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Effect of diet, location and sampling year on bioaccumulation of mercury, selenium and cadmium in pelagic feeding seabirds in Svalbard

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HIGHLIGHTS

- Biomagnification potential of Hg and Cd both in Arctic and Atlantic food webs.
- Trophic position explains Hg variation in kittiwakes but not in little auks.
- Selenium was associated with Hg in little auks, but not in kittiwakes.
- High Se:Hg molar ratios indicate low risk of Hg toxicity.

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ABSTRACT

Hepatic concentrations of mercury (Hg), selenium (Se) and cadmium (Cd) were determined in black-legged kittiwakes (*Rissa tridactyla*) and little auks (*Alle alle*) from two fjords in Svalbard (Kongsfjorden; 78°57′N, 12°12′E and Liefdefjorden; 79°37′N, 13°20′E). The inflow of Arctic and Atlantic water differs between the two fjords, potentially affecting element accumulation. Trophic positions (TP) were derived from stable nitrogen isotope ratios ($\delta^{15}N$), and stable carbon isotope ratios ($\delta^{13}C$) were assessed to evaluate the terrestrial influence on element accumulation. Mercury, Cd, TP and $\delta^{13}C$ varied significantly between locations and years in both species. Trophic position and feeding habits explained Hg and Cd accumulation in kittiwakes, but not in little auks. Biomagnification of Hg and Cd were found in the food webs of both the Atlantic and the Arctic fjord, and no inter-fjord differences were detected. The $\delta^{13}C$ were higher in the seabirds from Kongsfjorden than in Liefdefjorden, but this did not explain variations in element accumulation. Selenium concentrations were not influenced by Hg accumulation in kittiwakes, indicating baseline levels of Se in this species. In contrast, correlations between Hg and Se and lower Se:Hg ratios in little auks from Kongsfjorden than in Liefdefjorden indicate a more pronounced influence of Se–Hg complex formation in little auks feeding in Atlantic waters.

1. Introduction

Even after extensive regulations of anthropogenic Hg emissions over the past decades, Hg levels are increasing in Arctic seabirds and mammals (Braune et al., 2005; Riget et al., 2011; Dietz et al., 2013). Despite low emission in Arctic areas, an annual input of 90–450 metric tons of Hg from atmospheric deposition is estimated (Ariya et al., 2004; Skov et al., 2004). A large fraction is reemitted to the atmosphere, but still, a net input of Hg to Arctic ecosystems has been reported (Poissant et al., 2008). High Hg deposition during the Arctic spring overlaps with the spring bloom of phytoplankton, potentially increasing the assimilation of Hg in

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algae (Stern and Macdonald, 2005; Douglas et al., 2012). In turn, this could facilitate Hg accumulation in Arctic marine food webs. By using fatty acid markers unique for the Arctic copepod *Calanus glacialis*, Routti et al. (2012) found a coherence between high concentrations of Hg in polar bears feeding on a diet with a high influence of this Arctic copepod.

Selenium (Se) is an essential element and is therefore physiologically regulated within an optimal range. However, as Hg concentrations increase Se accumulation is enhanced by the formation of Hg–Se complexes, a process that protects cells and organisms against Hg toxicity (both organic and inorganic Hg; Khan and Wang, 2009).

Similar to Hg, Cd accumulates in Arctic seabirds despite low emission within the Arctic (Dietz et al., 1996; Savinov et al., 2003). Arctic atmospheric Cd concentrations are low (Berg et al., 2008), suggesting that most Cd found in Arctic marine biota are derived from geochemical processes of the ocean (MacDonald et al., 2000). Cd is naturally more abundant in the North Pacific than in the North Atlantic (by a factor of five), resulting in a net flux of Cd from the Pacific to the Atlantic side of the Arctic Ocean (Bruland and Franks, 1983; MacDonald et al., 2000). This may lead to higher Cd concentrations in Arctic water compared to Atlantic water. Cadmium is easily adsorbed to the chitinous surface of zooplankton, facilitating uptake in fish and birds (Dietz et al., 1996).

In a scenario of a changing climate, the species composition of the marine Arctic may shift towards Atlantic species (Falk-Petersen et al., 2007; Eriksen and Dalpadado, 2011). Such a shift has been observed in Kongsfjorden (Svalbard), due to unusually high influxes of Atlantic water (Willis et al., 2008; Gabrielsen and Hop, 2009). The change has persisted, as shown by abnormally large amounts of Atlantic species (Atlantic cod (*Gadus morhua*), capelin (*Mallotus villosus*), euphausiids and *Calanus finmarchicus*) in Kongsfjorden during the years 2007–2011 (Gabrielsen and Hop, 2009; Buchholz et al., 2012). During parts of this period black-legged kittiwakes (*Rissa tridactyla*) fed on capelin (*Mallotus villosus*) rather than their traditionally more important prey, the polar cod (*Boreogadus saida*), in Kongsfjorden (Gasbjerg, 2010).

Element concentrations correlate to trophic position (TP) in several Arctic seabird species (Atwell et al., 1998; Braune et al., 2005; Ricca et al., 2008). Studies of bioaccumulation in relation to diet commonly apply the ratios between stable isotopes of nitrogen ($^{15}N/^{14}N$) to determine TP as the heavy ^{15}N is enriched relative to the lighter ^{14}N in predators. (Minagawa and Wada, 1984; Hobson and Welch, 1992; Atwell et al., 1998; Power et al., 2002). The food web baseline is defined by $\delta^{15}N$ in organisms at the first trophic position (TP1), i.e. primary producers. Alternatively, $\delta^{15}N$ of primary consumers can be used to as a proxy for the second trophic position (TP2). Baseline $\delta^{15}N$ varies between locations and seasons, making it important to correct for the baseline when comparing accumulation of elements in different food webs (Cabana and Rasmussen, 1996). In Arctic food webs, the *Calanus* species may be used as TP2 organisms to estimate TP higher in the food web (Hobson and Welch, 1992). The carbon source of a food web can be derived from the ratio between stable isotopes of carbon ($^{13}C/^{12}C$) (DeNiro and Epstein, 1978; Post, 2002; Søreide et al., 2006). Enrichment of ^{13}C in inshore environments reflects a carbon source of terrestrial origin or a stronger coupling to the benthic environment (Hobson, 1999). Mercury accumulation may in some cases be explained by the carbon source of marine food webs (Ricca et al., 2008; Bond and Diamond, 2009).

Little auks (*Alle alle*) and black-legged kittiwakes are key species in Arctic marine ecosystems. The kittiwake is an opportunistic feeder preying on small pelagic fish like polar cod and capelin, as well as pelagic amphipods (*Themisto* spp.) and euphausiids (*Thysanoessa* spp.) (Mehlum and Gabrielsen, 1993). In contrast, little auks are specialist feeders, preying mainly on pelagic zooplankton like copepods, *Themisto* spp., *Thysanoessa* spp. and *Mysis* spp. (Mehlum and Gabrielsen, 1993). Copepods of the *Calanus* genus dominate the diet of little auks in the chick rearing period (Gabrielsen et al., 1991; Steen et al., 2007). Hence, kittiwake and little auk represent different trophic levels in the partial food web of the Arctic pelagic ecosystem.

The aim of the present study was to evaluate the influence of diet, feeding location and sampling year on accumulation of Hg, Cd and Se in Arctic pelagic seabirds. Samples of kittiwakes and little auks were collected in Liefdefjorden and Kongsfjorden at Svalbard. Kongsfjorden is dominated by Atlantic water while Liefdefjorden is dominated by Arctic water (Hallanger et al., 2011a). Furthermore, $\delta^{15}N$ and $\delta^{13}C$ were analyzed in muscle tissue of seabirds and in *Calanus glacialis* to examine the effects of TP and carbon source on element accumulation and biomagnification in the two fjords.

2. Methods

2.1. Field sampling

Kittiwakes and little auks were collected in the vicinity of two breeding colonies at Svalbard, one in Kongsfjorden (78°57′N, 12°12′E) and the other in Liefdefjorden (79°37′N, 13°20′E; Fig. 1). Sampling was carried out during the last two weeks of July 2008 and 2009. Ten free-ranging individuals of each species were collected outside the breeding colony at each location each year using a shotgun with non-toxic ammunition (steel/bismuth). Permission for birds sampling was granted by the Governor of Svalbard. Samples of the left pectoralis muscle and liver tissue were dissected out for stable isotope and element analysis, respectively. Sex and body mass was recorded. *Calanus glacialis* were collected for food web baseline reference in both fjords each year using Method Isaac Kidd (MIK) nets (1000 μm, whole water column). Only *C. glacialis* at developmental stage copepodite V (CV) was used in the assessment of trophic position. All samples were stored in plastic bags at −20 °C before transportation and analysis.

2.2. Element determination

Frozen liver tissue was lyophilized in acid washed polypropylene tubes (2 mL; Nalgene cryotubes, Thermo Scientific, Waltham, MA USA) with the screw cap partially open for a minimum of 24 h prior to digestion (CIT2, Leybold–Heraeus, Köln, Germany). Dry samples (0.15 g) were transferred to PTFE-vials (18 mL; UltraClave, MLS GmbH, Leutkirch, Germany) together with 2.3 g ultrapure water (Q-option, Elga Labwater, Veolia Water Systems LTD, UK) and 4.2 g concentrated nitric acid, HNO_3 (Scanpure, equal to ultrapure grade, Chem Scan, Elverum, Norway). Digestion was carried out using a high-pressure microwave emitter (Milestone Ultra Clave, EMLS, Leutkirch, Germany). The temperature was gradually increased from room temperature up to 250 °C within 1 h and thereafter gradually cooled down to the initial value within the next hour. The digested samples were diluted with ultrapure water in acid washed polypropylene vials (BD Falcon 50 mL conical, BD Biosciences, Bradford, MA, US) to a final volume of 60 mL and a final HNO_3 concentration of 0.6 M.

Total Hg, Cd and Se were determined by high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS, Thermo Finnigan model Element 2, Bremen, Germany). Instrument settings were described in detail by Sørmo et al. (2011). Samples were randomized with respect to sampling location and species. Three blank samples containing ultrapure water and HNO_3 were prepared in the same way as the samples (0.6 M in final solution). To account for potential carryover during digestion, the PTFE-vials