

LEVELS AND TRENDS OF POLYBROMINATED DIPHENYL ETHERS IN PORTUGUESE RIVER BASINS

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Introduction

Polybrominated diphenyl ethers (PBDEs) are globally distributed contaminants with a similar molecular structure to classical persistent organic pollutants (POPs), such as polychlorinated dibenzo-*p*-dioxins (PCDDs), furans (PCDFs) and biphenyls (PCBs). PBDEs have been shown to be present in many species and numerous temporal studies have indicated that PBDEs levels are rapidly increasing worldwide.¹

The main use of PBDEs is as flame-retarding additives to polymeric materials used in a range of applications including plastics, textiles and electronics. PBDEs are merchandised as technical mixtures of diphenyl ethers with a varying degree of bromination, containing mainly tetra to decabrominated diphenyl ether. At present the most predominant PBDE congener found in ambient air, soil, sediment and biota appear to be BDE 47, BDE 99, BDE 100 and BDE 209.²

It was once widely held that brominated flame retardants (BFRs) and, in particular, polybrominated diphenyl ethers (PBDEs) applications were non dispersive and environmental burdens would thus be minimal. However, growing evidences indicate that PBDEs are released in significant amounts. Despite low volatilities and water solubilities, PBDEs, are generally environmentally persistent, permitting eventual long-range transport. Abiotic media are their primary recipients, transporters and sinks. Hence examination of these media is crucial for identifying important PBDE source, trends and exposure scenarios.³

However, there is an evident lack of data on the levels and trends of PBDEs in Portugal. To our knowledge there are only one work about the contamination of sediment in five Portuguese rivers in 2001⁴, and another about the occurrence of PBDEs in river and coastal biota.⁵

The main objective of the present study was measure the concentrations of PBDEs in a number of surface sediments from Portuguese rivers between 2002 and 2004. Through this study, the temporal trend and spatial distribution of PBDEs in the sediments of Portuguese rivers will be revealed. Throughout this work, PBDEs levels have been compared to others studies to provide a global perspective on the PBDE contamination in Portugal.

Materials and Methods

Chemical reagents and standard solutions

PBDEs chemical standards were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). These standards included a standard solution (EO-4980) containing 39 PBDEs, 3 monoBDEs (BDE 1, BDE 2 and BDE 3), 7 diBDEs (BDE 7, BDE 8, BDE 10, BDE 11, BDE 12, BDE 13 and BDE 15), 8 triBDEs (BDE 17, BDE 25, BDE 28, BDE 30, BDE 32, BDE 33, BDE 35 and BDE 37), 6 tetraBDEs (BDE 47, BDE 49, BDE 66, BDE 71, BDE 75 and BDE 77), 7 pentaBDEs (BDE 85, BDE 99, BDE 100, BDE 105, BDE 116, BDE 119 and BDE 126), 5 hexaBDEs (BDE 138, BDE 153, BDE 154, BDE 155 and BDE 166) and 3 heptaBDEs (BDE 181, BDE 183 and BDE 190) and PCB 209 used as a internal standard.

Sample collection

The surface sediments were collected from 14 Portuguese rivers. These rivers are, from north to south, river Minho (flow of 300m³/s), Neiva, Cávado, Ave, Leça, Douro (flow of 450m³/s), Vouga (flow of 70m³/s), Mondego (flows of 80m³/s), Tejo (flows of 400m³/s), Guadiana (flows of 80m³/s), Sado (flows of 40m³/s),

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Arade, Formosa (flow of 70m³/s) and Benzafrim, and all discharge, except Guadiana, their waters to the Atlantic Ocean (Figure 1).



Fig. 1. Map of Portuguese rivers where surface sediments were collected.

The samples were transferred to the laboratory at a temperature of 4°C. Samples were freeze dried during four days. The lyophilized samples were homogenized and sieved through a stainless steel of 106 µm and stored in sealed containers at -20°C until analysis.

Sample preparation

Sample extraction was done using a pressurized liquid extraction (PLE) system (ASE 200, Dionex, Sunnyvale, CA, USA). Extraction cells (22 mL) were loaded by inserting two cellulose filters into the cell, 2 g of diatomaceous earth (Hydromatrix, Dionex, Sunnyvale, CA, USA.) and 1,5 g of sample. The sediment extraction was performed using a dichloromethane:hexane (1:1 v/v) mixture as solvent with two cycles at a pressure of 1500 psi and heated to 100 °C. The static time was 5 min, flush volume was 100 %, and the purge time 90 s. The final volume of the extract was approximately 33 mL and was therefore carefully evaporated to incipient dryness under a gentle stream of nitrogen and finally brought up to 500 µL with isoctane containing the recovery standard (PCB 209) for analysis by gas chromatography/mass spectrometry (GC/MS).

GC-NCI-MS analysis

Sample analysis for PBDEs was conducted using gas chromatography (Trace GC, ThermoFinnigan, USA.) with a mass spectrometer (Trace DSQ, ThermoFinnigan, USA.) operated in electron capture negative ionization (GC/ECNI-MS), equipped with a CP-SIL 8 CB Low bleed/MS (30m x 0.25 mm i.d., 0.25 µm film thickness) capillary column. 2µL of sample was injected using an autosampler with the injector operated in the splitless mode at 250 °C with a injection time of 1 min. Interface and ion source temperatures were set to 270 and 250 °C, respectively. The oven temperature was initially held at 110°C for 1 min and then ramped to 180°C (1 min) at a rate of 8°C/min, followed by a temperature ramp of 2°C/min to 240°C (5 min), and then to a final temperature of

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280°C (6 min) at 2°C/min. Methane was used as chemical ionization gas. The experiments were carried out by monitoring the two most abundant peaks from the mass spectra corresponding to $m/z = 79$ and 81.

Results and Discussion

PBDEs were detected in almost all the sediments samples (around 70%). Of the 39 congeners included in the analytical work, the most common PBDE detected were BDE 47, BDE 99 and BDE 100.

From the data obtained it is very clear that the north is much more contaminated with PBDEs than the south, which is not surprising, in fact the industries mainly related to textile, metal and paper, are located specially in the north of Portugal. These results are consistent with the results obtained in biota samples (*Barbus sp.*).⁵

Temporal monitoring of PBDEs levels in Portuguese sediments generally shows an increasing concentration trend, although the variability is large.

PBDEs profiles were calculated based only on 39 PBDEs from mono- to hepta-BDE. BDE 209 was not included in the profile to be able to compare with the commercial Penta-BDE (Bromkal 70-5DE) which consists of 24-38 % tetra-BDEs (especially BDE 47) and 50-60 % penta-BDEs (35 % of BDE 99 and 6,8 % of BDE 100)². As expected the congener specific profile in sediments from 2004 were very similar with the commercial Penta-BDE, where BDE 47 and BDE 99 are the most frequent congeners detected.

When the profiles obtained in sediments samples were very similar with the commercial mixture, imply a high degree of persistence of these compounds to degradation in the sediments. However, it's important to quantify the BDE 209, to see if the compounds detected are from the commercial Penta-BDE or the degradation of the commercial Deca-BDE.

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