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Polybrominated diphenyl ethers (PBDEs) in marine mammals from Arctic and North Atlantic regions, 1986–2009

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ABSTRACT

A selection of PBDE congeners was analyzed in pooled blubber samples of pilot whale (*Globicephala melas*), ringed seal (*Phoca hispida*), minke whale (*Balaenoptera acutorostrata*), fin whale (*Balaenoptera physalus*), harbor porpoise (*Phocoena phocoena*), hooded seal (*Cystophora cristata*) and Atlantic white-sided dolphin (*Lagenorhynchus acutus*), covering a time period of more than 20 years (1986–2009). The analytes were extracted and cleaned-up using open column extraction and multi-layer silica gel column chromatography, and the analysis was performed on a GC-MS system operating in the NCI mode. The highest PBDE levels were found in the toothed whale species pilot whale and white-sided dolphin, and the lowest levels in fin whales and ringed seals. One-sided analyses of variance (ANOVA) followed by Tukey comparisons of means were applied to test for differences between years and sampling areas. Due to inter-year sampling variability, only general comparisons of PBDE concentrations between different sampling areas could be made. Differences in PBDE concentrations between three sampling periods, from 1986 to 2007, were evaluated in samples of pilot whales, ringed seals, white-sided dolphins and hooded seals. The highest PBDE levels were found in samples from the late 1990s or beginning of 2000, possibly reflecting the increase in the global production of technical PBDE mixtures in the 1990s. The levels of BDE #153 and #154 increased relative to the total PBDE concentration in some of the species in recent years, which may indicate an increased relative exposure to higher brominated congeners. In order to assess the effect of measures taken in legally binding international agreements, it is important to continuously monitor POPs such as PBDEs in sub-Arctic and Arctic environments.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are aromatic compounds substituted with up to ten bromine atoms that have been used extensively as flame retardants in for example textiles, plastics, and electronics. Since most brominated flame retardants do not react with the material in which they are incorporated, an extensive usage on a global scale has caused a release of PBDEs into the environment. In the early 1980s, PBDEs were found by Andersson and Blomkvist (1981) in eel, pike, bream and sea trout from the Viskan–Klosterfjorden water system, close to Gothenburg in Sweden. Bioaccumulation in wildlife has since then been reported in numerous studies, even in places with no local point sources or industrial production (Law et al., 2003; Strandberg et al., 2001; ter Schure et al., 2004). Various detrimental effects related to PBDE exposure have been studied in recent years. Changes in neurobehaviour, effect on thyroid hormone levels and fetal toxicity have been observed in exposure studies of rodents (Darnerud, 2003; Eriksson et al., 2001). PBDEs have mainly been available in three technical mixtures, penta-BDE, Octa-BDE and Deca-BDE. The penta mixture consists primarly of tetra- (BDE #47), penta- (BDE #99, #100) and hexa- (BDE #153, #154) congeners, the octa mixture consists primarily of a hepta congener (BDE #183) and a few octaBDEs. DecaBDE consists primarily of the fully brominated BDE #209 (La Guardia et al., 2006). As a result of the ratification of the WEEE and RoHS directives, the penta- and Octa-BDE mixtures were banned in the European Union in 2004 and in 2009 they were added to

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the list of persistent organic pollutants (POPs) under the Stockholm convention. The DecaBDE mixture was banned from the Swedish market in the beginning of 2007 and from the whole of the European market in the middle of 2008 (Kemmlein et al., 2009). In order to assess the effect of measures taken in legally binding agreements, for example the LRTAP Protocol and Stockholm Convention, it is important to continuously monitor POPs such as PBDEs in remote environmental compartments. However, since POPs are long lived and globally distributed it may take several years before effects of implemented reduction measures can be evaluated. Many marine mammal species are suitable for studies of long-term exposure of chemicals in the marine environment since they feed at the top of the aquatic food chain and have a relatively long life-span. PBDE concentrations as high as 3000–5000 ng/g lipid weight (lw) have been reported in blubber of pilot whales from the Faroe Islands and sperm whales and harbor seals stranded along the Dutch coast (de Boer et al., 1998; Lindström et al., 1999). PBDEs have been hypothesized to be transported to remote regions like the Arctic by similar atmospheric pathways as PCBs, and that tetra- and penta-brominated PBDEs have accumulation potential comparable to that of hexa- to heptachloro biphenyls (Wania and Dugani, 2003). Although a general trend in the last decades has been that the traditional POPs have declined in arctic biota whereas the PBDEs have increased, PBDE concentrations have shown different patterns of change in different species and geographical areas (Braune et al., 2007; de Wit et al., 2006; Helgason et al., 2008; Rigét et al., 2010; Vorkamp et al., 2008). In the Canadian Arctic, an increase in PBDE levels was found in burbot liver, ivory gull eggs and East Canada beluga sampled in the period 1980–2006 (Braune et al., 2007; Stern and Tomy, 2007; Tomy et al., 2007). A possible decline or tendency to leveling off was found in West Canada ringed seal and eggs of thick-billed murre and northern fulmars between 2000 and 2006 (Braune, 2006, 2007; Ikonomou et al., 2005; Riget et al., 2006). In the Barents Sea region, temporal trend studies in seabird eggs indicate a rapid increase of PBDEs from 1983 to 1993, after which the concentrations leveled off (Helgason et al., 2010).

The aim of the present study was to provide information on PBDE levels in marine mammals from Arctic and North Atlantic regions over the last 20 years. The current data is based on analysis of selected PBDEs in blubber samples of seven whale and seal species sampled in East Greenland, Faroe Islands, Iceland, West Ice and Norway between 1986 and 2009.

2. Materials and methods

2.1. Sampling

Sampling parameters of pilot whale (*Globicephala melas*), ringed seal (*Phoca hisida*), minke whale (*Balaenoptera acutorostrata*), fin whale (*Balaenoptera physalus*), harbor porpoise (*Phocoena phocoena*), hooded seal (*Cystophora cristata*) and Atlantic white-sided dolphin (*Lagenorhynchus acutus*) are summarized in Fig. 1 and Table 1. In general, either length and/or teeth parameters were used for age determination in order to produce comparable pooled samples. The pools combined individuals of similar age/size and of a single sex in species where sex is known to influence the contaminant concentration. In order to minimize the variability stemming from age and sex-related processes, it was decided to perform the chemical analyses primarily on samples of males, and preferentially within a fixed age/size group. As a means also to minimize the variance in the data without increasing the number of samples to be analyzed, it was decided to analyze pooled samples, comprising 3–5 individuals of a predefined age/sex. Pooled samples can be used to reduce the biological variation, which is advantageous in the sense that the reduction of within group variation will increase the sensitivity of the experiment to changes between groups. Samples of Atlantic white-sided dolphin and pilot whale were taken in connection with the traditional drive hunts by sampling crews of the Environment agency and the Museum of Natural History in the Faroe Islands. The samples are part of larger collections of biological materials taken in the yearly drive fishery. Samples of minke whales were obtained by licensed whalers from southwest and central West Greenland between May and October 1998. The minke whales caught along the Norwegian coast were part of a scientific catch for the Marine mammal's program funded by the Research Council of Norway and obtained from the bio-bank at the Norwegian School for Veterinary Science (NVH). The whales were caught using a transect method by which the ship follows a certain predefined route, aiming at estimating the minke whale stock. The minke whales from Icelandic waters were derived from a scientific program carried out under the auspices of the Ministry of Fisheries in Iceland during 2003–2007. Altogether 200 animals were caught during these five years from all around Iceland by random sampling from small defined areas. Blubber samples of female hooded seal were made available from the bio-bank at the Norwegian School of Veterinary Science and from the institute of

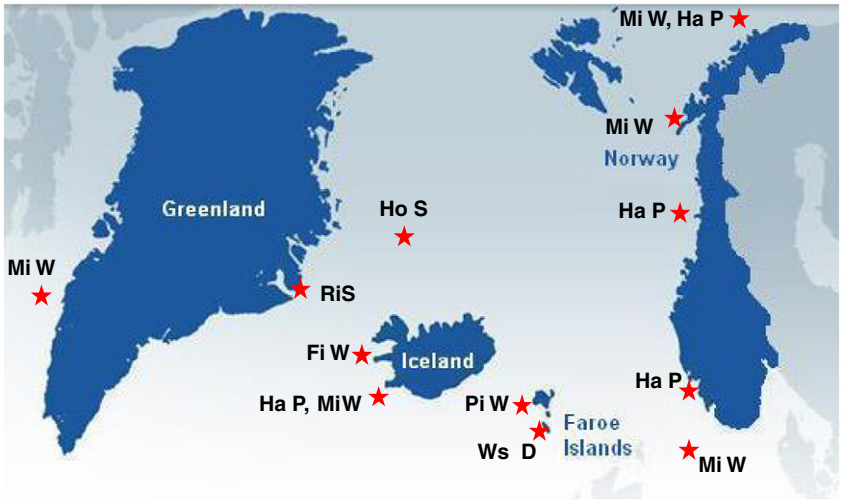

Fig. 1. Indicative map showing sampling locations of pilot whales (Pi W), minke whales (Mi W), hooded seals (Ho S), ringed seals (Ri S), harbor porpoise (Ha P), fin whales (Fi W) and white-sided dolphins (Wh d).