Biological transport of persistent organic pollutants (POPs) to Lake Ellasjøen, Bjørnøya (Bear Island), Norway

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Introduction

During recent years, multidisciplinary studies have been carried out on Bjørnøya (Bear Island, Norway) (Figure 1), elucidating the fate and the presence of persistent organic pollutants (POPs) in this pristine Arctic environment. High concentrations of POPs, like polychlorinated biphenyls (PCBs), dichloro-diphenyl-dichlorethane (DDE) and polybrominated diphenyl ethers (PBDEs) have been measured in sediment and biota from Ellasjøen[1,2], a lake located in the southern, mountainous part of Bjørnøya (Figure 1). In Lake Øyangen, located only 6 km north of Ellasjøen on the central plains of the island, levels of POPs are several times lower than in Ellasjøen[2].

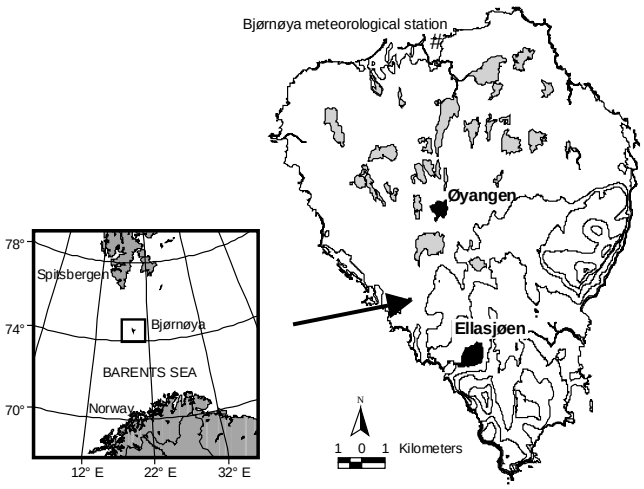

Figure 1. Bjørnøya with Lake Øyangen and Lake Ellasjøen.

One reason for the different POP contamination levels in Ellasjøen and Øyangen is probably differences in precipitation regime between the southern mountainous part of the island and the central plains further north, leading to differences in the deposition of air transported contaminants. Another possible source for contaminants to Ellasjøen is the large colonies of seabirds (mainly

kittiwake (*Rissa tridactyla)*, little auk (*Alle alle)* and glaucous gull (*Larus hyperboreus*)), which are situated close to the lake during the ice-free period (early June – October). These seabirds feed in the marine environment, and deposit large amounts of guano (excrements) directly into the lake or in the catchment area of the lake. Øyangen is not influenced by seabirds. There are two ways in which input from seabirds can lead to higher levels of POPs in Ellasjøen: 1) direct input of POPs through allochthonous material (guano, bird remains) or 2) a change in trophic state of the lake as a result of nutrient loadings from the seabirds.

Studies from the marine environment have shown an enrichment of the stable isotopes ^{15}N relative to ^{14}N, and ^{13}C relative to ^{12}C, in phytoplankton and zooplankton from areas affected by seabird guano (Wainwright *et al.* 1998). The input of guano to Ellasjøen could therefore affect the isotopic signatures of the organisms from the lake. It is also been established that changes in the relative abundance of the naturally occurring isotopes of nitrogen (N) and carbon (C) can be used as a method to characterise food web dynamics and trophic structure[3, 4]. The metabolic processes of animals enrich the heavy isotopes of N (^{15}N) and C (^{13}C), and the stable isotope ratio can therefore be used to construct simple food web models. Generally the $^{15}N/^{14}N$-ratio increases by 3 - 5 ‰ per trophic transfer[3, 4]. The magnitude of the heavy isotope enrichment is much smaller for carbon, so $\delta^{13}C$ is more often used to trace carbon sources, such as pelagic versus benthic[5] or marine versus terrestrial[6, 7].

The aim of the present study was to investigate the role of guano as a transport medium for POPs to Ellasjøen. Two main approaches were followed: 1) an investigation of the trophic status of Ellasjøen, as well as the reference lake, Øyangen, through analyses of stable isotopes of carbon and nitrogen, and 2) analyses of selected contaminants in lake biota and guano. If guano has a significant effect on the lake this would likely change the stable isotope values in the food chain in Ellasjøen compared to Øyangen. In addition the congener pattern in biota samples from Ellasjøen might be influenced by the pattern in guano more than by the pattern in precipitation.

Material and methods

Fieldwork

Particulate organic matter (POM), zooplankton (90% *Cyclops abyssorum*), chironomid larvae (*Chironomidae* sp.), tadpole shrimps (*Lepidurus arcticus*) and Arctic char (*Salvelinus alpinus*) were collected from Ellasjøen and Øyangen over a 3-years period (1999 – 2001), according to methods described in Evenset *et al.* (2004)[2]. In addition, fish that were sampled in 1996 was included in the data set. POM was used as a substitute for phytoplankton, although POM also contains small zooplankton and detritus. The invertebrate samples consisted of many pooled individuals. Muscle samples were taken from the dorsal axial muscle of the fish. Seabirds (little auk, kittiwake and glaucous gulls) were killed with a shotgun (1999 and 2001), and intestinal content (guano) was collected from the posterior part of the intestines. All samples were collected in July.

Chemical analyses

The biota and guano samples were analysed for stable isotopes of carbon and nitrogen. To reduce variability due to isotopically lighter lipids[8, 9] these were removed by Soxhlet extraction for two hours with a mixture of 93% dichloromethane (CH_2Cl_2) and 7% methanol (CH_2OH). The samples were then washed with 2N HCL for 5 minutes, dried over night at 105°C and homogenised. Samples (1 mg in Sn-capsules) were combusted with O_2 and Cr_2O_3 at about 1 700°C in a Carlo Erba, NCS 2500 elemental Analyser. NOx was reduced with Cu at 650°C. The combustion products N_2, CO_2 and H_2O were separated on a Poraplot Q column. N_2 and CO_2 were directly

transferred to a Micromass Optima mass spectrometer for quantification of $\delta^{13}C$ and $\delta^{15}N$. Isotopic composition is reported relative to N_2 in air.
Stable isotope values is expressed as δ values, given in parts per thousand:
$\delta(‰) = [(R_{(sample)} - R_{(standard)})/ R_{(standard)}] \times 1000$,
where R represent the ratio between heavy and light isotope, related to standard values of marine carbonate (Pee Dee Belemnite) for carbon or atmospheric air for nitrogen.
A selection of the samples were also analysed for PCBs (33 congeners) and DDTs (*o, p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT, *p,p'*-DDT) using the method described in Derocher *et al.* (2003)[10].

Statistical analyses
A Principal Component Analyses (PCA) was carried out to explore the relative contribution of each PCB-congener to the sum of PCBs (log-transformed data) in lake biota and guano. The analysis was performed using CANOCO, ver. 4.5.

Results and discussion

Stable isotopes
The food-chains in both the investigated lakes are short and the same species can generally be found in both lakes. However, the $\delta^{15}N$ values were significantly higher in biota from Ellasjøen than in corresponding samples from Øyangen (Table 1). The higher values are probably due to utilisation of nitrogen originating from seabird guano. An increase in $\delta^{15}N$ values in marine areas affected by seabird guano has previously been reported by Wainright *et al.* (1998)[7]. Guano from little auk and kittiwake had $\delta^{15}N$ values comparable to zooplankton and chironomids from Ellasjøen, while the $\delta^{15}N$ values in guano from glaucous gull were between the values of invertebrates and fish from Ellasjøen. $\delta^{15}N$ values in guano were higher than in all organisms from Øyangen.
Differences in stable isotopes of carbon often reflect different carbon sources (e.g. benthic versus pelagic) to the ecosystems in question. There was a difference in $\delta^{13}C$-values between the two lakes included in the present study, but the difference was less than for $\delta^{15}N$. Organisms from Ellasjøen had lower $\delta^{13}C$-values than corresponding organisms from Øyangen (Table 1). The $\delta^{13}C$-values in guano differed little between species (Table 1), but the values were generally higher than in lake biota. However, it is not likely that guano is a significant carbon source to lake organisms. The differences in $\delta^{13}C$-values between the two lakes are probably caused by differences in the importance of pelagic versus benthic primary production as a carbon source to organisms. Planktonic algae often have lower $\delta^{13}C$-values (-30 to -36 ‰) than benthic algae (-17 to -22 ‰)[11]. Øyangen is a shallow lake (max depth 5m) and it is therefore likely that the production of benthic algae is relatively high. Ellasjøen is much deeper (max depth 34 m) and has a small littoral zone that can be utilised by benthic algae. However, the large nitrogen inputs to Ellasjøen will sustain a large stock of planktonic algae (phytoplankton). The low $\delta^{13}C$-values in Ellasjøen are therefore probably due to a high production of pelagic algae, as opposed to Øyangen, where benthic production is more important.
Table 1. Stable isotopic composition of biological samples from Lake Ellasjøen and Lake Øyangen, as well as guano samples from the three seabird species that are most numerous around Ellasjøen.

Sample	n	$\delta^{15}N$ (‰)	$\delta^{13}C$ (‰)
Ellasjøen			
POM	4	5.2 ± 0.8	-30.8 ± 0.1
Zooplankton	3	12.2 ± 1.1	-31.9 ± 1.5
Chironomid larvae	13	12.7 ± 0.8	-27.5 ± 2.2
Arctic char	41	18.1 ± 1.5	-26.1 ± 1.7
Øyangen			
POM	4	-3.1 ± 1.8	-25.9 ± 0.2
Zooplankton	2	4.7 ± 0.9	-27.2 ± 5.1
Chironomid larvae	6	3.4 ± 0.9	-26.4 ± 1.3
Arctic char	45	8.9 ± 1.2	-20.4 ± 2.1
Guano			
Little auk	6	11.6 ± 0.7	-20.3 ± 0.7
Kittiwake	6	11.9 ± 0.4	-20.1 ± 0.4
Glaucous gull	5	14.8 ± 0.8	-20.5 ± 1.0

POPs

A selection of the samples that were analysed for stable isotopes were also analysed for PCBs (33 congeners) and DDTs (6 congeners). Average sum PCB and sum DDT for the different sample types are given in Table 2. Levels of both PCB and DDT were significantly higher in biota from Ellasjøen than in biota from Øyangen. PCB 153 was the dominating congener in biota from both lakes, followed by PCB 138 and 180. The persistent DDT-metabolite *p,p'*-DDE dominated in sum DDT, constituting from 94 - 99 % in biota from Ellasjøen and from 72 – 96 % in biota from Øyangen. Table 2. Average concentrations ± st.dev. in biological samples from Lake Ellasjøen and Lake Øyangen, as well as in guano from the three seabird species that are most numerous around Ellasjøen.

Sample	n	% lipid	Sum PCB (ng/g ww)	Sum DDT (ng/g ww)
Ellasjøen				
Zooplankton	2	2.2	26.2	2.2
Chironomid larvae	1	3.7	60.0	5.4
Arctic char	20	3.7 ± 3.9	2 389 ± 1 528	110.6 ± 98.3
Øyangen				
Zooplankton	1	0.6	1.6	0.16
Tadpole shrimps	1	2.4	5.6	0.53
Arctic char	16	1.8 ± 1.1	27.5 ± 37.7	3.5 ± 2.4
Guano				
Little auk	2	4.1	37.0	14.5
Kittiwake	5	3.7 ± 0.7	174.1 ± 53.2	11.7 ± 8.7
Glaucous gull	7	2.7 ± 1.5	1 653 ± 1 602	377.2 ± 272.4

Bjørnøya is a remote island, located more than 500 km from any known point source for POPs. The presence of POPs therefore suggests that these have been transported to the area by long-range transport. Ellasjøen receives more precipitation than Øyangen (Akvaplan-niva, unpublished data), and this can lead to a higher deposition of air-borne contaminants. Some of the concentration difference can therefore be due to the prevailing meteorological conditions. However, there are some differences in contaminant pattern and stable isotope ratios between the two lakes that cannot solely be explained by differences in deposition of air-borne contaminants. The result from the PCA-analyses showed that there was a difference in contaminant pattern between fish from Ellasjøen and Øyangen (Figure 2). Fish from Ellasjøen had a higher relative contribution of higher chlorinated and persistent PCBs (penta – hepta PCBs) than fish from Øyangen, which had a higher share of the tri – tetra PCBs (Figure 3). In addition, a higher proportion of DDT in the samples from Øyangen than in Ellasjøen, where the metabolite *p,p'*-DDE occurred in higher proportions, indicate that the source of contaminants may differ between the two lakes. The most persistent contaminants (e.g. higher chlorinated PCBs and *p,p'*-DDE) are less prone to long-range atmospheric transport, but have a stronger potential for bioaccumulation than the less lipophilic POPs (e.g. lower chlorinated PCBs)[12, 13, 14].

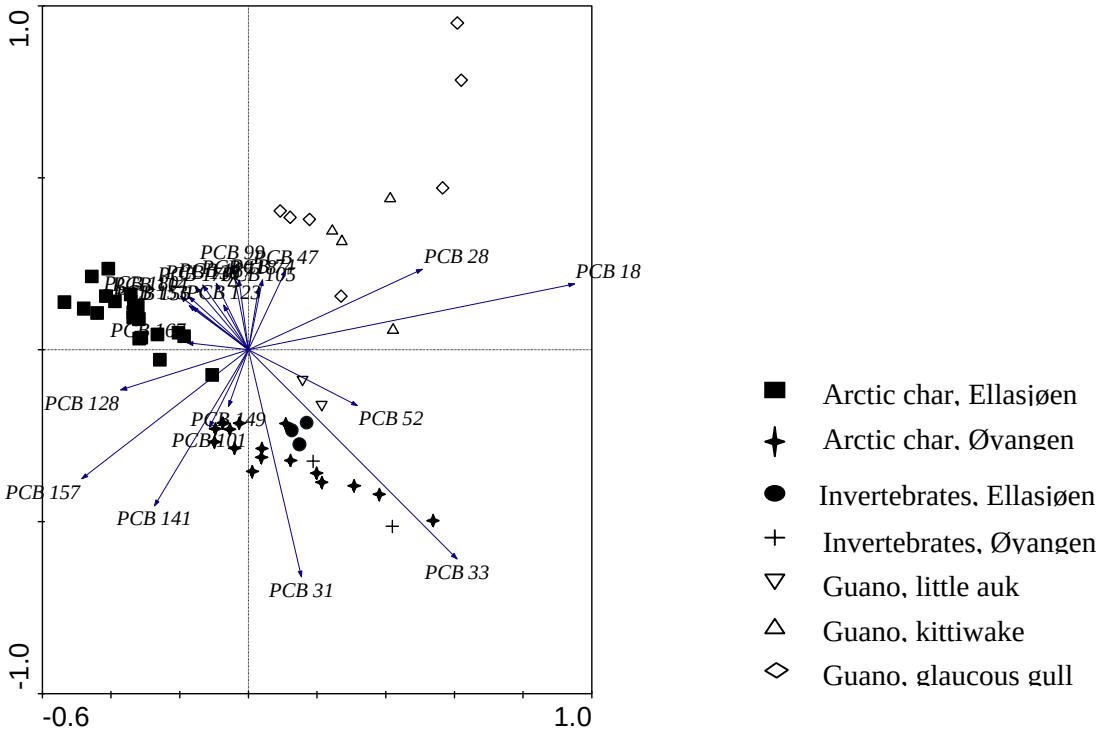

Figure 2. A PCA-plot (double-centred) showing the relative PCB contribution (log-transformed data) in lake biota from Ellasjøen and Øyangen, as well as guano from little auk, kittiwake and

glaucous gull. The first axis accounted for 40% of the variation in the data set whereas the second axis accounted for 30%.

Levels of PCB and DDT in guano varied between species, with the lowest levels in guano from the plankton-feeder little auk. In guano from kittiwake, a species that mainly feed on plankton and fish, the levels were higher, but the highest levels were measured in guano from the omnivorous species glaucous gull (Table 2). Contaminants transported by seabirds or excreted in seabird guano, have passed through parts of the marine food chain and have therefore gone through one or more bioaccumulation cycles. Bioaccumulation processes alter the contaminant pattern and increase concentrations, especially for the most persistent contaminants. This was clearly reflected in the guano samples, especially in the species feeding highest in the food-chain (glaucous gull). As in the biota samples from the lakes, the persistent congener PCB 153 dominated the samples, followed by PCB 138 and 180. The guano-samples from little auk had a higher relative share of the lower chlorinated PCBs than the guano samples from kittiwake and especially glaucous gull (Figure 2), which were more dominated by higher chlorinated congeners. In addition the persistent DDT-metabolite, *p,p'*-DDE, constituted from 98.7 – 100% of sum DDT in the guano samples. The contaminant pattern in biota samples from Ellasjøen was generally more similar to the contaminant pattern in guano than the samples from Øyangen were, although the guano samples had a very varying contaminant pattern. In Øyangen the composition of POPs in the whole lake system seemed to reflect atmospheric deposition as a contamination source[2, 15]. The relative importance of the two possible sources for POPs to Bjørnøya (guano and air-borne compounds) in currently being investigated through a separate project.
The high levels of POPs in Ellasjøen, the differences in contaminant patterns and stable isotope ratios between the two lakes, as well as the elevated levels of POPs in guano indicate that input from the large seabird colonies around the lake represent a significant source for POPs to Ellasjøen. The nutrient loadings from the seabirds has also obviously led to a change in trophic state of the lake, a factor which probably also has contributed to the enrichment of POPs in biota from Ellasjøen.

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