Temporal development of polybrominated diphenyl ethers (PBDEs) in ringed seals *(Phoca hispida)* and peregrine falcon *(Falco peregrinus)* eggs from Greenland

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Introduction

The increasing use of inflammable polymeric materials in various industrial branches has required the addition of flame retardants for safety reasons. Alaee et al. (2003) reported that the global market demand for brominated flame retardants increased by over 100% over a decade, from 145 000 tonnes in 1990 to over 310 000 tonnes in 2000. PBDEs are acknowledged as ubiquitous persistent pollutants, with a concerning resemblance to polychlorinated biphenyls (PCBs), regarding bioaccumulation and biomagnification and potential effects on hormone balances and neurobehavioural development.
The increased awareness of an environmental problem led to discontinuation in industrial production, first on a voluntary basis and eventually by political regulations. Since July of this year, the use of penta-BDE and octa-BDE has been banned in the European Union. At present, 10 states of the USA have taken measures against PBDE emissions, including phase-outs of PBDE-containing products (BSEF 2006). There are no restrictions on the use of deca-BDE (BDE-209), HBCD or TBBPA in the EU or North America.
Swedish and French studies have shown increasing concentrations of PBDEs in guillemot *(Uria algae)*, pike *(Esox lucius)* and mussels *(Mytilus edulis* and *M. galloprovincialis)* until the late 1980s or the 1990s, but decreasing or stagnating levels since then (Sellström et al. 2003, Kierkegaard et al. 2004, Johansson et al. 2006). Similarly, declining concentrations in Swedish human milk samples have been observed since the late 1990s (Meironyté et al. 1999). Studies from North America, however, have shown ongoing increases in biota since the 1970s or 1980s, e.g. in lake trout (*Salvelinus namaycush*) from the Great Lakes (Luross et al. 2000), beluga *(Delphinapterus leucas)* from the St. Lawrence Estuary (Lebeuf et al. 2004) and ringed seals from the Canadian Arctic (Ikonomou et al. 2002). Apparently, different trends exist in North America and Europe.
The presence of PBDEs in the Greenland environment has been shown previously (e.g. Vorkamp et al. 2004b). Geographical differences were found, with higher concentrations in East Greenland than in West Greenland, which is attributed to the compound transport from Europe/Asia and North America, respectively. This abstract summarises the knowledge presently available of temporal trends of PBDEs in Greenland biota, based on studies of ringed seal from East and West Greenland and peregrine falcon eggs.

Materials and Methods

Samples of ringed seal blubber from Ittoqqortoormiit (Central East Greenland) were available from the years 1986, 1994 and 1999-2004, as described by Rigét et al. (2006). Preliminary analyses of ringed seal blubber from Qeqertarsuaq (Central West Greenland) from the years 1982, 1986, 2001, 2002 and 2004 have been conducted. The peregrine falcon eggs originated from the three southernmost municipalities of Southwest Greenland, Nanortalik, Qaqortoq and Narsaq, and were

collected annually between 1986 and 2003, with exception of the years 1993, 1996 and 1997. Details on sample collection and bird identification are given by Vorkamp et al. (2005).
All chemical analyses were carried out at NERI and followed the procedures described by Vorkamp et al. (2004a). Briefly, the samples were homogenised, Soxhlet extracted with n-hexane:acetone (4:1) and purified on a multi-layered glass columns. After elution with n-hexane, the extracts were concentrated and kept in iso-octane. BDE-71 was used as a syringe standard for quantification, and BDE-77 was added prior to extraction to assess the recovery.

Results and Discussion

Ringed seals

The concentrations of PBDEs in ringed seals from West Greenland were an order of magnitude lower than in their counterparts from East Greenland. This is in agreement with findings for black guillemot liver (Vorkamp et al. 2004a), however, the difference was smaller for the black guillemots (only about factor 3). The same spatial trend has also been observed for organochlorine compounds, such as PCBs and toxaphene (Riget et al. 2004), indicating that PBDEs follow the same transport patterns. The results from East Greenland have been discussed in detail by Rigét et al. (2006).

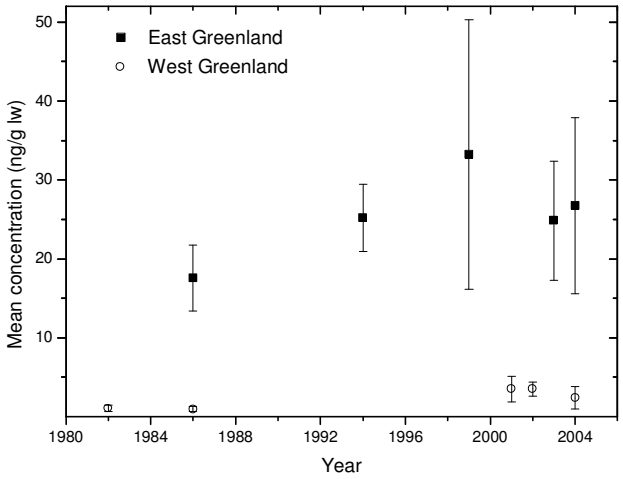

Figure 1: Mean concentrations and standard deviations of BDE-47 in ringed seal from East and West Greenland. N: 7-20, with N≥10 for most years.

Due to the low concentrations in the West Greenland seals, BDE-47 was the only congener above the detection limit in all samples. For this reason, the temporal trend in the ringed seals is only based on BDE-47 (Figure 1). Figure 1 shows the mean values and standard deviations of all samples analysed for one year. The same course in PBDE concentration will be seen when using median values or geometric mean values. There seems to be a tendency of increasing concentrations until approximately year 2000 or 2002/2003, after which the mean values are lower. Due to the large standard deviations, these trends are not statistically significant, and the apparent decrease since approximately 2002 has to be confirmed by future monitoring that will extend the present time series.
Different concentrations have previously been shown for male and female animals, probably caused by contaminant transfer from the mother to the offspring (e.g. Lindström et al 1999). The mean values of BDE-47 in male and female seals are not statistically different for any of the years studied (t-test, 5% level). The mean age of the East Greenland seals was generally between 3 and 6 years for each year, and seals from West Greenland were maximum one year old, except for few specimens. Ringed seals generally become sexually mature at the age of 3-5 (Smith 1973).

Peregrine falcon eggs

This dataset varies from the ringed seal in that respect that more individual years were studied, but less samples per year (N≤5). Therefore, all 37 samples are displayed in Figure 2, covering a period from 1986 and 2003, i.e. approximately the same time period that was studied for the ringed seals. In contrast to the seals and most other biota, the peregrine falcon eggs were enriched in the higher brominated congeners. BDE-153 was the dominant congener in the peregrine falcon eggs and accounted for 34% of the total concentration of 12 BDE-congeners, while BDE-47 only accounted for 6% (Vorkamp et al. 2005). This distribution had also been found in other birds of prey, such as merlins *(Falco columbarius)* and gyrfalcons *(Falco rusticolus)*, while e.g. eggs of sparrowhawk *(Accipiter nisus)* and white-tailed eagle *(Halliaeetus albicilla)* showed a predominance of BDE-47 (Herzke et al. 2001). These differences in congener pattern have been attributed to specific metabolisation processes (Law et al. 2003).

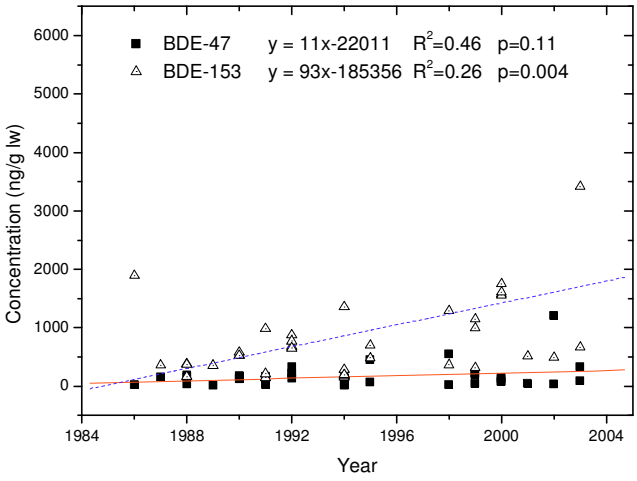

Figure 2: Concentrations of BDE-47 and BDE-153 in peregrine falcon eggs from Southern Greenland collected between 1986 and 2003 and results of the linear regression.

Compared with the ringed seals, the peregrine falcon eggs had considerably higher concentrations of BDE-47. It has repeatedly been shown that higher trophic levels animals from East Greenland have high body burdens of persistent contaminants, as a result of transport pathways and biomagnification (e.g Rigét et al 2004). However, the concentrations in the peregrine falcon eggs still exceed these levels, although biomagnification is less pronounced in the terrestrial than in the marine environment. However, the PBDE concentrations in the peregrine falcon eggs are likely to reflect the use of brominated flame retardants on the American continent, as peregrine falcons from Greenland migrate to Central and South America in winter. Moreover, during their summer stay in Greenland, the peregrines primarily prey on passerines and ptarmigans, which are expected to be low in PBDE concentrations. It seems likely that PBDEs in the ringed seals originate from long-distance transport to Greenland, while main exposure of the peregrine falcons happens during migration.

Based on linear regression, both congeners increase slightly over the study period, but the trend was only statistically significant (5% level) for BDE-153 (Figure 2). A statistically significant has also been shown for BDE-209 in the same samples. Due to the large variation in the dataset, the nature of the trend is not unambiguous, and an exponential increase could also be possible (Vorkamp et al. 2005). It also has to be noted that the trend is influenced by single samples with high concentrations, e.g. from the years 2002 and 2003. In contrast to the preliminary results for ringed seals and studies

from Europe (e.g. Meironyté et al. 1999; Sellström et al. 2003), the PBDEs do not seem to decrease or level off in the peregrine falcon eggs. As for the seals, continuing measurements will be necessary to assess the current and most recent development.

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