THE OCCURRENCE OF POLYBROMINATED DIPHENYL ETHERS (PBDES) IN RIVER AND COASTAL BIOTA FROM PORTUGAL

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INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are flame retardants used commercially as non-covalent additives in polymeric materials with half-lives on the order of 2-10 y. PBDEs, similar in molecular structure to polychlorinated dibenzo-p-dioxins (PCDDs), furans (PCDFs), and biphenyls (PCBs), are of concern due to their persistence, bioaccumulation, and possible adverse effects in wild life and humans[1].

Throughout this work PBDEs level determination in biota was developed for the first time in Portugal. The data obtained was important to provide a global perspective on the PBDEs contamination in Portugal and allows the comparison with studies made in other countries[1,3,4].

PBDEs have been reported in river and coastal sediments samples of the eight main rivers of Portugal[2].

Environmental levels of fourteen polybrominated diphenyl ethers (PBDEs) were analysed in a number of biota samples taken over a large geographic range covering five rivers and coastal areas of Portugal.

MATERIALS AND METHODS

Chemical reagents and standard solutions

The polybrominated diphenyl ether analytical standards solutions were purchased from RIVO. The components of these solutions were one tri-BDE (BDE 28), five tetra-BDE (BDE 47, BDE 66, BDE 71, BDE 75, BDE 77), four penta-BDE (BDE 85, BDE 99, BDE

100, BDE 119), three hexa-BDE (BDE 138, BDE 153, BDE 154) and one hepta-BDE (BDE 190). The concentrations of each compound ranged from 50 ng/mL to 600 ng/mL.

Five different solutions were prepared in order to check the linearity of the method. These solutions contained 14 PBDE congeners, at different concentrations ranging between 5 and 50 ng/mL.

Solvents (dichloromethane, hexane and methanol) for organic trace analysis were purchased from Riedel de-Häen.

Sample collection

The biota samples were collected from coastal areas (mussels- *mytilus galloprovincialis*) and from five Portuguese rivers (fishs - *barbus sp.*). These rivers are, from north to south, river Douro (450m^3/s), Mondego (80m^3/s), Tejo (400m^3/s), Guadiana (80m^3/s) and Sado (40m^3/s), and all discharge their waters to the Atlantic Ocean.

The samples were transferred to the laboratory at a temperature of 4ºC. All fish samples were divided in two, one was the body muscle and the other was the liver. Then all samples (fish body muscles, fish liver, and mussels) were frozen at -20ºC before being freeze dried. The lyophilized samples were grounded and homogenized by sieving through a stainless steel and stored in sealed containers at -20ºC until analysis.

Sample preparation

Samples were Soxhlet extracted (0,5 g muscle, 0,3 g liver) in hexane:dichloromethane (1:1) during a period of 24 hours. The extract was rotaevaporated nearly to dryness (2 mL) and sample clean up was performed with a Florisil cartridges. Cartridges were placed on a Baker SPE apparatus connected to a vacuum system. The cartridges were conditioned with 20 mL hexane:dichloromethane (19:1). Afterwards, 2 mL of sample extract was placed on the top of the cartridge and eluted by gravity with 20 mL hexane:dichloromethane (19:1) and 20 mL hexane:dichloromethane (1:2). Samples were finally concentrated to almost dryness and reconstituted in 1 mL isooctane.

GC-NCI-MS analysis

GC-NCI-MS was performed on a ThermoFinnigan Trace GC gas chromatograph connected to a ThermoFinnigan Trace DSQ (USA) mass spectrometer. A CP-SIL 8 CB Low bleed/MS (30m x 0,25 mm i.d., 0,25 µm film thickness) capillary column was used with helium as the carrier gas. The temperature program was from 110ºC (held for 1 min) to 180ºC (held for 1 min) at 8ºC/min, then from 180ºC to 240ºC (held for 5 min) at 2ºC/min, and then from 240ºC to 280ºC (held for 6 min) at 2ºC/min. The operating conditions were as follows: ion source temperature 250ºC and methane 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

The used method allows the determination of 14 PBDEs congeners in river and coastal biota samples from different parts of Portugal. In all of the samples analysed we found at least one PBDE.

Tetrabromodiphenyl ether (BDE 47) was found in all samples, has reported in other works[1,3,4,5], mainly due to the fact that BDE 47 is one of the major component of Bromkal 70-5DE (BK70), which was used in many countries.

Pentabromodiphenyl ether (BDE 100) was detected in several samples, especially in Mondego river.

The major values of PBDEs were found in fish's liver. High lipid contents in liver might be the main reason why the average concentrations of PBDEs in liver were larger than those in the fish muscle.

CONCLUSIONS

It is not known whether the contamination of low brominated congeners in fish and mussels was caused by "tetra-BDE" that had been discharged into the environment in the past, or it is caused by ongoing contamination resulting from effluence from resin products buried in landfills or from debromination of highly brominated diphenyl ethers[3]. The presence of lower brominated PBDEs congeners in Portuguese biota indicate that effort should be directed to study possible environmental transformation of higher brominated congeners. This will improve the existing knowledge on the persistence, degradation and fate of these compounds in the environment.

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