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Bromine content and brominated flame retardants in food and animal feed from the UK

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HIGHLIGHTS

- Current data on PBDEs, HBCD and TBBP-A in food and animal feed.
- Screen for emerging/novel BFRs in food.
- Organic bromine content of foods.

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ABSTRACT

Current occurrence data for polybrominated diphenyl ethers (PBDE) and hexa-bromocyclododecane (HBCD) measured in most commonly consumed foods ($n = 156$) and animal feeds ($n = 51$) sampled in the UK, demonstrates an ongoing ubiquity of these contaminants in human and animal diets. PBDE concentrations for the sum of 17 measured congeners ranged from 0.02 ng/g to 8.91 ng/g whole weight for food, and 0.11 ng/g to 9.63 ng/g whole weight for animal feeds. The highest concentration ranges, and mean values were detected in fish, processed foods and fish feeds. HBCD diastereomers (alpha-HBCD was the most commonly detected) generally occurred at lower concentrations (from <0.01 ng/g to 10.1 ng/g for food and <0.01 ng/g to 0.66 ng/g for animal feed) and less frequently than PBDEs, but tetra-bromobisphenol A which was also measured, was rarely detected. The total bromine content of the samples was also determined in an attempt to use a mass balance approach to investigate some of these samples for the occurrence of novel and emerging BFRs. Although the approach was further refined by measuring organic bromine content, the concentrations of bromine were too high (in most cases by orders of magnitude) to allow use of the approach. A selected sub-set of samples was screened by GC–MS, for the presence of novel/emerging brominated flame retardants (PBT, TBX, PBEB, DBHCTD, HCTBPH and OBTMPI) but these were not detected at the higher limits of detection that result from full scan (GC–MS) screening. This data will contribute to the EU wide risk assessment on these contaminants.

1. Introduction

Brominated flame retardants (BFRs) are used (either chemically bonded, or more commonly, as additives) in industrial and domestic polymeric materials, in order to delay the onset of fire. Historically, the most commonly used BFR was polybrominated diphenyl ether (PBDE) mixtures, but as concern about potential and reported toxicological effects have been studied and reported over the last 15 years or so, the three main commercial PBDE mixtures, Penta-BDE, Octa-BDE and Deca-BDE have been progressively phased out of use in some parts of the world (notably the EU and some states in the US). Similarly restrictions on use or bans are considered for other high volume BFRs such as hexa-bromocyclododecane (HBCD) due to widespread environmental presence and potential toxicity, and restrictions on usage will apply within the EU from later in 2015. It is thus established that PBDEs and HBCD/tetrabromobisphenol A (TBBPA) have been widely used and these compounds formed the focus of this study. Despite bans or restricted use over the last few years, PBDEs and HBCD continue to be found routinely in foods, and this investigation was designed to provide current levels and to evaluate any declining trends as a result of these actions.

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It was inevitable that the industrial and commercial demand arising from the bans would be filled by an increasing number of alternative flame retardants in order to comply with fire safety regulations, and many other classes of BFRs exist as detailed in a publication by Bergman et al., 2012. Some of these more recently introduced BFRs such as hexabromobenzene (HBB), bis (2, 4, 6-tribromophenoxy) ethane (BTBPE) and decabromodiphenyl ethane (DBDPE) have already been the subjects of investigation and have been detected in the environment (Shi et al., 2009; Körner et al., 2011, Yang et al., 2012) and in some foods (Fernandes et al., 2010; Tlustos et al., 2010). This is unsurprising, given that as additives, they have a greater potential for release, and also, they have similar properties to PBDEs (chemical stability arising from halogenated aromaticity and low aqueous solubility). Similarly, there are a number of other more recent BFR chemicals that have been introduced, and with limited resources, it would prove difficult to fully investigate all of these compounds. A more targeted approach would be to focus on those BFRs where some information on environmental persistence, bioavailability and toxicity was available. Additionally, occurrence in biota or indeed food would provide further indication. The European Food Safety Authority (EFSA) has recently published an opinion (EFSA, 2012) which takes many of these considerations into account. Based on high overall persistence (>500 days), the potential for bioaccumulation and identification in the environment or food, a set of novel/emerging BFRs was identified as being worthy of further investigation for occurrence in food:

- hexabromobenzene (HBB)
- 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE)
- 5,6-dibromo-1,10,11,12,13,13-hexachloro-11-tricyclo[8.2.1.02,9] tridecene(DBHCTD)
- 1,2,3,4,7,7-hexachloro-5-(2,3,4,5-tetrabromophenyl)-bicyclo [2.2.1]hept-2-ene (HCTBPH)
- pentabromotoluene (PBT)
- pentabromobenzyl acrylate (PBB-Acr)
- pentabromoethylbenzene (PBEB)
- 1,2,4,5-tetrabromo-3,6-dimethylbenzene (TBX)
- decabromodiphenyl ethane (DBDPE)
- octabromotrimethylphenyl indane (OBTMPI)

A further two BFRs, N,N'-ethylenebis(tetrabromophthalimide) (EBTEBPI) and hexabromocyclodecane (HBCYD), with high persistence and bioaccumulation potential have not been identified in the environment or in food. It was also noted that although the modeling used by EFSA did not indicate high bioaccumulation potential, decabromodiphenyl ethane (DBDPE) and octabromotrimethylphenyl indane (OBTMPI) were likely to be bioaccumulative, because their molecular mass was not high enough to prevent bioavailability (EFSA, 2012).

As with other mass produced chemicals, the occurrence of BFRs in food is also influenced by environmental persistence, proximity to areas of high usage and recycling or disposal, and in the case of foods of animal origin, uptake and metabolism rates. This study aimed to determine the current occurrence levels of PBDEs and HBCD in food and animal feed that is commercially available in the UK, and to investigate whether a mass balance approach (a large discrepancy between the bromine content of a sample and the sum of the known BFRs e.g. PBDEs and HBCDs, could indicate the presence of other brominated compounds including emerging/novel BFRs) could be used to identify any novel or emerging BFRs. The study is timely, given the request by the European commission to member states (European Commission, 2014), to investigate the occurrence of a range of BFRs in food, in order to carry out a more robust risk assessment on dietary exposure.

2. Sampling and analysis

2.1. Sampling

Just over 400 samples of food (297) and animal feed (105) were collected during 2013, following a structured sampling plan which included a wide range of commonly consumed foods that were available from retail outlets in the UK. Animal feeds were similarly selected from commercial sources in the UK. The principle food groups were eggs, processed meats, poultry and carcase meats, milk and dairy products, offals, and shellfish, processed foods (of vegetable origin) and others including fruit, vegetable and bread. The fish samples that were included were all sourced from UK and proximate marine waters (Fernandes et al., 2015b). The animal feeds were mainly fish feeds, compound feeds for dairy, cattle, sheep, poultry and pigs, oilseeds, legumes, grasses, cereals and cereal by-products.

The samples were stored under appropriate conditions (most food samples were frozen) prior to analysis. Sample preparation for animal feeds consisted of homogenisation by milling and blending as required, to provide particle sizes of <1 mm. Some food samples were processed to isolate edible portions (in the case of shellfish and fish or meat on the bone) followed by grinding and thorough homogenisation. Where required food samples were then freeze-dried. The resulting powders were re-homogenised and aliquots used for analysis of bromine, followed by PBDE and HBCD analysis.

2.2. Analysis

Total bromine content was measured in all samples; a more specific measure of organic bromine (bromine compounds extractable by organic solvents) was measured in a smaller subset of 47 samples.

The following BFRs were targeted for quantitative analysis in 207 samples:

PBDE congeners: IUPAC numbers 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, 183 and 209.

PBB congeners: IUPAC numbers 15, 49, 52, 77, 101, 126, 169,153 and 209.

α-HBCD, β-HBCD and γ-HBCD, Pentabromocyclododecene (PeBCD) and TBBPA.

A sub-set of 30 samples was screened by gas chromatography-mass spectrometry GC–MS (full scan) for the presence of emerging and novel BFR compounds.

2.3. Analysis of total and organic bromine (bromine extracted using organic solvents)

Total bromine was analysed using tetramethyl ammonium hydroxide digestion followed by internal standardisation with Scandium and Antimony. For organic bromine measurements, sample aliquots were first extracted with a hexane/dichloromethane mix. The extracts were concentrated and then treated as for total bromine. Measurement for both procedures was carried out using Inductively Couple Plasma – MS (ICP-MS) using an Agilent 7700 ICP-MS with collision cell. More detail on these procedures is given in Fernandes et al., 2015.

2.4. Analysis of PBDEs, HBCD and TBBPA

The method used for the preparation, extraction and analysis of samples for PBDEs has been reported previously (Fernandes et al., 2004, 2008). In brief, samples were fortified with 13C-labelled analogues of target compounds and exhaustively extracted using mixed organic solvents. Extracts were concentrated and purified