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Nitrogen and sulfur isotopes predict variation in mercury levels in Arctic seabird prey

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ABSTRACT

Mercury (Hg) biotransformation and biomagnification are processes that affect Hg burdens in wildlife. To interpret variation in Hg in seabird eggs, used as Hg bioindicators in the Arctic, it is important to understand how Hg biomagnifies through the food web. We evaluated the use of δ^{34}S, along with other commonly used stable isotope signatures (δ^{15}N and δ^{13}C), for the determination of possible sources of Hg in an Arctic food web (56 individuals of 15 species of fish and invertebrates). Hg correlated with δ^{34}S ($R^2 = 0.72$). When the combined effects of δ^{34}S and δ^{15}N were considered in mixed-effects models, both δ^{34}S and δ^{15}N together described Hg patterns in Arctic food webs better than either isotope alone. Our results demonstrate the usefulness of δ^{34}S to account for variation in Hg among marine animals and to study the possible underlying effects that MeHg production may have on Hg pathways in Arctic ecosystems.

1. Introduction

Human activity directly and indirectly produces multiple sources of pollutants that are affecting and modifying the environment (Persson et al., 2013; Rockström et al., 2009). For example, mercury (Hg) deposition has increased three-fold since preindustrial times (Driscoll et al., 2013; Selin, 2009). Currently, 1900–4000 t are released into the atmosphere every year from human primary sources (Driscoll et al., 2013; Selin, 2009). Hg poses a special threat to polar regions (Fort et al., 2014; Kirk et al., 2012). Hg speciation between its volatile and deposited forms can lead to processes such as global distillation and mercury depletion events during which Hg is transferred from equatorial or temperate regions into polar environments (Ariya et al., 2004; Braune et al., 2015; O'Driscoll et al., 2005; Rigét et al., 2011; Skov et al., 2004). Between 208 and 305 tons of Hg are deposited each year in the Arctic due to these types of processes despite local emissions in the region being low (Ariya et al., 2004; Skov et al., 2004). Mercury is most toxic in its organic form, methylmercury (MeHg), which is also easily assimilated and bioaccumulated by organisms (Dietz et al., 2013; Liu et al., 2008).

Animals, particularly seabirds, can be used to monitor contaminants in ecosystems because they can integrate signals over large foraging areas and return to a central site (colony) where they can be sampled relatively easily (Elliott and Elliott, 2013, 2016; Furness and Camphuysen, 1997). Dietary analyses can be used to determine whether increasing Hg concentrations in animal tissue are due to an increase of available MeHg in the ocean or due to changes in the animal's feeding habits (Elliott and Elliott, 2016; Kidd et al., 1995; McKinney et al., 2010, 2015). Stable isotope ratios have been widely used as indicators of trophic level and feeding location when quantifying Hg in tissues (Atwell et al., 1998; Nisbet et al., 2002; Overman and Parrish, 2001; Vo et al., 2011).

The δ^{15}N ratio (^{15}N to ^{14}N, expressed in relation to an international isotopic reference) is an index of the relative trophic position of an organism as ^{15}N content increases with trophic level (Carr et al., 2017; Hobson et al., 1994). As differences in dietary trophic level can explain significant proportions of Hg variation, especially when temporal trends are being studied, correcting for the δ^{15}N ratio can help to control for this confounding effect (Fig. 1: 'trophic position hypothesis'; Bentzen et al., 2016; Kidd et al., 1995; McKinney et al., 2012; Vo et al., 2011). Another commonly used isotope signature is the ratio of ^{13}C to ^{14}C, δ^{13}C (as expressed relative to an international isotopic reference), which can describe changes in food sources associated with habitat to a greater degree than trophic level. For example, benthic feeding organisms are enriched in ^{13}C compared to pelagic feeders (Carr et al., 2017; Hobson et al., 1994; Nisbet et al., 2002) and terrigenous organic carbon is associated with lower δ^{13}C values compared to marine carbon (Foster et al., 2012; Schell et al., 1998). Differential feeding from

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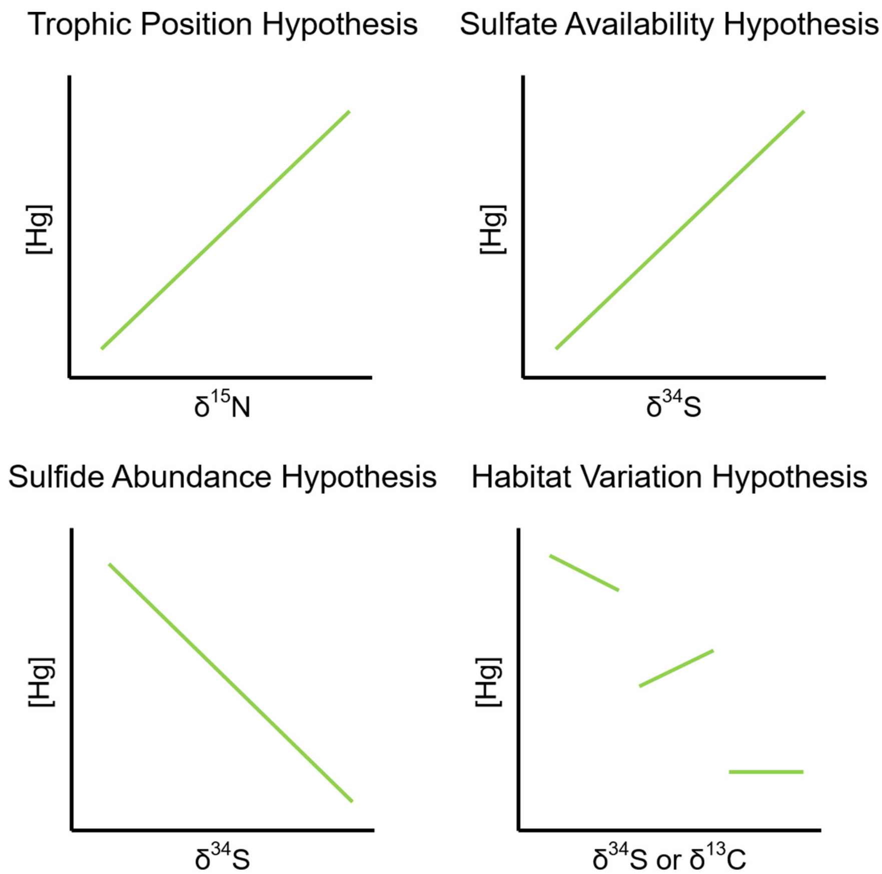

Fig. 1. Hypotheses for relationship between Hg and isotopes tested within this paper: trophic position hypothesis, sulfate availability hypothesis, sulfide abundance hypothesis, and habitat variation hypothesis.

diverse habitats may cause variation in the Hg concentrations uptaken (Fig. 1: 'habitat variation hypothesis'). Specifically, if Hg levels are higher in one habitat (i.e. benthos) than another habitat (i.e. pelagic waters), due to long range transport or other mechanisms, then an association between Hg and isotopic values might be expected. For example, fish that were originally river residents had higher Hg than other fish caught in the same rivers and that migrated from a lake; $\delta^{13}C$ and $\delta^{34}S$ (see below) could distinguish between the river residents and the lake migrants (Carr et al., 2017). These commonly used ratios can help to elucidate observed differences in Hg concentrations that are the result of the animal's feeding habits but fail to account for an important aspect of the mercury cycle that is independent of top predator's life history, the production of MeHg.

Sulfate-reducing bacteria (and iron-reducing or methanogenic bacteria, to a lesser extent) are the main drivers of the conversion of inorganic Hg into MeHg in many environments (Driscoll et al., 2013; Morel et al., 1998; Selin, 2009). These bacteria, which inhabit anoxic aquatic environments, use sulfate as the final electron acceptor for respiration and can methylate Hg during the process, presumably by the involvement of the acetyl-coenzyme A pathway (Parks et al., 2013; Pollman and Axelrad, 2014; Selin, 2009). The central role played by the sulfate-reducing bacteria suggests that the production of MeHg is not limited by the initial concentration of inorganic Hg but rather by sulfate concentrations and, thus, sulfate reduction rates. The addition of an inhibitor of sulfate reduction to anoxic sediments led to an almost complete reduction of MeHg production (Compeau and Bartha, 1985). Similarly, no methylation occurred in cultures of sulfate-reducing bacteria where no sulfate was added (King et al., 2000). Increased concentration of available sulfate in sediments and lakes led to an increase in MeHg production (Gilmour et al., 1992). As these bacteria respire, sulfur in the water column is converted from sulfate to sulfide causing the remaining sulfate to become enriched in the heavier sulfur isotope, ^{34}S (Krouse and Mayer, 2000; Peterson and Fry, 1987). This makes the ^{34}S to ^{32}S ratio as expressed relative to an international isotopic reference, $\delta^{34}S$, useful for the detection of sulfate reduction and, thus, mercury methylation via sulfate-reducing bacteria, so that variation in environmental MeHg levels can be accounted for (Fig. 1: 'sulfate availability hypothesis'; Elliott and Elliott, 2016). Conversely, if sulfate-reducing bacteria are limited by factors other than sulfate, we may expect a negative relationship between $\delta^{34}S$ and Hg (Carr et al., 2017; Fry and Chumchal, 2012). High levels of sulfide associated with low $\delta^{34}S$ values could be indicative of the active presence of sulfate-reducing bacteria (which, if limited by factors other than sulfate abundance, would convert most sulfate into sulfide) leading to higher methylation rates and thus, higher Hg bioaccumulation potential (Fig. 1: 'sulfide abundance hypothesis').

Thick-billed murres (*Uria lomvia*) are a key monitoring species for mercury in the Canadian Arctic (Braune, 2007; Braune et al., 2016). A recent study showed that variation in Hg among both thick-billed murres and their prey was associated with variation in $\delta^{15}N$ (Braune et al., 2014a, 2014b). A dietary shift towards prey lower in $\delta^{15}N$ masked an increase in Hg across time, and accounting for variation in $\delta^{15}N$ improved assessment of Hg trends over time (Braune et al., 2014b). Our study aims to compare the usefulness of $\delta^{34}S$, along with $\delta^{15}N$ and $\delta^{13}C$, for the determination of Hg bioaccumulation sources in Arctic food webs. To this end, we sampled individuals from 15 species of fish and invertebrates that are common prey of thick-billed murres breeding at Coats Island in northern Hudson Bay. We predicted that Hg levels would be associated with both sulfate availability ($\delta^{34}S$) and trophic position ($\delta^{15}N$).