Polybrominated diphenylethers in biota from Bjørnøya (Bear Island)

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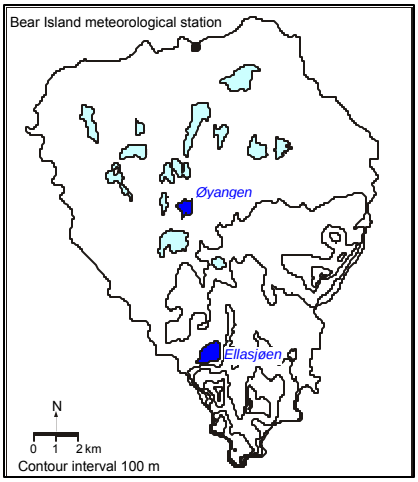
Introduction

Bjørnøya (Bear Island, Norway) is situated about 500 km North off the Norwegian mainland halfway between Norway and Spitsbergen (74°N, 19°E; Figure 1). Recently, environmental studies have been performed on Bjørnøya, elucidating the fate and the presence of persistent organic pollutants in a pristine Arctic environment.

During these previous studies, it was shown that land locked Arctic char (*Salvelinus alpinus*) from Lake Ellasjøen (21 m.a.s.l.) on Bjørnøya was contaminated with some of the highest concentrations of PCB in freshwater fish from Arctic areas[1]. However, in samples from Lake Øyangen (ca. 6 km north of Lake Ellasjøen, 33 m.a.s.l.) concentrations were on the same level or lower than the concentrations found in samples from other Arctic areas (e.g. the Canadian Arctic). These level differences are probably caused by large seabird colonies (mainly glaucous gulls, kittiwake and little auk) close to Lake Ellasjøen. These birds drop large amounts of guano into the lake, and considerable concentrations of POPs have been found in guano samples from both kittiwake and glaucous gull. In contrast, no significant bird activities exist around Lake Øyangen. In addition, Lake Ellasjøen is situated in the mountainous southern part of the Island. This special geographic position lead to increased precipitation (rain, snow) and fog events at Lake Ellasjøen compared to Lake Øyangen. This may lead to an increased deposition of airborne contaminants in the Ellasjøen catchment area.



For PBDE no significant source exists within the European Arctic; and PBDE are hypothised to get transported via long-range transport to Bjørnøya. Another possible source for contamination may be the large colonies of seabirds, nesting on the island during the summer months. Within a comprehensive research programme at Bjørnøya, co-ordinated by Akvaplan-niva and funded jointly by the Research Council of Norway and the State Pollution Control Authority of Norway (SFT), samples from selected species of a typical freshwater food web and from seabirds were collected at Lakes Ellasjøen and Øyangen and analysed for the content of selected brominated flame retardants (BFR) in the laboratories of the Norwegian Institute for Air Research (NILU).

Figure 1: Bjørnøya (Bear Island, 74ºN, 19ºE) and the sampling sites Lake Øyangen and Lake Ellasjøen

Material and Methods

The method is described in more detail elsewhere[5], but briefly: about 1 to 15 g of the respective biological sample was homogenised with the 10-fold of pretreated sodium sulfate (8h heated at 650ºC). The mixture was transferred to a glass column (300 x 50 mm) and the internal standard mixture containing ^{13}C-labeled BDE 28, 47, 99, 153 and 183 was added on top of the column. The lipophilic compounds were eluted by a slow flow of 150 mL cyclohexane/aceton (1:3, *v,v*) (Suprasolv quality, Merck, Darmstadt, Germany). After volume reduction to 1 mL, lipids were removed using gel permeation chromatography (GPC) on 50 g Biobeads SX-3 (Biorad, Hercules, CA) with dichloromethane as eluent on a pre-packed commercially available Environgel GPC system (Waters, Milford, CA, USA). The BFR fraction was cleaned additionally on 1.5g pretreated florisil (8h heated at 650ºC and deactivated with 0.5 v-% water) with 8 mL n-hexane/dichloromethane. Before quantification, octachloronaphthalene was added as recovery standard. All ^{13}C isotope labelled standards were purchased at Cambridge Isotope Laboratories (CIL, Andover, MA). An aliquot of 2 µl of the sample extract was injected on-column for gas chromatographic separation (Fisons 8560 Mega II, Milan, Italy) on a 30m DB5MS capillary column (id: 0.25 mm, film thickness: 0.25 µm, J&W, Folsom, CA). The following temperature program was employed for the separation: Initial temperature 70ºC (2 min isotherm), heating rate 15ºC/min to 180ºC, heating rate 5ºC /min to final temperature 280ºC (10 min isotherm) [5]. BDE 28, 47, 71, 77, 99, 100, 138, 153, 154 and 183 were analysed.

Low resolution mass spectrometric detection in electron impact mode (GC/LRMS-EI: MD800, Finnigan, San Jose, CA) was used for quantification. Single Ion monitoring (SIM) was employed for separation and quantification of the PBDE in the samples. For the here described method, the detection limits for all BFR were determined between 0.01 and 0.3 ng/g ww for all biota samples analysed. In several sampling campaigns (1998-2003), PBDE levels were determined in two pooled zooplankton samples (Lake Øyangen: 10g, Lake Ellasjøen 12g); one pooled sample of chironomids (*Chironomidae sp.)* from Ellasjøen and of tadpole shrimps (*Lepidunes arcticus*) from Øyangen; 4 Arctic char (AC), Lake Øyangen (Ø) and 6 Arctic char (separate fish), Lake Ellasjøen (ES). Additionally, two pooled and two individual intestinal content samples, 3 muscle samples and 15 liver samples were collected from glaucous gull (GG , *Larus hyperboreus*; near Lake Ellasjøen). Intestinal content samples and muscle tissue were collected from kittiwake (K, *Rissa tridactyla*, 3; 3 respectively) and little auk (LA, *Alle alle*, 1; 3 respectively) as well. The levels are presented in figure 2.

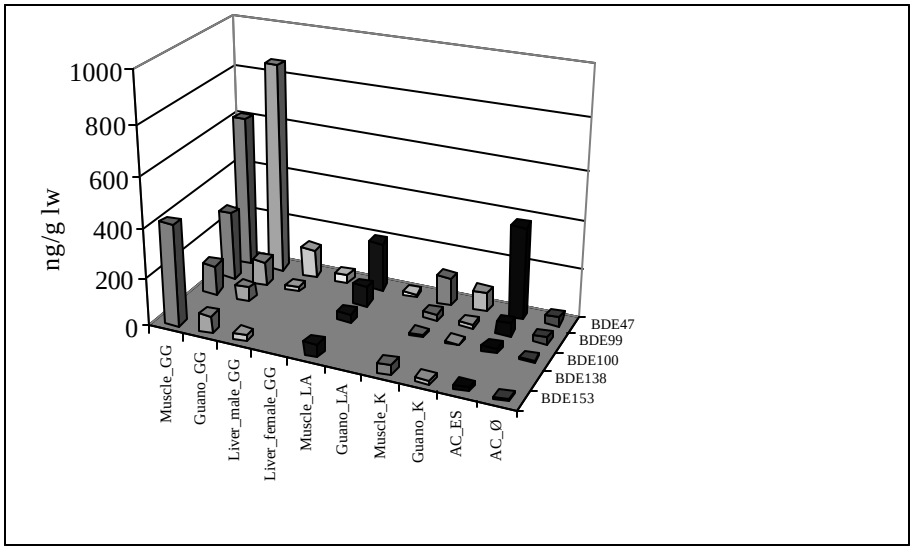


Figure 2: PBDE levels in biota from Bjørnøya in ng/g lw
(GG: glaucous gull; LA: little auk; K: kittiwake; AC: arctic char; ES: Ellasjøen; Ø: Øyangen)

Results and discussions

From ten PBDE congeners analysed, only the congeners 28, 47, 99, 100, 153, were found in the biota samples from Bjørnøya. The levels for all zooplankton, chironomids and tadpole shrimps collected at both locations were very low (from less than LOD to 7 ng/g lw). The levels found for the fish samples from Lake Øyangen were also very low, often not exceeding the detection limits. The highest PBDE concentration was found for BDE47 in the Arctic char muscle (50 ng/g lw). This general low levels found in biota from Lake Øyangen confirm the already reported findings for PCB. However, considerably higher PBDE levels were found for biota samples from the Lake Ellasjøen area. BDE 47 and 99 were identified as the most abundant PBDE congeners in all Lake Ellasjøen samples (figure 2). The PBDE levels found for Artic char from Ellasjøen with up to 420 ng/g lw are in the same order of magnitude as levels reported from a densely populated area in Scandinavia, Lake Vättern, in southern Sweden, confirming the high contaminated state of this pristine region [3]. Muscle tissue and guano from glaucous gull represent the most contaminated sample materials ever collected from Arctic seabirds. However, the BDE 47 concentrations found in the glaucous gull muscle tissue (median 620 ng/g lw) are not unusual high compared to literature values reported for muscle tissue from top predators like the osprey (1800 ng/g lw) from Sweden[8] but very few data are available so far on seabird tissue. Surprisingly high concentration of BDE 153 was detected in muscle samples of glaucous gull (420 ng/g lw).

Seabird guano must be considered as one of the major PBDE sources for the Lake Ellasjøen fresh water system. To estimate the contribution from guano to the PBDE contamination of the Lake Ellasjøen, the total amount of guano deposited in the Lake Ellsjøen was estimated. Kittiwake is with about 300 000 individuals one of the dominating seabird species on Bjørnøya. Birds were counted on and above the lake on several occasions (May- September) from 2000 to 2003. At any time during the ice-free season from 200 (early June and September) to 4000 (July, August) kittiwakes are on and above Ellasjøen. Based on literature about guano production in this species, it was estimated that 11 500 kg guano is dropped into the lake each year from this species. The total breeding population of glaucous gull on Bjørnøya is about 2 000 pairs[6]. About 70 birds are continuously in or above the lake, during the summer months. However, glaucous gull has a body mass that is about 4 – 5 times the body mass of kittiwakes. Therefore, glaucous gull consumes on average 3.4 times the amount of food consumed by kittiwakes[7], resulting in 3.4 times the amount of excreted material, summing up to 1 650 kg guano deposited into the lake. All population estimates for little auk are very rough. The total population on Bjørnøya has been reported to range between 10 000 – 100 000 pairs. No population estimates have been carried out in the colony that breeds at the edge of Ellasjøen. However, PBDE levels are low in guano from this species. Additionally, little auk deposits guano in the cliffs surrounding the lake. Only a small part of this guano is expected to reach the lake and the contribution from this species is expected to be low. Figure 3 illustrates the levels of PBDE in guano and the relative contribution to the PBDE contamination of the Lake Ellasjøen in relation to the number of bird per species and time spend in or above the lake in the pie-diagram calculated from the sumPBDE concentrations on wet weight basis. We estimated, that glaucous gull deposits 18 mg sumPBDE per year in the lake Ellasjøen, whilst kittiwake deposits 53 mg sum PBDE in the lake during the same time. Regardless to the fact that the guano dropped by kittiwake is almost five times lower contaminated with sumPBDE compared to glaucouss gull, guano of kittiwake contributes with approximately 75% to the PBDE contamination of the Lake Ellasjøen because of the much higher number of individuals, thus explaining the elevated PBDE levels in Arctic char from Lake Ellasjøen.

In addition, the local differences in the PBDE levels between the two locations, Lake Øyangen and Lake Ellasjøen, situated in about 6 km distance from each other, are remarkable and demonstrate impressively the important influence of locally defined ecological, geographical and meteorological factors like, precipitation, presence of local nesting cliffs and, the drainage of guano into the freshwater habitat. Such small-scale habitat specific differences are very difficult to estimate, document and report.

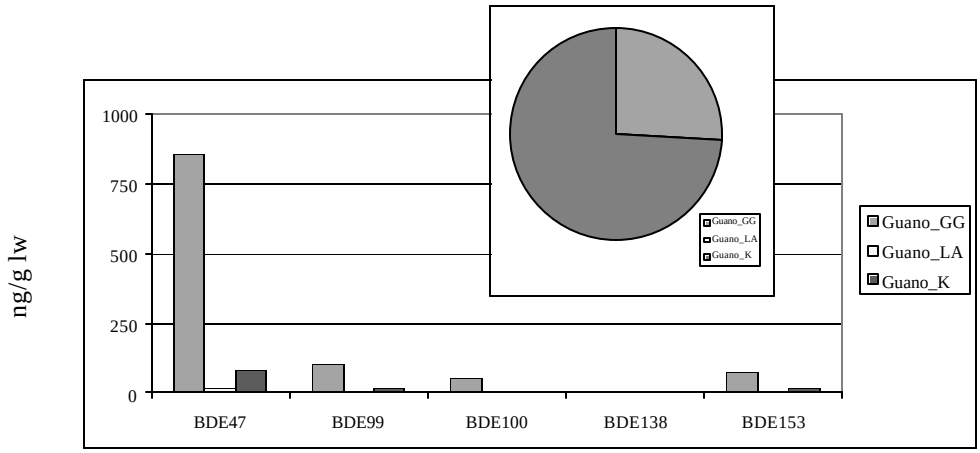


Figure 3: PBDE in guano of glaucous gull, little auk and kittiwake in ng/ g lw and relative contribution of sumPBDE in to the Lake Ellasjøen during one season calculated from wet weight levels (%)

Acknowledgement

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References

1. Skotvold T, Wartena EMM and Schlabach M (1998) *Organohalogen Comp*. 39: 411.
2. Bustnes JO, Erikstad KE, Bakken, Mehlum, F, Skaare, JU (2000) *Ecotox*. 9/ 3: 179.
3. Sellstrom U, Jansson B., Kierkegaard A., de Witt C. Chemosphere 1993; 26(9):1703-1718.
4. Sellstrom U, Kierkegaard A, de Witt C, Jansson B. Env Tox and Chem 1998; 17(6):1065-1072.
5. Herzke D, Gabrielsen GW, Evenset A, Burkow IC. Environmental Pollution 2002; 121: 293-300.
6. Mehlum, F. & Bakken. *Seabirds on Islands Threats, Case Studies and Action Plans*. Birdlife International. 1994.
7. Mehlum, F & G.W. Gabrielsen. Energy expenditure and food consumption by seabird populations in the Barents Sea region. in: *Ecology of Fjords and Coastal Waters*. Elsevier. 1995; 457-470.
8. Sellstrom U, Jansson B., Kierkegaard A., de Witt C. Chemosphere 1993; 26(9):1703-1718.