TEMPORAL TRENDS OF POLYBROMINATED DIPHENYL ETHERS IN SE BAFFIN BELUGA: INCREASING EVIDENCE OF LONG RANGE ATMOSPHERIC TRANSPORT

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Introduction

Polybrominated diphenyl ethers (PBDEs), sometimes referred to as brominated diphenyl oxides, are produced and used as flame retardants. They are used in relatively high concentrations in electronic equipment such as computers and television sets, building materials, plastics, textiles, carpets, cars, aircraft and in many other applications[1]. When used as additive flame retardants, PBDEs can migrate out of the products and cause a diffuse contamination of the environment during the entire lifetime of the flame retardant product[2].

PBDEs containing predominantly penta-, octa- and decabromophenyl ethers are commercially produced. Each of these products, in particular PeBDE and OBDE, are mixtures of many PBDE congeners[1,3]. Total consumption of PBDEs world-wide doubled from approximately 20,000 to 40,000 tonnes/year over the eight year period from 1984 to 1992. DeBDE is the most commonly used product, corresponding to 75% of global PBDE production in 1992. Since that time, the demand for brominated flame retardants has increased in countries such as the USA and Japan and continues to rise[1].

PBDEs are similar in behavior and toxicity to well-known environmental contaminants such as PCBs and DDT[1]. However, while the ban of the production and usage of these major organochlorine contaminant groups has resulted in a decline in environmental levels[4,5], PBDE concentrations are increasing[1,2]. A recent study reports that concentrations of PBDEs in breast milk from healthy native Swedish mothers living in the Stockholm region, increased 60-fold over the 25 year period from 1972-1997, a doubling every five years[6]. PBDEs have also been measured in fish, fish eating birds and marine mammals from remote areas[1] and in air samples (gas phase) collected from Alert, NWT[7].

Marine mammals are exploited by many communities throughout the Arctic. These animals occupy high trophic levels in marine food webs and so accumulate (relatively) high concentrations of persistent organohalogens[4]. Because of their known persistence and tendency to bioaccumulate and their continued release into the environment, large quantities of PBDEs could eventually reach the Arctic marine environment where they then could pose an increasing risk to aquatic biota and to the people living in Arctic communities. The aim of this study was to document the temporal trends of PBDEs in Arctic marine ecosystems so as to determine whether levels in marine mammal tissues, and thus exposure to people living in Arctic communities who consume them as

part of their traditional diet, are increasing or decreasing with time. The presence of PBDEs in SE Baffin beluga provides further evidence in support of atmospheric transport of PBDEs to the Arctic.

Methods and Materials

Collections: Blubber samples from beluga in the Clearwater Fjord area of Cumberland Sound (1982 and 1986) were obtained by DFO personnel (Winnipeg, MB) with the cooperation of local hunters. As part of an ongoing whale sampling and stock identity program, supported by the Nunavut Wildlife Management Board (NWMB) and DFO, samples from the southern coastline in Cumberland Sound (1992, 1996 and 1997) were collected by hunters during their subsistence hunts using standardized whale kits. Blubber, kidney, liver, ovaries and uterus, muscle and the lower jaw, as well as morphometric data were collected for each animal. All samples were shipped frozen to the Freshwater Institute and stored at - 40°C until analysis. Animals were aged by thin sectioning a canine tooth from the rear of the lower jaw and counting growth layer groups (GLG) in the dentine using transmitted light[8].

Analysis: Blubber samples were partially thawed, and 2 grams were combined with anhydrous Na_2SO_4 (heated at 600°C for 16 hours before use). The mixture was then extracted twice with hexane in a small (50 mL) ball mill, centrifuging and decanting the hexane between extraction's. Extractable lipids were determined gravimetrically on a fraction (1/10) of the extract. 300 mg of each sample extract was sent to IOS for PBDE analysis. Samples were spiked with a suite of internal standards and processed for GC/HRMS analysis using the methodology described by Ikonomou *et al*[9]. Quantitation was based on custom standard solutions prepared by Cambridge Isotope Laboratories.

Statistics: All univariate analyses was performed with lipid normalized log10 transformed data to adjust for skewness. ANCOVA was used to assess the effects of year to year collections (temporal trends), age of the animals and age*year interactions (homogeneity of slope between age and [PBDE]) using the model [PBDE] = year age age*year, where [PBDE] = log concentration of individuals PBDE congeners or homologue groups. Differences between collection years were examined with paired comparisons of age adjusted least squared mean concentrations[10]. Only results for animals older than two years of age will be included in the analysis of covariance because of the large variation in concentrations seen in younger animals[11].

Results and Discussion

In total, blubber samples from 51 male beluga (> 2 years of age), collected at four different time periods (1982, n=8; 1986, n=15; 1992, n=11; 1997, n=17) and covering a 15 year time span, were analyzed. Temporal trends of lipid normalized (age adjusted least square mean) PBDE homologue group and congener concentrations are shown in Figure 1. Since 1982, the levels of the major PBDE homologue groups and congeners in the SE Baffin beluga have increased significantly. Concentrations of PBDE47 (2,2',4,4'-TeBDE), the most predominant PBDE congener residue in the beluga blubber, increase 6.5-fold over this 15 year time period (Table 1). These results almost certainly reflect the increase in industrial usage of PBDEs world wide. Figure 2 shows the % contribution of the major PBDE congeners and homologue groups to total PBDE in the beluga for each time point (age adjusted). Over the fifteen year time span from 1982 to 1997, contributions of the TrPDE and TePDE homologue groups to total PBDEs have declined by ~50 and 7%,

respectively. Conversely, PePDE and HxPDE contributions have increased by ~20 and 80%, respectively. This change in the SE Baffin beluga PBDE composition is most likely driven by the shift in composition of commercial PBDEs to higher brominated mixtures[1,3].

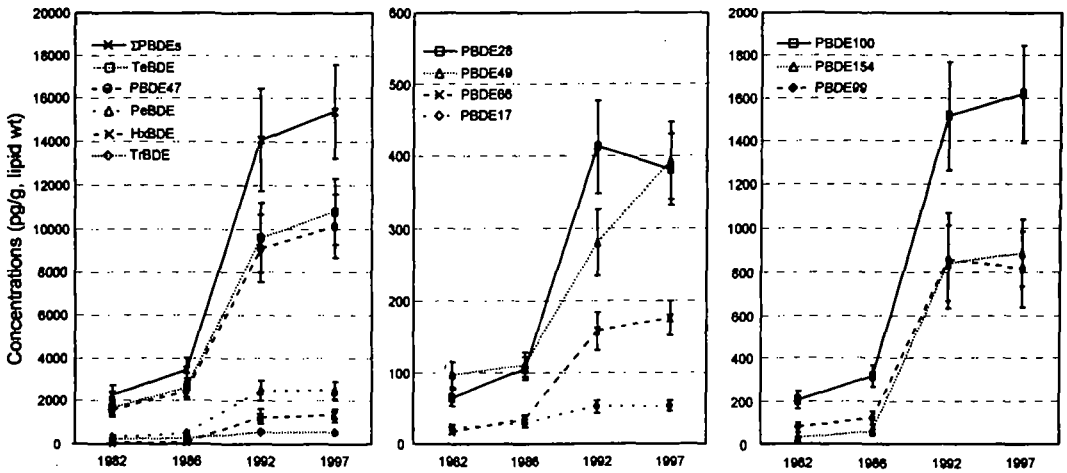

Figure 1. Temporal trends of lipid normalized (age adjusted least square mean) concentrations of PBDE homologue groups and major congeners in male SE Baffin beluga blubber samples.

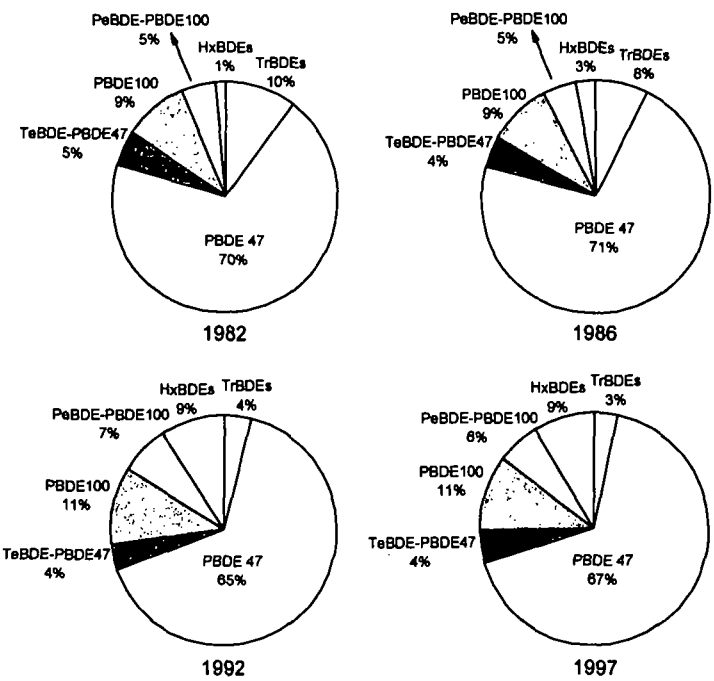

Figure 2. PBDE composition in male SE Baffin beluga blubber samples Collected in 1982, 1986, 1992 and 1997 (age adjusted).

Table 1. Factor increases of major PBDE homologues and congeners between time points. Italicized numbers indicate that least square mean concentration differences were significant by t-test at $p < 0.05$

Time	PBDE congeners								PBDE homologues				
period	17	28/33	47	49	66	99	100	154	Tr	Te	Pe	Hx	ΣPBDE
82-86	1.3	*1.6*	*1.6*	1.2	*2.0*	1.6	1.5	*2.1*	1.1	*1.6*	1.5	*3.0*	1.5
82-92	*2.3*	*6.4*	*5.9*	*2.9*	*9.3*	*10.8*	*7.4*	*29.0*	*2.4*	*5.8*	*7.9*	*40.7*	*6.2*
82-97	*2.3*	*5.9*	*6.5*	*4.1*	*10.3*	*10.3*	*7.9*	*30.6*	*2.3*	*6.5*	*8.0*	*42.2*	*6.8*
86-92	*1.8*	*3.9*	*3.7*	*2.5*	*4.6*	*6.9*	*4.8*	*14.1*	*2.1*	*3.7*	*5.2*	*13.6*	*4.1*
86-97	*1.8*	*3.6*	*4.1*	*2.5*	*5.1*	*6.6*	*5.1*	*14.9*	*2.0*	*4.1*	*5.3*	*14.1*	*4.5*
92-97	1.0	0.9	1.1	1.4	1.1	0.9	1.1	1.1	0.9	1.1	1.0	1.0	1.1

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