Determination of Polybrominated Diphenylethers (PBDEs) and other Halogenated Components in Sediments Collected in Pakistan

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Introduction

Polybrominated diphenylethers (PBDEs) are widely used as flame retardants in polymer materials, textiles, electronic boards and various other materials. Technical PBDE preparations are produced as mixtures of mainly penta-, octa- or decabrombiphenyl ethers[1]. PBDEs are structurally similar to other environmental pollutants like dioxins and PCBs, they are lipophilic and persistent components and widespread in the environment.

Environmental monitoring of persistent organic pollutants (POPs) and particularly PBDEs, PCDDs/PCDFs and the dioxin-like PCBs is quite expensive and requires specialized laboratory facilities ideally equipped with High Resolution Mass Spectrometry (HRMS) instrumentation. Hence, by far the majority of work on PBDEs, PCDDs/PCDFs and dioxin-like PCBs has been carried out in industrialized countries in Europe, North America and Japan. In contrast there is very little – or no information available on the levels of these chemicals in the environment of developing nations and to our knowledge no data are available on the levels of these chemicals in the environment in Pakistan.

Methods and Materials

Samples

For the purpose of this study sediment samples were collected from 9 locations following a transect of the Indus River (5 Locations) and in the vicinity of the industrial areas of Karachi Harbor and Gizri Creek, a key industrialized area on the major urbanized area of Pakistan's coastline.

Analytical Methods

For analysis freeze-dried, homogenized samples were send to the ERGO Laboratory in Hamburg. All analyses were performed following the isotope dilution method. Ten native standards (BDE Nos. 17, 28, 47, 66, 99, 100, 138, 153, 154, 183) were obtained from Cambridge Isotope Laboratories, Andover, USA. One native standard (BDE No. 209) was from Wellington Laboratories, Guelph, Canada. Six internal C^{13} labeled standards (BDE Nos. 28, 47, 99, 153, 154 and 183) were delivered by Wellington,

Canada, one (BDE No. 209) was from Cambridge. Solvents were delivered by Promochem (cyclohexane, dichloro methane) and Mallinckrodt (toluene). Silica gel, aluminia oxide, sodium sulfate were obtained from Merck.

Table 1: Sediment samples from Pakistan

Code	Station	Salinity	Pool (No of samples)	Description
PK 1	Indus River	Fresh water	Samples from Indus River up stream	Collected at different barrages at Indus River
PK 2	Indus River	Fresh water	dto	dto
PK 3	Indus River	Fresh water	dto	dto
PK 4	Indus River	Fresh water	dto	dto
PK 5	Indus River	Fresh water	dto	dto
PK 6	Indus River, down stream	Oceanic	Indus River down stream, entrance of the sea (pool of 2 samples)	
PK 7	Korangi Creek area	Estuarine	Pool of 4 samples	Including steel mill area and Port Qasim Area.
PK 8	Gizri Creek	Estuarine	Pool of 2 samples	During low tide receiving untreated Industrial and Domestic waste in area
PK 9	Karachi Harbour	Oceanic	Pool of 4 samples	About 15 km area within Karachi harbour

A total of 2 g sediment was mixed with sodium sulfate. Before extraction a mixture of 7 internal BDE standards was added to the sample (100 pg / sample for each congener with the exception of Deca-BDE: 10,000 pg). For soxhlet extraction toluene was applied. Extracts were concentrated to dryness and subject to purification using a multicolumn system consisting of sulfuric acid on silica, activated silica gel and aluminia oxide columns. The final extract was reduced in volume by a stream of nitrogen, the final volume was 50 µl containing C^{13} labeled BDE 139 (Wellington) for recovery standard.

The measurements were performed using high-resolution gas chromatography /high resolution mass spectrometry (HRGC /HRMS, HP 5890 coupled with VG Autospec) at RP = 10 000 using a DB 5 (30 m, 0.25 mm ID, 0.1 µm film) column for gas chromatographic separation. The two most abundant masses were used for measurement (M^+ for Tri- and Tetra-BDE, and $M\text{-}2BR^+$ for Penta- to Deca-BDE). The identification of BDEs was based on retention time and isotope ratio. The quantification was performed using internal and external standards.

Reduction of solvents and control of blank data is an important step in quality control when analyzing PBDEs at ultra trace levels. Solvents and reagents were tested before the laboratory procedures. All glassware was rinsed by solvents prior to use. Silica gel and sodium sulfate were pre-washed. To reduce the risk of contamination, rotary

evaporators were not used. No plastic equipment was used. For quality control reasons a laboratory blank and a QC pool was run with the batch of nine samples. Quantification was only done if sample data was at least twice the blank value.

Results and Discussion

The results of the investigation are presented in table 2.

Table 2. Concentrations of PBDE congeners in sediment samples from Pakistan, (ng/g dry matter) totals are given as upper bound values.

Sample	BDE No.										
	17	**28**	**47**	**66**	**99**	**100**	**153**	**154**	**183**	**209**	**Total BDEs**
PK 1	n.d. (0.002)	n.d. (0.007)	n.d. (0.024)	n.d. (0.002)	n.d. (0.012)	n.d. (0.002)	n.d. (0.002)	n.d. (0.002)	n.d. (0.003)	n.d. (0.020)	0.08
PK 2	n.d. (0.002)	n.d. (0.007)	n.d. (0.020)	n.d. (0.002)	n.d. (0.014)	n.d. (0.002)	n.d. (0.002)	n.d. (0.002)	n.d. (0.003)	n.d. (0.020)	0.07
PK 3	n.d. (0.002)	n.d. (0.007)	n.d. (0.024)	n.d. (0.002)	n.d. (0.014)	n.d. (0.002)	n.d. (0.002)	n.d. (0.002)	n.d. (0.002)	n.d. (0.10)	0.16
PK 4	0.003	n.d. (0.007)	0.025	n.d. (0.002)	0.020	0.005	0.003	0.003	0.015	1.74	2.45
PK 5	n.d. (0.002)	n.d. (0.006)	n.d. (0.024)	n.d. (0.002)	n.d. (0.012)	n.d. (0.002)	n.d. (0.002)	n.d. (0.002)	n.d. (0.003)	n.d. (0.04)	0.06
PK 6	n.d. (0.002)	n.d. (0.007)	n.d. (0.024)	n.d. (0.002)	0.013	n.d. (0.004)	n.d. (0.003)	n.d. (0.003)	0.003	n.a.	0.06
PK 7	n.d. (0.002)	n.d. (0.005)	0.24	n.d. (0.002)	0.030	0.003	0.003	0.004	0.005	0.88	1.17
PK 8	0.028	0.08	0.15	0.011	0.22	0.046	0.029	0.031	0.043	5.85	6.49
PK 9	0.018	0.07	0.10	0.007	0.13	0.024	0.020	0.021	0.046	6.68	7.12

n.d. = not detected, limit of detection in (LOD) n.a. = not analyzed

Nearly all 6 samples collected at the Indus River area (one exception: PK 4) do not show any or nearly any PBDE contamination. The highest concentrations were found in samples collected in the Karachi area/harbor. In all cases the most prominent congener was Deca-BDE.

Table 3. PBDEs in sediment samples, other studies, in ng/g, dry matter, values given as mean and (range)

Area	Author	n	BDE 47	BDE 99	BDE 209
EU, estuaries	Kierkegaard et al., 1997 [3,4]	22	0.76(<0.2–5.8)	0.87(<0.2–6.9)	95(<0.5-1,700)
Sweden, rivers	Sellström et al., 1998 [5]	9	10(<2-50)*	15(<2-63)*	1770(<20-16,000)*

Japan, Osaka Bay	Sakai et al., 2002 [6]	8	n.r.	n.r.	<6-910
Austria, Rivers	Mosche et al., 2003 [7]	13	0.45 (0.1-3.4)	0.46 (0.1-3.9)	n.a.
Denmark, marine and freshwater	Platz et al., 2001 [8]	16	0.3 (<0.03-1.12)	0.5 (0.04-2.2)	4.6 (<1.3-21.5)
North-America	Muir et al., 2003 [9]	8	n.a.	n.a.	15.3 (<0.1-112)

* = data based on ignition loss n.a. = not analysed n.r. = not reported

Our data are in agreement with data published by other investigators as given in Table 3. On the other hand data found for Pakistan are much lower compared to sediment samples from Europe, Japan and the United States.

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