Brominated flame retardants in deep water fish species collected off the west coast of Scotland

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INTRODUCTION

Deep water (> 1000 m) fish have a high potential for the accumulation of semivolatile, persistent organic pollutants (POPs), such as brominated flame retardants (BFRs), because many deep water species are longer lived and feed at higher tropic levels than shallow water fish. BFRs include polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD) and tetrabromobisphenol-A (TBBP-A). All are persistent, toxic and have the potential to bioaccumulate and are, therefore, included on the OSPAR List of Chemicals for Priority Action.

BFRs reduce fire hazards by interfering with the combustion of polymeric materials and can be classed as additive or reactive materials. Reactive BFRs are chemically bonded into plastics. Additives, such as PBDEs and HBCD, are added to polymers and resins and are thought to be more easily released to the environment when compared to reactive BFRs. TBBP-A is used as both a reactive and an additive BFR. Commercial PBDE mixtures are classified according to their degree of bromination. The penta BDE mixture is mainly used in furniture and upholstery, the octa mixture in plastics and the deca mixture in textiles. Penta and octa formulations of PBDEs, and HBCD, were manufactured by the Great Lakes Chemical Company at Newton Aycliffe, County Durham in the north east of England. Manufacture of PBDEs at this plant ceased in 1996 and for all BFRs on 23 December 2003.

HBCD and TBBP-A are currently among the most widely used BFRs, with an estimated global use of 16,700 and 130,000 tonnes, respectively. As the usage of HBCD and TBBP-A began more recently relative to PBDEs, and they continue to be produced, it is possible that concentrations in the environment will rise. HBCD has been produced in the UK and although TBBP-A has not, it is imported.

Deep water fish [roundnose grenadier (*Coryphaenoides rupestris),* black scabbard (*Aphanopus carbo),* and black dogfish (*Centroscyllium fabricii*)] collected on the west coast of Scotland during 2006 were analysed for halogenated persistent organic pollutants. This report presents the preliminary BFR data in these three species of deep water fish.

Materials and Methods

In 2006, three species of deep water fish were taken by the research vessel FRV *Scotia* from the Rockall fishing area, to the west of Scotland (Fig. 1) at depths between 1000 and 1500 m. Liver and fish flesh were sub sampled for contaminant analysis. Fish flesh was not collected from black dogfish. The total lipid content was determined using the Smedes method[1]. Samples were extracted by Pressurised Liquid Extraction (PLE) (Fig. 2). An appropriate amount of tissue, equivalent to a maximum 300 mg lipid, was mixed with anhydrous sodium sulphate (~ 40 g). For PBDEs, this was spiked with a recovery standard (CB198) and refrigerated overnight before being ground to a fine powder. Thirty (30) g of 5% deactivated alumina was added to the PLE cell as a fat retainer. Samples were extracted using an oven temperature of 60^{o}C and a pressure of 1500 psi. The extraction solvent used was *iso*-hexane. The cleaned-up extracts were concentrated by Syncore and reconstituted in *iso*-hexane prior to analysis. The concentration and composition of the PBDEs, namely BDE17, 28, 75, 49, 71, 47, 66, 77, 100, 119, 99, 85, 154, 153, 138, 183 and 190, were determined by gas chromatography-electron capture negative ion mass spectroscopy (GC-ECNIMS) using an HP6890 Series gas chromatograph interfaced with an HP5973N MSD, fitted with a cool on-column injector. 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 (ions equating to bromine) for all PBDEs.

A separate sample was extracted by PLE for the analysis of HBCD and TBBP-A (Fig. 2). Labelled internal standards were added prior to extraction (^{3}H-α-, β- and γ-HBCD and ^{13}C-TBBP-A). For HBCD the amount of fat retainer was reduced to 5 g as recoveries of HBCD were poor using 30 g of deactivated alumina. For TBBP-A the fat retainer had to be omitted to achieve good recoveries. Any remaining lipid and other co-extractives were separated from HBCD and TBBP-A using gel permeation chromatography (GPC). A PE

Sciex API 150 (Perkin Elmer, Maclesfield, UK) single quadropole mass spectrometer equipped with an electrospray source was utilised for the analysis. The LC mobile phase used was acetonitrile/ water, using ammonium acetate as a modifier. A 150 x 2.00 mm ID column packed with 3 μm particles coated with a C_{18} stationary phase was used.

An internal standard method using a six-point calibration curve was used for quantification. The ions monitored were *m/z* 641.0 (HBCD), 658.2 (^{3}H-HBCD), 543.1 (TBBP-A) and 554.8 (^{13}C-TBBP-A) with a dwell time of 150 ms A laboratory reference material and procedural blank was analysed with each batch of samples and the results monitored on Shewhart control charts.

RESULTS AND DISCUSSION

The mean % lipid in the livers of the black dogfish, black scabbard and roundnose grenadier was 5.7%, 13.7% and 57.8%, respectively. The roundnose grenadier liver had the highest lipid content, although it was very variable, ranging from 28.0 to 83.0% by weight. The PBDE concentrations in the liver were positively correlated with the lipid content. Muscle tissue from the black scabbard and roundnose grenadier were also collected for analysis. The lipid content in the fish muscle of these two species was similar with means of 1.07 and 0.92% for black scabbard and roundnose grenadier, respectively. There was no correlation between lipid content and PBDE concentrations in the fish muscle.

PBDE concentrations were normalised to the % lipid to take into account the different lipid content of the three species. Mean total PBDE concentrations (sum of 17 congeners) in the liver of the three deep water fish were 11.7, 34.5 and 50.5 μg/kg lipid weight for black dogfish, black scabbard and roundnose grenadier, respectively, with only 2 samples of roundnose grenadier giving a concentration greater than 100 μg/kg lipid weight (Fig. 3). The roundnose grenadier gave the highest mean concentration; however, there was no significant difference in the total PBDE concentrations (on a lipid weight basis) between the three species ($p < 0.05$, ANOVA). There was no significant difference in the PBDE concentrations in flesh and liver when normalised to lipid content ($p < 0.05$, ANOVA). PBDE concentrations in the fish muscle were below the limit of quantification (LoQ) for most congeners with totals ranging from < LoQ to 229.6 μg/kg lipid weight, with only one sample having a concentration greater than 100 μg/kg lipid weight. PBDE concentrations were similar in the two species with means of 45.8 μg/kg lipid weight and 36.0 μg/kg lipid for the black scabbard and roundnose grenadier, respectively. The PBDE profile in both the muscle and liver was typical of other studies with BDE47, 99 and 100 dominating the profile (Fig. 3). BDE17, 75, 71, 77 119, 183, 190 were detected in only a few instances.

Only one published study on PBDEs in deep water fish could be found[2]. Ten different species of deep water fish (whole fish) from the Sulu Sea, western Pacific, collected at depths of up to 1015 m were analysed for organohalogen contaminants, including PBDEs. Concentrations of all contaminants were very low compared to other studies and PBDE concentrations (sum of 14 congeners) ranged from 0.85 to 2.1 μg/kg lipid weight. Concentrations in the deep sea fish from the FRS study were lower than found in plaice liver from the former sewage sludge dump site in the Clyde (90.8 – 2,154 μg/kg lipid weight) and at the Pladda reference site (35.2 – 560.5 μg/kg lipid weight)[3]. Higher concentrations have also been found in the liver of four different populations of Atlantic salmon, with mean total PBDE concentrations (BDE47, 99 and 100) ranging from 50 to 263 μg/kg lipid weight[4].

As yet there are no assessment criteria available for PBDEs and therefore the environmental significance of these concentrations cannot be assessed.

HBCD and TBBP-A were below the LoQ (0.3 μg/kg wet weight) in all samples regardless of tissue type.

References

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Figure 1 West of Scotland deep sea *FRV* Scotia trawl sites (♦)

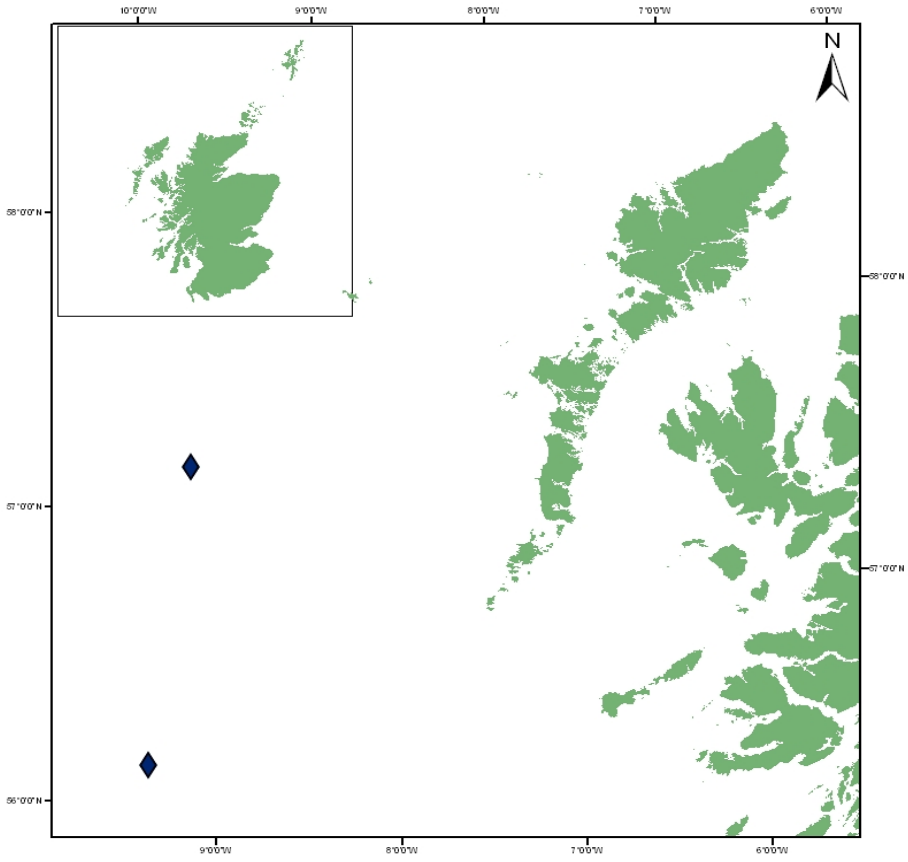

Figure 2 Schematic of the Pressurised Liquid Extraction (PLE) cell used for the extraction of PBDEs, HBCD and TBBP-A from biota.

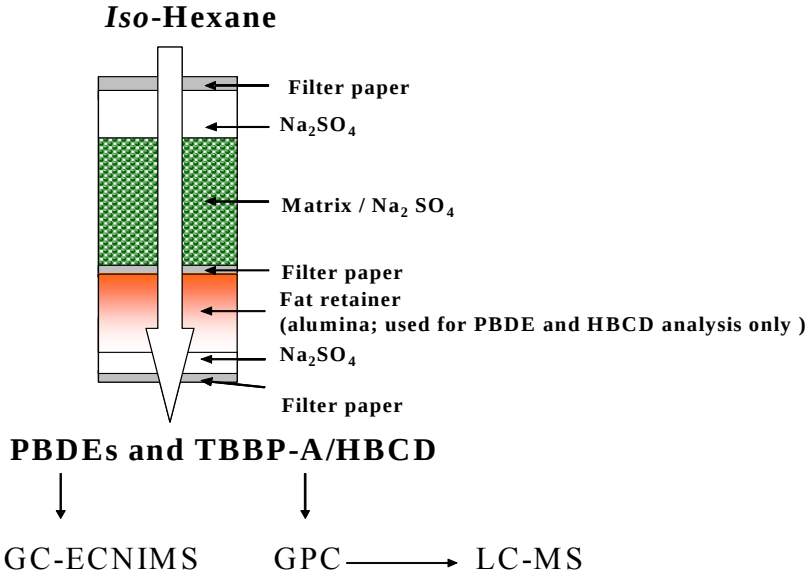

Figure 3 Concentrations (µg/kg lipid weight) for the total PBDE (sum of 17 congeners) and the dominant congeners (BDE47, BDE99 and BDE100) in the liver of deep water fish. The fish were collected from the Rockall fishing area, which is to the west of Scotland in 2006 from depths of 1000 – 1500 m. The circle is the mean concentration and asterisks are outliers.