CHLOROBORNANES IN BIOTA SAMPLES, RELATED TO A TYPICAL FRESHWATER FOOD WEB AT BJØRNØYA (BEAR ISLAND)

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Introduction

Within the past decade, multidisciplinary studies have been performed on Bjørnøya (Bear Island, Norway) elucidating the fate and the presence of persistent organic pollutants in this pristine Arctic environment. High concentrations of conventional persistent pollutants like polychlorinated biphenyls (PCB) were found in biota samples reaching the region probably via long-range transport [1]. Subsequently, bioaccumulation throughout the food webs into the top predators resulted in toxic concentration levels. Correlations between high POP burden and reduced physiological fitness were found for glaucous gulls (*Larus hyperboreus*) on Bjørnøya [2]. This species as one of the major predators in the Arctic is a good indicator for contaminant accumulation. 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 belonging to a typical freshwater food web were collected at Lake Ellasjøen and analysed for the content of chlorobornanes in the laboratories of the Norwegian Institute for Air Research (NILU). In addition, gut samples from glaucous gull were taken and analysed, since guano input from seabirds like gulls into the freshwater system cannot be neglected as possible POP source. Bjørnøya is situated about 500 km North off the Norwegian mainland halfway between Norway and Svalbard (figure 1).

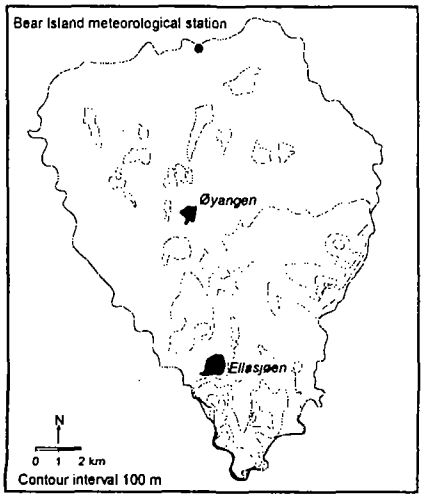

Figure 1: Bjørnøya (Bear Island, 74°N, 19°E) and the sampling sites Lake Øyangen and Lake Ellasjøen

During previous studies, it was shown that land locked Arctic char (*Salvelinus alpinus*) from Lake Ellasjøen (21 m.a.s.l.) on Bear Island was contaminated with some of the highest concentrations of PCB in freshwater fish in the Arctic [1]. However, samples from Lake Øyangen (ca. 6 km North of Lake Ellasjøen, 33 m.a.s.l.) were on the same level or lower than the concentrations found in samples from the Canadian Arctic. These level differences were thought to be mainly due to the fact that large nesting colonies of little auk (*Alle alle*) exist close to Lake Ellasjøen. In addition large numbers of kittiwakes (*Rissa tridactyla*) and glaucous gulls using the Lake as resting area. Thus, guano of the seabirds released into the freshwater system might contribute significantly to the high POP levels found. At Lake Øyangen, however, no significant seabird activities exist. In addition, Lake Ellasjøen is situated in the mountainous southern part of the Island (figure 1). This special geographic position probably leads to increased precipitation (rain, snow) and fog events at Lake Ellasjøen compared to Lake Øyangen. Lake Øyangen, the second sampling site, is situated about 6 km North of Lake Ellasjøen in the central plains of Bjørnøya. Based on these clearly defined geographic and ecological differences it was obvious for the project group to perform, also for chlorobornanes, a level and pattern comparison.

Material and Methods

About 1 to 15 g of the respective biological sample was homogenised with the 10-fold of pretreated sodium sulfate (8h heated at 650°C). The mixture was filled into a glass column (300 x 50 mm) and the internal standard mixture containing ^{13}C-labeled hexachlorobenzene (HCB), hexachlorocyclohexane (HCHs), dichlorodiphenyltrichloroethane (DDE) and polychlorinated biphenyls (PCBs) was added on top of the column. The lipophilic compounds were eluted by a slow flow of 150 mL cyclohexane (Suprasolv quality, Merck, Darmstadt, Germany). After concentration to 1 mL, lipids were removed by gel permeation chromatography (GPC) on 50 g Biobeads SX-3 (Biorad, Hercules, CA) with cyclohexane/ethylacetate (50/50). The POP fraction was cleaned additionally on 30g pretreated alumina (8h heated at 850°C and deactivated with 5 v-% water) with the following mobile phase: n-hexane and n-hexane/methyl-t-butyl ether (MTBE) (50/50). Before quantification 1,2,3,4-tetrachloronaphthalene (TCN) was added as recovery standard. All ^{13}C isotope labeled standards were purchased at Cambridge Isotope Laboratories (CIL, Andover, MA). 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 70°C (2 min isotherm), heating rate 15°C/min to 180°C, heating rate 5°C /min to final temperature 280°C (10 min isotherm).

Table 1: Chlorobornanes selected for analysis in the Bjørnøya biota samples.

Parlar no.	AV-name [3]	Scientific name
# 26	B8-1413	2-endo,3-exo,5-endo,6-exo,8,8,10,10-octachlorobornane
# 32	B7-515	2,2,5-endo,6-exo,8,9,10-heptachlorobornane
# 38	B8-789	2,2,5,5,9,9,10,10-octachlorobornane
# 40	B8-1414	2-endo,3-exo,5-endo,6-exo,8,9,10,10-octachlorobornane
# 44	B8-2229	2-exo, 5,5,8,9,9,10,10-octachlorobornane
# 50	B9-1679	2-endo,3-exo,5-endo,6-exo,8,8,9,10,10-octachlorobornane
# 51	B8-786	2,2,5,5,8,9,10,10-octachlorobornane
# 58	B9-715	2,2,3-exo,5,5,8,9,10,10-nonachlorobornane

# 62	B9-1025	2,2,5,5,8,9,9,10,10-nonachlorobornane
# 69	B10-1110	2,2,5,5,6-exo,8,9,9,10,10-decachlorobornane

Low resolution mass spectrometric detection in negative ion chemical ionisation mode (GC/LRMS-NICI: MD800, Finnigan, San Jose, CA) was used for quantification. Single Ion monitoring (SIM) was employed for recording and quantification of the chlorobornanes in the samples. In table 1, the chlorobornane congeners chosen for analyses, one hepta-, five octa-, three nona-, and one decachlorobornanes, are listed. For the here described method, the detection limits for all chlorobornanes were determined between 0.01 and 0.3 ng/g ww for all biota samples analysed. The selected samples are listed in table 2.

Table 2: Eleven samples chosen for chlorobornane analysis.

Lake Øyangen	**Lake Ellasjøen**
1ZPØ-98 = Zooplankton No. 1, 1998, 1PCØ-98 = Pooled Arctic char No. 1 (3 fish), 1998, 1PCØ-99 = Pooled Arctic char No. 1 (3 fish), 1999, 2PCØ-99 = Pooled Arctic char sample No. 2 (3 fish, 1999, 1SCØ-98 = Pooled stomach content from Arctic char, 1998, mainly *Lepidurus spec.*	1ZPE-99 = Zooplankton No. 1, , 1999, 1ACE-99 = Arctic char No. 1, 1999, 2ACE-99 = Arctic char No. 2, 1999, 3ACE-99 = Arctic char No. 3, 1999, 1SCE-99 = Pooled stomach content from Arctic char, 1999, mainly *Chironomidae,* 1GGE-99 = Glaucous gull gut, pooled from 15 gulls, 1999.

Results and discussions

From the nine chorobornane congeners analysed, only three, the congeners #26, #40, and #50, were found in considerable amounts in the analysed biota samples from Bjørnøya. The levels found for all samples from Lake Øyangen were very low, often not exceeding the detection limits, the highest chlorobornane concentration was found for #50 in the 1PCØ-98 sample (2.7 ng/g wet weight). This general low levels found at Lake Øyangen confirm the already reported findings for for PCB, were also low levels were found in Lake Øyangen biota samples. However, similar with the PCB investigations reported earlier [1], considerably higher chlorobornane levels were found for biota samples from the Lake Ellasjøen catchment area. Whereas almost no chlorobornanes were found for zooplankton from Lake Øyangen, for congener #50, a level of 1.2 ng/g ww was determined in Lake Ellasjøen zooplankton and a significant increase from zooplankton (sum #26+#40+#50: 1.2 ng/g ww) to Arctic char (average sum: #26+#40+#50: 8.1 ng/g ww) was found for the Lake Ellasjøen samples. Glaucous gull gut, (sum #26+#40+#50: 84.2 ng/g ww) from Lake Ellasjøen was highest contaminated. The congeners #26 and #50 were found as the most abundant chlorobornanes in both Lake Ellasjøen and Lake Øyangen samples (figure 2). In general, chlorobornane sum concentration for zooplankton (Ice Island: 2 ng/g ww) and Arctic char (Greenland: 13 ng/g ww), reported in the literature are similar with those found at Lake Ellasjøen [4]. Although significant differences were found between Lake Øyangen and Lake Ellasjøen samples, the highest chlorobornane contamination, found in the pooled glaucous gull gut sample, cannot be considered as unusual high compared to published literature date reported for Arctic marine top predators. A comprehensive review article presents levels up to 4000 ng/g ww (sum chlorobornanes) for marine mammals [4]. However, based on the results of the present study, glaucous gull guano was identified as one of the major chlorobornane sources for the Lake Ellasjøen fresh water system. The distinct local chlorobornane level differences between the two sites, demonstrate impressively the important influence of locally defined and restricted ecological,

geographical and meteorological environmental factors on the overall contaminant levels (e.g., precipitation, presence of local seabird nesting colonies and resting areas). Based on these assumptions, sea birds at Bjørnøya function effectively as transport link for persistent organic pollutants from the marine into the freshwater ecosystem. Such a "sea bird" linkage between freshwater and marine ecosystems is common not only for Arctic regions. Therefore it can be assumed that also in other locations seabird guano might be evaluated as contamination source for persistent pollutants.

For chlorobornanes, no significant primary source exists within the European Arctic. The only source for chlorobornanes at Bjørnøya is, therefore, long-range transport. As additional conclusion, the here presented results are a further indication for the importance of long-range transport processes as important sources for persistent contaminants in Arctic regions.

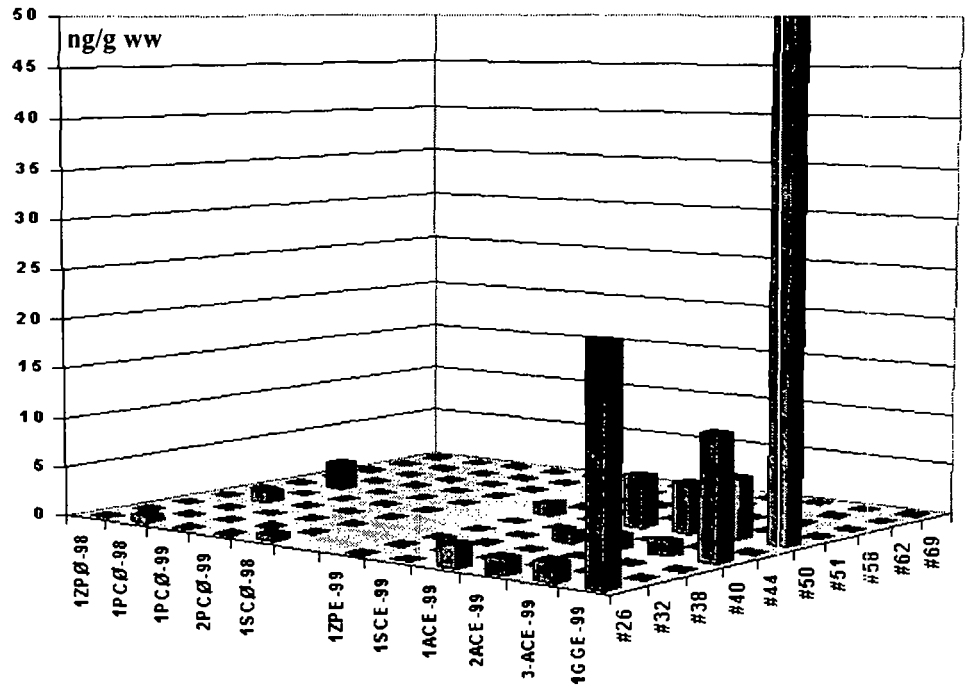

Figure 2: Chlorobornanes in selected biota samples from Lake Øyangen and Lake Ellasjøen (Bear Island). Abbreviations: see table 2.

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