

Polybrominated Diphenyl Ethers - Environmental Contaminants of Concern

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Background

Brominated flame retardants (BFRs) include a large number of different types of brominated substances, used extensively in polymers and textiles to prevent ignition and to slow down the initial phase of a developing fire (1). One class of BFRs is polybrominated diphenyl ethers (PBDEs). The annual global consumption of PBDEs was in 1992 estimated to be 40,000 tons. PBDEs are commercially produced in mixtures with different degrees of bromination, known as penta-, octa- and decaBDE, corresponding to 10, 15 and 75 %, respectively of the total PBDE consumption (2,3). The composition of one commercial PBDE product was recently described in detail (4). Only a limited number of the theoretically possible PBDE congeners are present in each commercial PBDE product, most likely depending on *ortho/para*-directed substitution caused by the ether oxygen and also due to the steric hindrance. PBDEs may be characterized as persistent and highly lipophilic substances, with low vapor pressure, similar to well-known environmental contaminants such as polychlorinated biphenyls (PCBs).

PBDEs are frequently used as additives in plastic materials for electronic and electrical goods (TV-sets, computers, fax machines and housings of electrical appliances) and in textiles (3). The use of PBDEs as additives makes those articles vulnerable to leakage from the plastic materials and textiles where they may be used.

PBDEs were reported as environmental pollutants in pike from the Swedish River Viskan in 1981 (5). Since then, PBDEs have been reported as pollutants in fish (5-11), birds (9), and mammals (9) as well as in sediments (6, 7). Most recently, high concentrations of PBDEs were reported in salmon (*Salmo salar*) from the Baltic (10), but high levels are also present in Steelhead trout from Lake Michigan (unpublished). The levels of 2,2',4,4'-tetraBDE (BDE-47*) were reported to be in the range 280-1200 ng/gm Harbor seal blubber (13). The concentrations of BDE-47 have been reported to be approximately 2 ng/g (l.w.) both in human blood (14-16) and in mothers' milk (17). It is alarming that the PBDE levels are increasing over time as have been shown in mothers' milk (17).

In biota, among all PBDE congeners, BDE-47 seems to be present at the highest concentrations. Other PBDE congeners found in the environment are 2,2',4,4',5-pentaBDE (BDE-99), 2,2',4,4',6-pentaBDE (BDE-100), 2,2',4,4',5,5'-hexaBDE (BDE-153), and 2,2',4,4',5,6'-hexaBDE (BDE-154) (9,10, 13-17). In addition, a heptaBDE has been identified in trout from Lake Ontario, USA (8). Typical levels in a few selected materials are summarized in Table 1.

Table 1. Concentrations (ng/g lipid weight (l.w.)) of PBDEs in humans and wildlife.

Species	Locality	Tissue	PBDE concentration (ng/g l.w.)			Reference No.
			BDE-47	BDE-99	BDE-100	
Human	Sweden	Plasma	1.6	n.a.	n.a.	(14-16)
Human	Sweden	Milk	2.2	0.4	0.5	(17)
Salmon	Baltic Sea	Muscle	200	54	47	(10)
Herring	Bothnian Sea	Muscle	82	14	27	(9)
Grey seal	Baltic Sea	Blubber	650	38	40	(9)

PBDE standards

PBDEs are commercially produced by direct bromination of diphenyl ether in the presence of a catalyst. Methods that are much more specific are in general necessary for synthesis of pure individual PBDE standards.. The standards listed in Table 2 are available from Cambridge Isotope Laboratories, Inc.

Table 2. PBDE congeners that have been synthesized. Compounds present in the commercial pentaBDE product, Bromkal 70-5DE, are given in bold italics.

BDE No.	No. of Br	Structure	BDE No.	No. of Br	Structure
1	1	2	47	4	2,2',4,4'
2	1	3	51	4	2,2',4,6'
3	1	4	66	4	2,3',4,4'
7	2	2,4	71	4	2,3',4',6
8	2	2,4'	75	4	2,4,4',6
10	2	2,6	77	4	3,3',4,4'
11	2	3,3'	85	5	2,2',3,4,4'
12	2	3,4	99	5	2,2',4,4',5
13	2	3,4'	100	5	2,2',4,4',6
15	2	4,4'	116	5	2,3,4,5,6
17	3	2,2',4	119	5	2,3',4,4',6
25	3	2,3',4	138	6	2,2',3,4,4',5'
28	3	2,4,4'	140	6	2,2',3,4,4',6'
30	3	2,4,6	153	6	2,2',4,4',5,5'
32	3	2,4',6	154	6	2,2',4,4',5,6'
33	3	2',3,4	155	6	2,2',4,4',6,6'
35	3	3,3',4	166	6	2,3,4,4',5,6
37	3	3,4,4'	181	7	2,2',3,4,4',5,6
			190	7	2,3,3',4,4',5,6

* Since the symmetries are the same, the BDE congeners have been numbered according to the BZ system for PCBs (12)

Analysis of PBDEs in environmental samples

The general procedure for analysis of PBDEs includes extraction and lipid weight determination. Lipids are preferably removed from the extract by partitioning between n-hexane and concentrated sulfuric acid, or by gel permeation chromatography. Further clean-up of the samples may be performed on a small silica gel/sulfuric acid column (18-21). Analysis using gas chromatography/mass spectroscopy (GC/MS) may be performed using the negative ions formed by electron capture reactions at chemical ionization (ECNI), scanning for m/z 79/81, representing the bromine ion (22) or by GC/HRMS (17). If gas chromatography with electron capture detector (GC/ECD) is used, it is necessary to remove the more abundant polychlorinated biphenyls that otherwise would interfere with the analyte. This may be done using high pressure liquid chromatography to collect a PBDE fraction that can be analyzed using GC/ECD (10). A typical chromatogram (GC/MS (ECNI)) of lipids extracted from salmon muscle is shown in Figure 1. The identities of the PBDE congeners are given by their BDE-numbers (Table 2).

Acknowledgment

The work on PBDEs has been supported by the Swedish EPA, EU (Environment and Climate Program for Research).

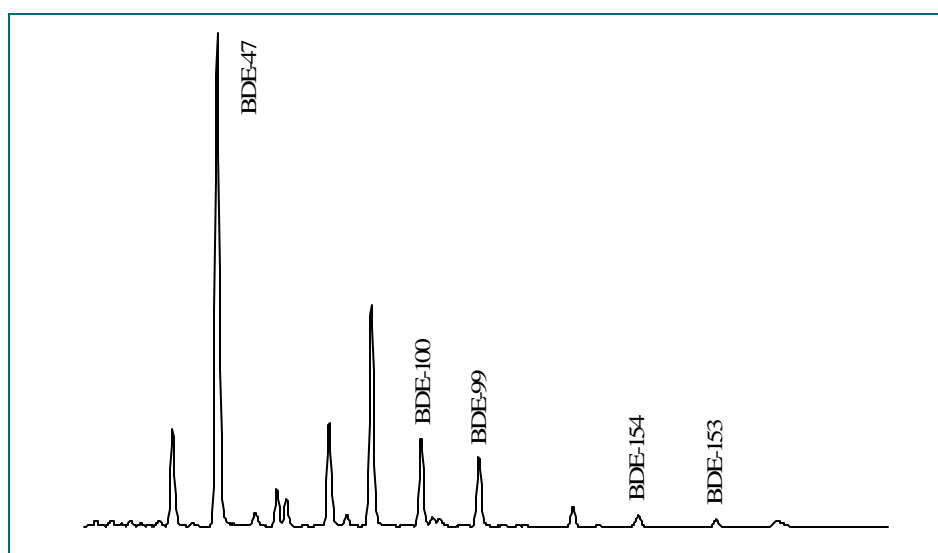


Figure 1

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