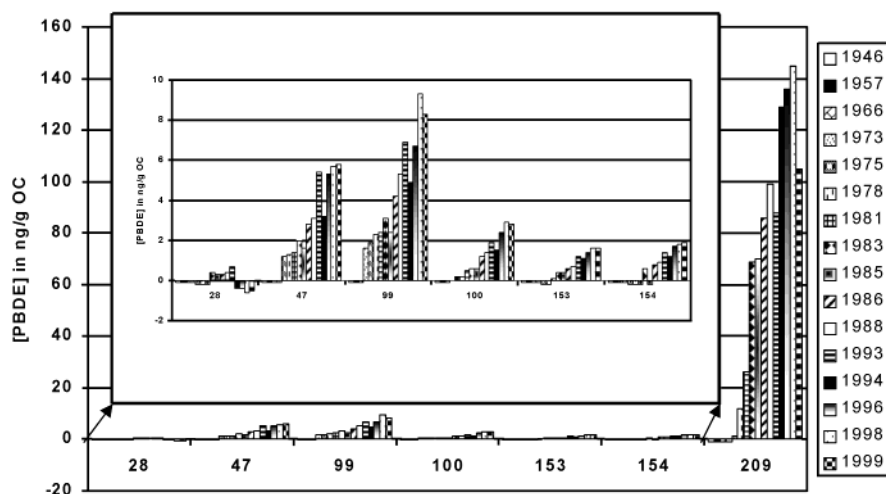


FIGURE 3. PBDE concentrations in  $\text{ng g}^{-1}$  total organic carbon (TOC) in dated layers from a sediment core from the Drammenfjord, Norway. The insert shows the values of the BDEs 28–154 on an enlarged scale. Concentrations below the limit of detection (LOD) are given as the negative value of the LOD.

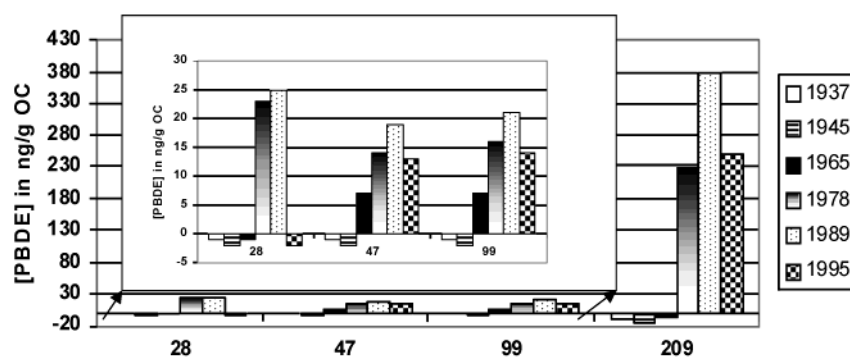


FIGURE 4. PBDE concentrations in  $\text{ng g}^{-1}$  total organic carbon (TOC) in dated layers from a sediment core from "De Vlieter" in the Western Wadden Sea. The insert shows the values of the BDEs 28, 47, and 99 on an enlarged scale. Concentrations below the limit of detection (LOD) are given as the negative value of the LOD.

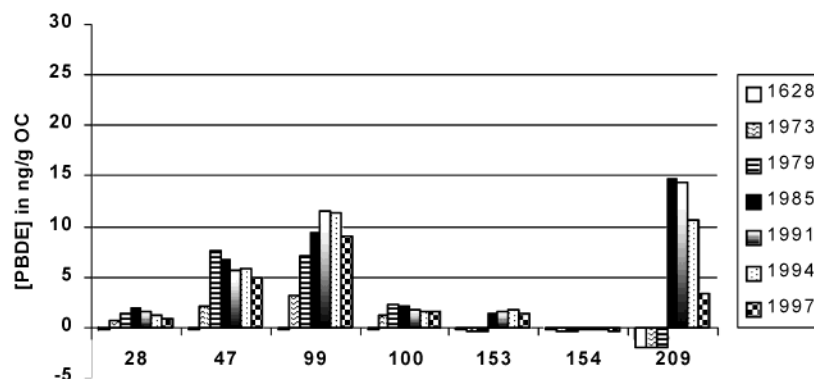


FIGURE 5. PBDE concentrations in  $\text{ng g}^{-1}$  total organic carbon (TOC) in dated layers from a sediment core from the freshwater Lake Woserin, Mecklenburg-Vorpommern, Germany. Concentrations below the limit of detection (LOD) are given as the negative value of the LOD.

for naturally produced methoxylated and hydroxylated PBDE derivatives (sponges *Dysidea* spp. and *Tedania ignis*), and polybrominated hydroxylated phenoxydiphenyl ethers (brown alga *Cystophora congesta* and the acorn worm *Ptychodera flava*) (17).

**Comparison with Other Data.** There is only one published case on the levels of individual BDE congeners in a dated sediment core available for comparison with our data (6). This core was taken in the Bornholm Deep in the Baltic Sea, close to the south coast of Sweden and the island of Bornholm. The concentrations reported for the different sediment layers covered the period between 1930 and 1987. BDE47, BDE99, and an unknown penta-BDE congener (probably BDE100)

were already detected between 1930 and the first half of the 1970s, but the concentrations remained at very low levels ( $0.05\text{--}0.22 \text{ ng/g}$  loss on ignition (LOI), representing the organic fraction of the sediment layer). The levels of these tetra- and penta- BDEs started to increase from the early 1970s onward and reached the highest value of  $2.9 \text{ ng/g}$  LOI in the top layer, which represented 1987. The rapid increase of the BDE concentrations since the 1970s corroborates with our data, but their presence before 1965 is in contrast with our findings. Because production of the penta-BDE mix did not start before 1970, the low levels in the older sediment layers may be caused either by natural production of these compounds, or by processes disturbing the initial laminar

sedimentation. BDE209 concentrations were not yet determined in this core.

**Potential Sources of PBDEs in Relation to Modes of Transport.** The PBDEs detected in different sediment cores can have been transported either via the atmosphere or via water currents and suspended particles. In the case of Lake Woserin, there are no industrialized tributaries to the lake. In this case, atmospheric input is the most probable route of PBDEs transport to the lake. In the case of the Wadden Sea and the Drammenfjord, the situation is different because both areas are in close contact with major industrial areas via water currents. High levels of BDE209 were found in sediments of the Belgian/Dutch river Scheldt, whereas intermediate levels were found in sediments from the Rhine–Meuse estuary (18). Low levels of all PBDE formulations were present in the Scandinavian rivers Göta, Glomma, Skien, and Otra (18). The Drammenfjord is a branch of the partly heavily industrialized greater Oslofjord, including the city of Drammen at the head of the fjord. Thus, a PBDE input from local sources via the dissolved phase or suspended particles is much more likely for these two areas than for Lake Woserin. In this respect, the relatively low levels of BDE209 compared to that of the lower brominated BDE congeners in Lake Woserin may indicate that atmospheric transport is a less important route for the relatively nonvolatile BDE209 than it is for the lower brominated congeners. However, expansion of the current data set is necessary to substantiate this conclusion.

**Possible Importance of Environmental Degradation Processes.** The congener pattern of the tri- to hexa-BDE congeners in our three recent sediment cores still showed a high resemblance to their pattern in the industrial penta-BDE mixtures of the different manufacturers. Also, the GC/NCI-MS chromatograms did not show any peaks of brominated compounds that were not present in either the penta-BDE formulation or the deca-BDE formulation. Thus, degradation processes in these marine sediments are probably not very important. Alternatively, degradation processes of BDE209 could directly produce the identical congeners as dominating in the penta-BDE mixture, but that would result in ratios between the tri- to hexa-BDE congeners clearly different from those in the technical penta-BDE formulation. This is not the case. As a last possibility, degradation processes might produce compounds other than PBDEs, analyses of which were beyond the scope of this study.

The results of this work show that BDE congener concentrations show time-dependent patterns in these cores. The majority of the BDE congeners were first observed around 1970, but BDE209 appeared about a decade later. This is in agreement with the industrial production figures for the commercial penta-mix and deca-mix PBDE formulations (1). The systematic absence of BDE183 indicates that the environmental occurrence of the octa-PBDE mixture is presently negligible in the areas investigated. In the cores from the western Wadden Sea and Lake Woserin, the TOC-normalized concentrations of the tetra- to hexa-brominated BDEs were leveling off, whereas those in the Drammenfjord were still increasing at the end of the 1990s. In contrast, the concentrations of BDE209 had decreased in the most recent layer of all three cores.

There is no evidence from the deeper (older) sediment layers from these cores, or from the ancient marine sediments of the Kimmeridge Clay formation, for the natural production of the BDE congeners determined in this study.

## Acknowledgments

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Center of Potsdam, Germany. We wish to express our gratitude to the crew of the NIOZ R/V *Pelagia* for their sampling of the core in the Drammenfjord. This cruise was financed by The Netherlands Organization for Scientific Research (NWO), for which they are kindly acknowledged. The suggestions of Dr. R. J. Law of the Centre for Environment, Fisheries and Aquaculture Sciences (Burnham on Crouch, Essex, UK) resulted in a considerable number of improvements in the present version of the manuscript. This project was financed by the Bromine Science and Environmental Forum (BSEF), Brussels, Belgium.

## Supporting Information Available

Four tables with the TOC-normalized concentrations of the different BDE congeners and the TOC contents of the different sediment slices of the sediment cores analyzed. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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