POLYBROMINATED DIPHENYL ETHERS (PBDEs) IN THE FIRTH OF CLYDE IN RELATION TO SEWAGE SLUDGE INPUT

L. Webster, M. Russell, F. Adefehinti, E. J. Dalgarno, and C. F. Moffat
FRS Marine Laboratory, PO Box 101, 375 Victoria Road, Aberdeen, UK

Introduction

Brominated flame retardants (BFRs) have been used as flame retardants in textiles, plastics and electronics for several decades. Polybrominated diphenyl ethers (PBDE) were one of the most widely used groups of BFRs. PBDEs are persistent and toxic, with a potential for bioaccumulation, and can undergo long range atmospheric transport. As such they are included on the Oslo and Paris Commission (OSPAR) List of Chemicals for Priority Action (OSPAR 2001). At present there is little information on environmental concentrations of PBDEs in Scotland and though not produced in Scotland these compounds have been produced in the UK and have been detected in the UK environment (Law et al. 2006).

The penta mixture, used in furniture and upholstery, contains mainly tetra- and penta-BDEs and the octa mixture, used in plastics contains mainly hexa- to hepta-BDEs. BDE209 is the dominant congener in the deca mixture and is used mainly in textiles (OSPAR 2001). On 30 January 2001 the European Commission issued a proposal to ban the penta technical mixture. This ban was finally put in place on 15 August 2004, restricting the use of the penta and octa technical mixtures. Although penta and octa BDE technical mixtures have been phased out in Europe, production and use continues in other parts of the world such as Asia. PBDEs can be released to the environment during their production and while manufacturing other products, and during disposal of products containing theses chemicals. In addition, PBDEs may continue to leak out of treated material.

Due to its industrial legacy, the Clyde is arguably Scotland's most heavily contaminated water body. Effluent and accidental discharges from engineering works, military bases, textile and paper industries have all resulted in environmental contamination of the area. One of the most concentrated inputs of contaminants into the Firth of Clyde was as a result of sewage sludge dumping. Sewage sludge was disposed of annually at Garroch Head, south of the Isle of Bute, from 1904 up to 1998 when disposal ceased in order to meet the UKs' obligations under the EC Urban Waste Water Treatment Directive 91/271/EEC. Sewage sludge contains significant quantities of contaminants. Chlorobiphenyls (CBs) have been monitored in plaice liver from Garroch Head and a reference site (Pladda) since 1992 and in sediment since 1999 (Fig. 1) (Webster et al. 2005). PBDEs were measured in some of these plaice liver (1996 – 2005) from Garroch Head and at Pladda. Core samples collected from Garroch Head in 2003 were also analysed for PBDEs.

Materials and Methods

Due to the possibility of photolytic degradation special precautions were observed when analysing PBDEs. Incoming light was minimised in the laboratory by placing UV filters on the windows and lights were kept turned off. A laboratory reference material (LRM) and procedural blanks were run with each batch of samples. This method is accredited to ISO 17025 by the United Kingdom Accreditation Services (UKAS).

Biota

Lipid content was determined using a modified Smedes method (Smedes 1999). An appropriate amount of tissue (equivalent to 300 mg lipid) was mixed with sodium sulphate (~20 g), spiked with recovery standard (CB198), and left overnight before being ground to a fine powder. Samples were then extracted using an accelerated solvent extraction system (ASE300, Dionex).

Sediment
Sediment was freeze dried and ground and an aliquot (10-20 g) was spiked with recovery standard before being extracted using an accelerated solvent extraction system (ASE300, Dionex).

Accelerated solvent extraction (ASE)
Fat retainer (5% deactivated alumina) was added to the ASE tubes before the biota/sodium sulphate mixture, or freeze dried sediment, precluding the need for a separate clean up step. Samples were then extracted using an oven temperature of 60°C and a pressure of 1500 psi. Five minutes heating was followed by 2 x 5 min static cycles. The cell flush was 50% total cell volume with a 120 second purge (using nitrogen) at end of each sample extraction. The extraction solvent used was *iso*-hexane. For sediment samples copper powder was added to the ASE collection bottles to remove sulphur. Following ASE extraction, the extracts were reduced in volume to ~0.5 ml at 20ºC using a Turbovap and analysed by gas chromatography-negative chemical ionisation mass spectrometry (GC-NCIMS).

Analysis by gas chromatography-negative chemical ionisation mass spectroscopy (GC-NCIMS)
The concentration and composition of the PBDEs were determined by GC-NCIMS using an HP6890 Series gas chromatograph interfaced with an HP5973N MSD, fitted with a cool on-column injector. A Thames Restek STX-500 column (STX-500, 30 m x 0.25 mm i.d., 0.15 µm film thickness, Thames Restek, Buckinghamshire, U.K.) was utilised, fitted with a Thames Restek Siltek (0.53 mm i.d) 5 m pre-column. The carrier gas was helium, set at a constant pressure of 15 psi. Methane was used as the reagent gas at a pressure of 1.6 bar. The transfer line was held at 280°C and the ion source at 150°C. Injections were made at 120°C and the oven temperature held constant for 2 minutes. Thereafter the temperature was ramped at 15°C min^{-1} up to 205°C, followed by a ramp of 6°C min^{-1} up to a final temperature of 330°C. The MS was set for selective ion monitoring (SIM) with a dwell time of 50 ms. Ions monitored were *m/z* 78.9 and 80.9 for all PBDEs, and for BDE209 *m/z* 486.7 and 488.7 were also monitored.

Results and Discussion
The preliminary data presented here are from flatfish (plaice - *Pleuronectes platessa*) and sediment from Garroch Head in the Firth of Clyde. Concentrations for the ΣBDEs (BDE17, 28, 75, 49, 71, 47, 66, 77, 100, 119, 99, 85, 154, 153, 138, 183, 190) in Garroch Head plaice liver sampled between 1996 and 2005 ranged from 4.1 µg kg^{-1} wet weight in a sample collected in 2001 to 407.3 µg kg^{-1} wet weight in a sample collected in 1996 (Fig. 2). There was a significant downward trend in the median ΣBDE concentration with time ($p < 0.01$). Of the 17 congeners analysed all were detected in Garroch Head fish liver, although not in all samples. Similar to other studies BDE 47 was the dominant congener, accounting for more than 40% of the total in all but one sample. BDE209 was also found in some of the Garroch Head plaice liver, with concentrations ranging from <LoD to 389.9 µg kg^{-1} wet weight in a sample collected in 2005. BDE209 is not normally found in biota, this is thought to be because it is not bioaccumulated due to its large molecular size, or due to degradation. BDE209 was found in procedural blanks (1.3 - 3.7 ng ml^{-1}), however, concentrations in the plaice liver were still considerably higher than found in the blanks, therefore, BDE209 is present in plaice liver from this highly contaminated site. BDEs were also measured in plaice liver collected from a reference site at Pladda. Concentrations were lower than at Garroch Head, with the ΣBDEs ranging from 2.08 - 65.64 µg kg^{-1} wet weight. BDE209 was also found at low levels in these samples, however these results should be treated with caution due to the blank problems for BDE209.

Five cores were collected from Garroch Head. A 2 cm thick slice was taken from the top of each core, then 4 cm slices thereafter. Table 1 indicates the sections which have been analysed for PBDEs to date and concentrations for the ΣBDE and BDE209 are shown in Fig. 3. Highest concentrations were found in the top 2 cm, with a significant downward trend ($p < 0.01$) in cores GH-A and GH-B. This trend is also evident in the other three cores but the analysis is not yet complete. BDE209 was the dominant congener in all Garroch Head sediments (Fig. 3), ranging from 2.32 to 98,125 µg kg^{-1} dry weight. No cores were collected from the Pladda reference site but grab sediments (n=3) collected in 2005 have been analysed for PBDEs, with the ΣBDE being < 0.03 µg kg^{-1} dry weight. BDE209 ranged from 3.5 to 5.5 µg kg^{-1} dry weight .

References

Law RJ, Allchin CR, deBoer J, Covaci A, Herzke D, Lepom P, Morris S, Tronczynski J, deWit CA. 2006. Chemosphere 64:187-208.

OSPAR Commission, 2001 (2004 update). OSPAR Commission, London.

Smedes F. 1999. Analyst 124:1711-1718.

Webster L, Phillips LA, Russell M, Dalgarno EJ, Moffat CF.2005, J. Environ. Monit. **7**:1378–1387.

Table 1 Garroch Head core sections collected in 2003 and analysed for PBDEs

	Depth in core (cm)									
Core	**0-2**	**2-6**	**6-10**	**10-14**	**14-18**	**18-22**	**22-26**	**26-30**	**30-34**	**34-38**
GH-A										
GH-B										
GH-C										
GH-D										
GH-E										

analysed	**awaiting analysis**	**no sample**

Figure 1 Map showing the locations of the Garroch Head former sewage sludge dump site and the reference site at Pladda

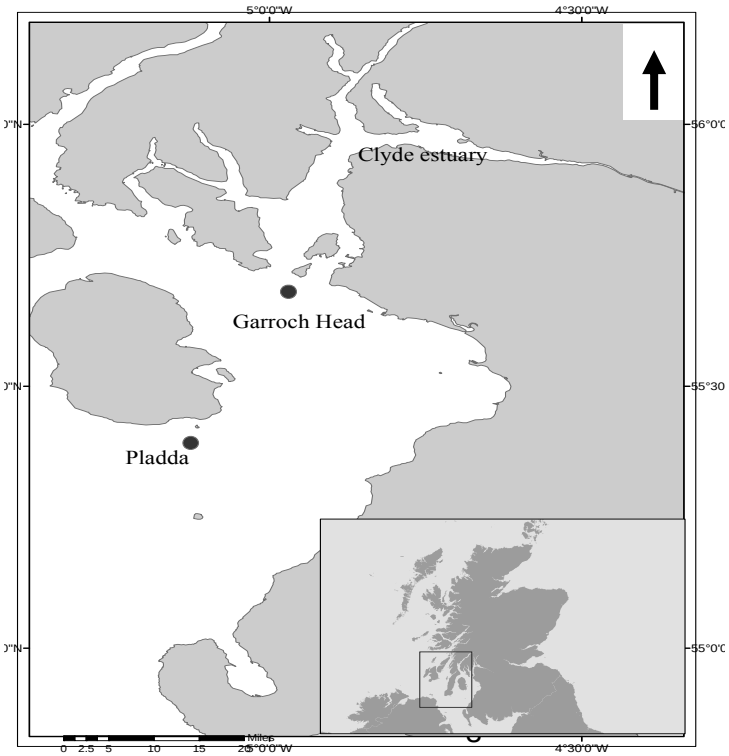

Figure 2 Total PBDE (sum of 17 congeners) concentrations (µg kg^{-1} wet weight) in plaice liver collected from Garroch Head and Pladda in the Firth of Clyde between 1996 and 2005.

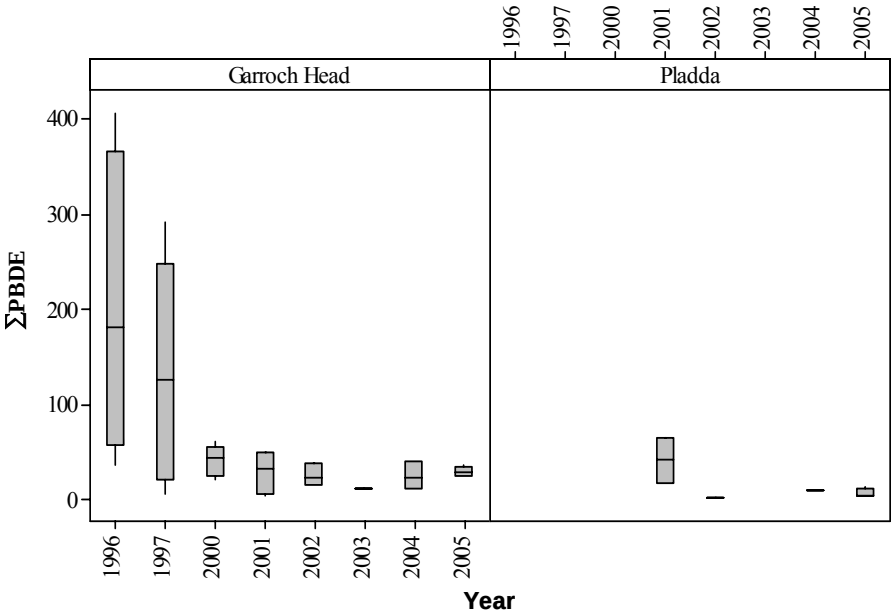
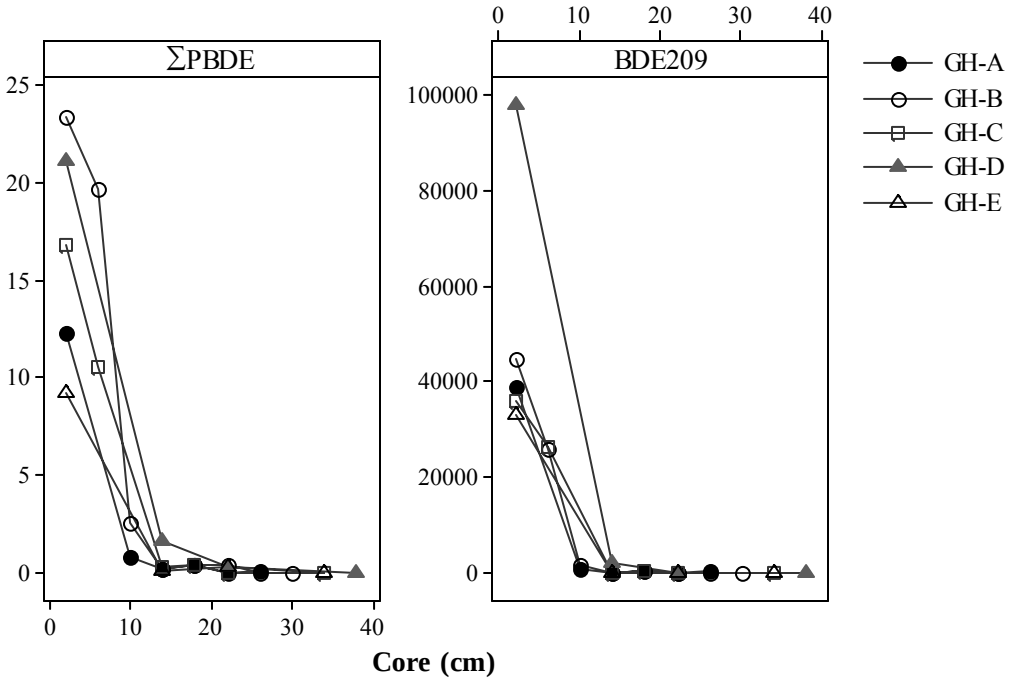
Figure 3 Total PBDE (sum of 17 congeners) and BDE209 concentrations (µg kg^{-1} dry weight) in five sediment cores (GH A – E) collected from Garroch Head and in 2003.