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Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) in seven different marine bird species from Iceland

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HIGHLIGHTS

- High levels of PBDEs were found in marine bird eggs from remote areas in Iceland.
- High levels of HBCDD were found in marine bird eggs from remote areas in Iceland.
- Results indicating different sources and/or usage patterns of the two BFRs.
- Contribution of individual PBDEs to the sum different between the bird species.

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ABSTRACT

Data on distribution, concentration and trends of polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) is scarce in biota from the sub-Arctic region of the Atlantic. The present study is an investigation on PBDE and HBCD concentrations in eggs from seven marine bird species from Iceland, i.e. common eider (*Somateria mollissima*), arctic tern (*Sterna paradisaea*), guillemot (*Uria aalge*), fulmar (*Fulmarus glacialis*), lesser black-backed gull (*Larus fuscus*), great black-backed gull (*Larus marinus*) and great skua (*Stercorarius skua*). Concentrations of sum PBDEs ranged from 44 ng g^{-1} fat in eider eggs to 2400 ng g^{-1} fat in great skua eggs. The contribution of different PBDE congeners to the sum concentration differed between species. Concentration of HBCDs (sum of α–,β– and γ–HBCD) ranged from 1.3 ng g^{-1} fat in arctic tern eggs to 41 ng g^{-1} fat in great black-backed gull. PCA on PBDE and HBCD shows different trends between the two BFR groups, further indicating different sources/usage. Investigations on any potential health or population effects of environmental pollutants on the great skua are advised since both the PBDE and HBCD concentrations are high.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) have widely been used as additive brominated flame retardants (BFR) mainly in plastics and textiles (EFSA 2011a,b). PBDEs have been produced since the 1970s and have been found in many environmental compartments (de Wit et al., 2010; Xiao et al., 2012). Their extensive use and reported adverse effects (reviewed in Letcher et al., 2010) have led to a restriction or phase-out of the technical mixtures PentaBDE and OctaBDE in both Europe and North America, while DecaBDE is still used. Recently, the European Food Safety Authority (EFSA) published opinions on both PBDEs and HBCDs and risk related to these two groups in food and their occurrence in the environment (EFSA, 2011a,b), where concerns were raised for the potential health risk for humans due to PBDE-99 in Europe. In Europe, PBDEs have partially been replaced by HBCD, but that replacement must be considered questionable as HBCD, like the PBDEs, is persistent, bioaccumulative and toxic. Today, there are no restrictions on the production or use of HBCD and the total release of HBCDs into the environment is increasing within the EU (ECHA, 2009). However, HBCD has been proposed to be included in the Stockholm Convention on persistent organic pollutants (Stockholm Convention). Levels of sum of ten PBDEs show a decreasing temporal trend in marine mammals from the Arctic environment (Rotander et al. 2012; Vorkamp et al., 2011), while trends of tetra- to heptaBDEs and HBCDs seem, depending upon the matrix (air, sediment or biota), to be leveling off or showing increasing trends in the Arctic envi-

Abbreviation: BFR, brominated flame retardant; GC, gas chromatograph; MS, mass spectrometer; HBCDs, hexabromocyclododecanes; PBDEs, polybrominated diphenyl ethers; PCBs, polychlorinated biphenyls; SIM, selected ion monitoring.

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ronment (Vorkamp et al., 2011). These BFRs are still major environmental pollutants and therefore it is important to monitor their trends in the environment.

Some but still limited data is available on the occurrence and distribution of PBDEs and HBCDs in the Icelandic environment (Jörundsdóttir et al., 2009; Rotander et al., 2012; Strid et al., 2010; Thron et al., 2004). In Iceland, located in the sub-Arctic region of the North Atlantic Ocean, the number of bird species is rather low but the sizes of the populations are sometimes extensive (e.g. common eider) and the country is an important breeding area for several migrating bird species (Petersen, 1998). Birds, and especially marine birds, are in many cases top predators which make them vulnerable against persistent organic pollutants that bioaccumulate in the food chain, such as PBDEs and HBCDs. The North-Atlantic receives BFR via long-range transport as well as from local usage. Reports from the Arctic show a ubiquitous presence of PBDEs and HBCD at all trophic levels (de Wit et al., 2010). Previous studies on the levels of PBDEs and HBCDs in similar bird species from other North-Atlantic regions have been published, e.g. Sørmo et al. (2011) report sum of eight PBDEs in herring gull (*Larus argentatus*) liver ranging from 135 to 985 ng g^{-1} fat. Carlsson et al. (2011) report on series of persistent organic pollutants, such as PBDEs, in eggs of common eider (*Somateria mollissima*) and herring gull from the Swedish West coast where the PBDEs contribute to <10% of the total contaminant load.

An extensive study on several chlorinated pollutants and their metabolites in seven Icelandic bird species showed high levels of polychlorinated biphenyls (PCBs) and DDTs in eggs of some of the investigated species, such as the great skua (*Stercorarius skua*). These findings raised concerns and calls for investigations on the birds health status (Jörundsdóttir et al. 2010). As a continuation of the evaluation of persistent organic pollutants in birds from remote areas of Iceland, the objective of the present study was to investigate the distribution and concentration of the brominated flame retardants PBDEs and HBCDs. The same egg samples from seven marine bird species from Iceland were used as in the previous published study. The present study was conducted to further evaluate the environmental situation in a sub-Arctic region where information on environmental pollutants is scarce.

2. Materials and methods

2.1. Samples

Eggs from guillemot (*Uria aalge*) and fulmar (*Fulmarus glacialis*) were collected at the Vestmannaeyjar Islands, South Iceland. Eggs of arctic tern (*Sterna paradisaea*), common eider, great black-backed gull (*Larus marinus*), and lesser black-backed gull (*Larus fuscus*) were collected near Sandgerði, Southwest Iceland, and great skua eggs were collected from the sands near Kvísker, Southeast Iceland. All eggs were collected in the years 2002–2004. The sampling locations (Fig. 1), were all remote and therefore site related effect is limited. Difference in long-range transport deposition between the sampling sites is believed to be non-significant. No ethical permits are required for egg collection or export of samples for scientific purpose from these species in Iceland. The samples were prepared at the Swedish Museum of Natural History (Stockholm, Sweden), where the content of the eggs was removed through a drilled hole in the shell. The egg content was thereafter homogenized and stored at −80 °C until taken out for analysis.

2.2. Chemicals

A mixture of 13 PBDE congeners (PBDE-47, -77, -99, -100, -128, -139, -153, -154, -203, -206, -207, -208, -209) was prepared in house (Eriksson et al., 2003; Marsh et al., 1999; Örn et al., 1996) and mixed with 4'-methoxy-2,3',4,5',6-pentabromodiphenyl ether (4'-MeO-PBDE121), synthesized in house (Marsh et al., 1998).This mixture was used as an external standard for analysis of PBDEs. α-, β- and γ-HBCD were purchased from Cambridge isotope laboratories (CIL, Andover, MA, USA), mixed together with 4'-MeO-PBDE121 and used as an external standard for analysis of HBCD. 3,3',4,4'-Tetrabromodiphenyl ether (BDE-77) and 4'-MeO-PBDE121 were used as surrogate and volumetric standards, respectively,. PBDE congeners are numbered according to the same system as used for PCBs (Ballschmiter et al., 1993).

All solvent used were of the highest quality available. The silica gel 60, 70–230 mesh from Merck (Darmstadt, Germany) used for clean up was activated over night at 300 °C before being impregnated with sulfuric acid.

2.3. Instruments

Analysis were performed on a gas chromatograph (Varian 3400 gas chromatograph, Palo Alto, California, USA) coupled to a mass spectrometer (GC/MS) (Finnigan MAT SSQ 710, ThermoFinnigan, San Jose, CA, USA) with a septum equipped temperature programmable injector and an auto sampler (CTC A200S). Helium was used as carrier gas and methane as reagent gas at 5.6 torr. A non-polar capillary column was used (DB-5 HT, 15 m, 0.25 mm i.d., 0.1 μm phase thickness, J&W Scientific, Folsom, CA, USA). The ion source temperature was 200 °C and the transfer line 290 °C. The instrument was operated in the electron capture negative ionisation mode and the electron energy was 70 eV. The PBDE congeners and HBCD isomers were analysed with selected ion monitoring (SIM) by scanning for the negative bromide ions, m/z 79 and 81.

2.4. Extraction and clean up method

The extraction method used is described in detail by Jensen et al. (2003), but due to the small sample amount the solvent volumes were scaled down to 1/10 of the volume presented by Jensen et al. (2003). The extractions were performed in test tubes according to Jörundsdóttir et al. (2009), where the method was validated for eggs. Briefly, the surrogate standard, PBDE-77 was added to the egg homogenate and the sample extracted with *n*-hexane:acetone (2:5, 4 mL). After mixing and separation, the organic phase is transferred to a new test tube. The egg homogenate was then extracted twice with *n*-hexane:methyl-*tert*-butyl ether and the combined extracts washed with 5 mL of 0.1 M phosphoric acid in an aqueous 0.9% sodium chloride solution. The solvent was evaporated and the lipids determined gravimetrically. The lipids were re-solved in *n*-hexane and a cleanup step was performed with potassium hydroxide in ethanol:water (1:1) (2 mL, 0.5 M). The sample was then treated with sulfuric acid in order to separate lipids from analytes. For further clean up a layered silica gel column was used, with silica gel (0.1 g) in the bottom and silica gel treated with sulfuric acid (1 g, 2:1 w/w) on top. The column was pre-eluted with *n*-hexane:dichloromethane (8 mL, 1:1) and the analytes eluted with *n*-hexane:dichloromethane (8 mL, 1:1). An additional clean up step was performed, using a silica gel column (0.7 g) where a fraction of *n*-hexane (4 mL) was first eluted containing most of the PCB and pesticides and then the PBDEs and HBCD were eluted with dichloromethane (8 mL) as the mobile phase. The volumetric standard, 4'-MeO-PBDE121, was added prior to analysis.

2.5. Quality control

Before extracting the samples, a pilot study was conducted in order to investigate which surrogate and volumetric standard was most suitable. Blank solvent samples were extracted and

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