Title: Geographical Investigation for polybrominated diphenylethers in fish collected from UK and proximate marine waters

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Abstract:

The purpose of this study was to investigate the occurrence of a range of regulated and emerging organic environmental contaminants in commonly consumed marine fish species that are considered to be at the highest risk of non-compliance, with existing regulatory limits for contaminants such as dioxins and PCBs. As part of the study, data on polybrominated diphenlyethers (PBDEs) was collected. The study provides current information on levels of occurrence, allowing the geographical identification of locations that show higher contaminant levels and also facilitating the estimation of human exposure as a result of consumption.
Two hundred fish samples were collected, the majority from UK marine waters, but extending to Norwegian waters in the North and to the Algarve in the South. The main species targeted were sardines, sprats, sea bass, mackerel, herring, grey mullet, but other species such as turbot, halibut, various shark species (dogfish, spurdog), etc. were also included.
PBDEs were observed in all samples with all measured congeners, with the exception of BDE-126, being detected. The concentrations range from 0.04 µg/kg to 8.87 µg/kg whole weight for the sum of all measured PBDE congeners. Concentrations appear to vary depending on species and location. The high frequency of PBDE occurrence makes it prudent to continue the monitoring of these commonly consumed marine fish species.

Introduction:

Marine environments are recognised sinks for a range of environmental contaminants, and uptake and bioaccumulation by various fish and shellfish species has been widely documented. Consequently, consumption of marine fish and shellfish has been shown to make a significant contribution to human exposure of a range of environmental contaminants.
In an effort to reduce or prevent inputs that could cause pollution, affect human health or adversely impact legitimate uses of the marine environment, the Marine Strategy Framework Directive encourages collaboration and coordination between individual EU Member States with the aim of protecting and preserving marine ecosystems. In the context of the present study, one of the targets for good environmental status under the directive is the limiting of contamination in fish and other seafood along with compliance with maximum contaminant levels established by European Commission regulation, or other relevant standards.
PBDEs are mass produced brominated flame retardants (BFRs) that were incorporated into a number of commonly used commercial materials such as plastics, rubbers, textiles and electronic components. As these are open-ended applications, the BFRs are available to diffuse out of materials into the environment, and this can occur during manufacture, use and disposal of the product.
Polybrominated biphenyls (PBBs) have physico-chemical and toxicological properties that are similar to their chlorinated analogues. They were produced commercially as flame retardant chemicals (BFRs) long before the large volume production of the more familiar BFRs such as PBDEs and HBCD.

Both PPBs and PBDEs are recognised to be persistent, bio-accumulative and toxic, with the potential to undergo long-range transport.
Emerging toxicological data shows that PBDEs can cause liver and neurodevelopmental toxicity and affect thyroid hormone levels. Additionally, they may be particularly harmful during a critical window of brain development during pregnancy and early childhood (Rose and Fernandes 2012). Their occurrence in food has been investigated (FSA 2006, Fernandes et al 2009). In comparison to polybrominated biphenyls (PBBs), they show more frequent and abundant occurrence. Fish, and in particular oily fish species, generally tend to show higher levels of contamination than other food types.
This paper provides results of PBDE data obtained from a study to investigate the occurrence of a range of regulated and emerging organic environmental contaminants in commonly consumed marine fish species in UK and proximate marine waters.

Methods and Materials:

Approximately 200 samples were collected from UK and proximate marine waters, including the North Sea and the Greater North Sea sub-region extending up to Norway, the Irish sea and the Celtic sea sub-regions extending off the North-Western coast of France, and the European coastal North Atlantic regions, including Biscay and extending as far south as the Algarve. On receipt at the laboratory each prepared sample was given a unique laboratory reference number and the sample details were logged into a database.
Sample preparation mirrored domestic consumption practices. Depending on the species, samples were dissected to collect edible muscle tissue and exclude skin, bones and organs. However for some species such as sprats, whole fish were used. The selected tissue (or whole fish) was minced, homogenised by blending then freeze-dried. Freeze dried samples were stored at -18°C and re-homogenised before analysis.
The method used for the preparation, extraction and analysis of samples has been reported previously (Fernandes et al 2004; 2008). In brief, samples were fortified with ^{13}C-labelled analogues of target compounds and exhaustively extracted using mixed organic solvents. PBDEs and ortho substituted PCBs/PBBs were separated from non-ortho substituted PCBs/PBBs, PCDD/Fs and PBDD/Fs by fractionation on activated carbon. The two fractions were further purified using adsorption chromatography on alumina. Analytical measurement was carried out using high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS). The analysis is accredited (UKAS) to ISO 17025 standards, with the inclusion of an in-house reference material and method blanks which were evaluated prior to reporting of sample data and used to determine the limits of detection.
PBDE congeners analysed~~:~~ (IUPAC numbers 17, **28**, **47**, **49**, 66, 71, 77, 85, **99**, **100**, 119, 126, **138**, **153**, **154**,**183** and **209**) include those specified in European commission recommendation 2014/118/EU which are given in bold font.
PBB congeners: IUPAC numbers 15, 49, 52, 77, 80, 101, 126, 153, 169 and 209.

Results & Discussion:

PBDEs were observed in all samples with all measured congeners being detected except BDE-~~-~~126. A summary of the data is presented in Table 1. There are only minor differences between the average values for both the sum of the 17 congeners and the sum of the 10 congeners specified in the EC recommendations, which confirms a more informed choice of congeners for the EU list. The concentrations range from 0.04 µg/kg to 8.87 µg/kg whole weight for the sum of all measured PBDE congeners (0.04 µg/kg to 8.63 µg/kg for the EU listed PBDEs). The highest average values were observed for herring, sea bass, mackerel and sprat (2.08, 2.0, 1.45 and 1.27 µg/kg respectively). PBBs were detected less frequently and at lower concentrations, confirming a trend observed in other studies (Fernandes et al 2008, 2012) The highest value observed was 0.65 µg/kg for BB-52 for grey mullet from France. In general, most of the higher positive values for PBBs were observed for samples

taken from French waters and from the southern coast of England. This may reflect a higher utilisation of PBBs in France relative to the UK.

This study has characterised PBDEs in a number of commonly consumed fish species, taken from marine waters around the UK and from other proximate fishing areas from which retail fish in the UK is commonly sourced. The high frequency of PBDE occurrence make it prudent to continue the monitoring of these commonly consumed marine fish species from the point of view of public health, as well as the status of the marine environment.

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Table 1 Summary of PBDE concentrations µg/kg whole weight

PBDE Concentrations, µg/kg whole weight	Sardines (n=16)				Mackerel (n=41)				Herring (n=19)				Grey Mullet (n=26)			
	MIN	**MEDIAN**	**MEAN**	**MAX**	**MIN**	**MEDIAN**	**MEAN**	**MAX**	**MIN**	**MEDIAN**	**MEAN**	**MAX**	**MIN**	**MEDIAN**	**MEAN**	**MAX**
Sum measured PBDEs	**0.14**	**0.39**	**0.50**	**2.18**	**0.15**	**1.24**	**1.45**	**3.86**	**0.61**	**1.14**	**2.08**	**8.87**	**0.09**	**0.58**	**1.10**	**5.41**
***Sum PBDEs (EU list)**	**0.13**	**0.38**	**0.49**	**2.12**	**0.14**	**1.16**	**1.35**	**3.65**	**0.58**	**1.10**	**2.00**	**8.63**	**0.08**	**0.57**	**1.08**	**5.36**
	Sprat (n=25)				Sea Bass (n=25)				Turbot (n=16)				Shark-various spp (n=14)			
	MIN	**MEDIAN**	**MEAN**	**MAX**	**MIN**	**MEDIAN**	**MEAN**	**MAX**	**MIN**	**MEDIAN**	**MEAN**	**MAX**	**MIN**	**MEDIAN**	**MEAN**	**MAX**
Sum measured PBDEs	**0.33**	**1.09**	**1.27**	**4.59**	**0.28**	**1.75**	**2.00**	**5.71**	**0.07**	**0.33**	**0.37**	**0.84**	**0.04**	**0.13**	**0.54**	**2.02**
***Sum PBDEs (EU list)**	**0.31**	**1.05**	**1.23**	**4.56**	**0.27**	**1.73**	**1.97**	**5.64**	**0.06**	**0.31**	**0.35**	**0.79**	**0.04**	**0.12**	**0.51**	**1.91**

*- Sum BDE-28, 47, 49, 99, 100, 138, 153, 154, 183 and 209 (EU recommendation 2014/118/EU)