

## RESEARCH/REVIEW ARTICLE

# Some like it cold: microbial transformations of mercury in polar regions

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Microbiology; mercury biogeochemistry; redox transformations; polar regions; methylation.

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**Abstract**

The contamination of polar regions with mercury that is transported from lower latitudes as inorganic mercury has resulted in the accumulation of methylmercury (MeHg) in food chains, risking the health of humans and wildlife. While production of MeHg has been documented in polar marine and terrestrial environments, little is known about the responsible transformations and transport pathways and the processes that control them. We posit that as in temperate environments, microbial transformations play a key role in mercury geochemical cycling in polar regions by: (1) methylating mercury by one of four proposed pathways, some not previously described; (2) degrading MeHg by activities of mercury resistant and other bacteria; and (3) carrying out redox transformations that control the supply of the mercuric ion, the substrate of methylation reactions. Recent analyses have identified a high potential for mercury-resistant microbes that express the enzyme mercuric reductase to affect the production of gaseous elemental mercury when and where daylight is limited. The integration of microbially mediated processes in the paradigms that describe mercury geochemical cycling is therefore of high priority especially in light of concerns regarding the effect of global warming and permafrost thawing on input of MeHg to polar regions.

Over the last few decades, concerns for the vulnerability of polar regions to organic and inorganic contaminants that originate in lower latitudes have increased. Mercury (Hg) is among the most serious of these contaminants due to its accumulation in polar food chains and the resulting health risks to both humans and wildlife (Macdonald et al. 2005; Dietz et al. 2009). Following natural and anthropogenic emissions, Hg is transported over long distances and globally distributed in its elemental form, Hg(0), which is also referred to as gaseous elemental Hg or GEM (Steffen et al. 2007; Pirrone et al. 2010). It is oxidized in the atmosphere and deposited via dry (aerosols) or wet (rain and snow) deposition to terrestrial and aquatic ecosystems. Asia is the dominant

source of GEM to the Arctic (Durnford et al. 2010), rendering this region particularly vulnerable as emissions from Asia are expected to increase in coming decades (Streets et al. 2009). The Antarctic is contaminated from sources in Africa, Australia, and South America (Dommergue et al. 2010). Mercury deposition to polar regions is enhanced by springtime atmospheric Hg depletion events (MDE) in the High Arctic (Schroeder et al. 1998; Lindberg et al. 2002), sub-Arctic (Dommergue et al. 2003), and Antarctic (Ebinghaus et al. 2002) regions, resulting in rapid and massive deposition of ionic Hg, Hg(II), from the atmosphere (Brooks et al. 2006; Skov et al. 2006). This springtime deposition is thought to be due to the oxidation of GEM by halogen

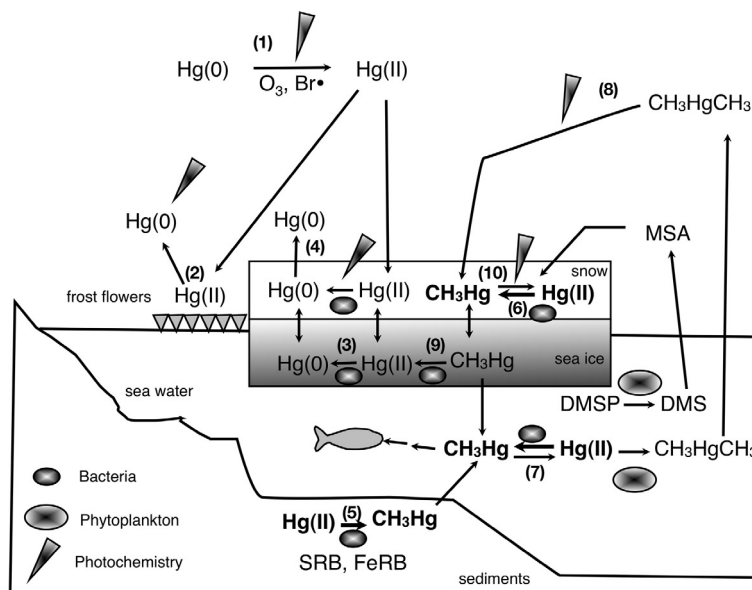
radicals and oxidized forms of halogens formed in sea salt aerosols by photochemical transformations (Lindberg et al. 2002; Brooks et al. 2006; Ariya et al. 2008).

How atmospherically deposited Hg(II) is converted to the potent neurotoxic compound methylmercury (MeHg) is the topic of this review. Our concerns in relation to MeHg production and its availability to polar food chains (Wren 1986) are due to human consumption of contaminated seals and whales (Macdonald et al. 2005) and to possible neurological damage in apex predators such as polar bears (Basu et al. 2009). In humans, MeHg manifests its toxicity in a variety of symptoms ranging from mild numbness of the extremities, blindness, impaired development of language, attention and memory skills (Krummel et al. 2005), and in severe cases, death (Clarkson 2002; Mergler et al. 2007).

Recent research has shown that Hg found in the highest trophic levels of Arctic food chains is almost exclusively present in the methylated form (Campbell et al. 2005; Loseto et al. 2008) and that blood and fatty tissues of native human populations have elevated levels of Hg (Van Oostdam et al. 2005; Butler Walker et al. 2006; Johansen et al. 2007; Donaldson et al. 2010). Thus, the impact of Hg contamination in the Arctic is

similar to that described in temperate zones of the world, raising the critical question of how Hg(II), entering polar regions through atmospheric deposition, becomes available for accumulation as MeHg in food webs. The answers to this question are found in the dynamics of the polar Hg biogeochemical cycle (Fig. 1), i.e., within-ecosystem transformations play a critical role in the toxicity and distribution of Hg. Post-depositional Hg processes must therefore be understood before we can link Hg deposition to Hg burdens in polar biota (Macdonald & Loseto 2010).

In temperate zones, microbial activities critically impact MeHg accumulation by carrying out biochemical transformations. Recent reviews on Hg cycling in the environment (Fitzgerald et al. 2007; Poissant et al. 2008; Selin 2009) and on the role of microbes (Barkay et al. 2003; Barkay et al. 2005) are available. Microbes are broadly distributed in polar environments, including air (Polunin & Kelly 1952), snow (Larose, Berger et al. 2010), coastal lagoons (Poulain, Ni Chadhain et al. 2007), soil (Connell et al. 2008), sea ice (Collins et al. 2010; Koh et al. 2010), marine sediments (Yergeau et al. 2009) and the water column (Galand et al. 2009). Bacteria and bacteriophages have also been documented in frost



**Fig. 1** The biogeochemical cycle of mercury in coastal marine environments in polar regions. Major reaction and transport pathways, provided as numbers in parentheses in the figure, are: (1) atmospheric oxidation of Hg(0) to Hg(II); (2) photoreduction of newly deposited Hg(II) to Hg(0); (3) biological reduction of Hg(II) to Hg(0); (4) evasion of Hg(0) to the atmosphere; (5) methylation of Hg(II) to CH<sub>3</sub>Hg by sulfate-reducing bacteria (SRB) and iron-reducing bacteria (FeRB); (6) methylation of Hg(II) to CH<sub>3</sub>Hg by aerobic pathway and/or by photomethylation in snow; (7) methylation of Hg(II) to CH<sub>3</sub>Hg by algae and phytoplankton in the water column; (8) photochemical degradation of diMeHg in the atmosphere; (9) biological demethylation of CH<sub>3</sub>Hg to Hg(II); and (10) photochemical demethylation of CH<sub>3</sub>Hg in snow. Methylation pathways are highlighted by bold lettering. Note that these reactions and pathways may take place in various compartments of polar regions; for the sake of simplicity they are only marked in a representative compartment in the figure (see text for details). Dimethylsulfoniopropionate is abbreviated to DMSP, dimethylsulfide to DMS and methylsulfonic acid to MSA.

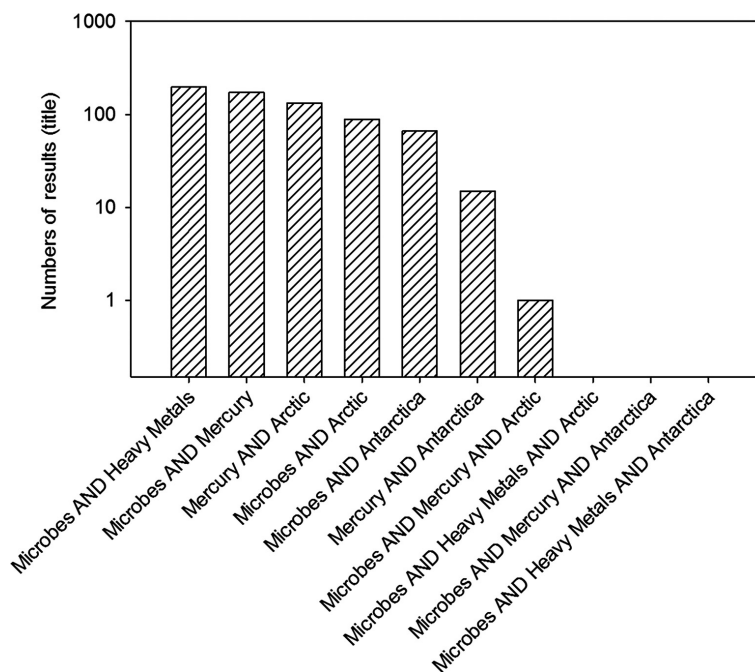
flowers (Bowman & Deming 2010), where Hg concentrations (as high as  $5 \text{ nmol L}^{-1}$  or  $1 \text{ } \mu\text{g L}^{-1}$ ) are more than 10 times higher than in MDE snow (Douglas et al. 2005; Douglas et al. 2008) and almost a 1000-fold higher than in Arctic inland locations (St. Louis et al. 2005). Because microbial activities have been documented in samples collected in both the Arctic (Kirchman et al. 2007; Yergeau et al. 2009) and the Antarctic (Manganelli et al. 2009), albeit at rates lower than those in temperate regions, research on microbial activities in polar regions should be an important component of efforts directed towards the understanding of how Hg biogeochemistry is related to MeHg accumulation. This need is highlighted by the paucity of published peer-reviewed publications on the interactions of microorganisms with Hg in polar regions. While the numbers of papers describing Hg or microbes in polar regions are in the hundreds, search engines have only picked up a single publication when the terms “microbes” OR “bacteria” OR “archaea” AND “mercury” AND “arctic” were used, and none when “antarctic” was replaced with “arctic” (Fig. 2).

Here we update our 2007 review paper and consider the most recent information on Hg in cold environments together with relevant information from research on Hg and microbiology in temperate environments. We synthesize these sources of information to propose

junctures where microbes critically affect the geochemical cycle of Hg in polar regions (Fig. 1) and identify research questions that address gaps in our understanding of how microbes modulate the toxicity and mobility of Hg in the Arctic and Antarctic regions (Table 1).

### Microbial transformations of mercury in polar environments

Our current view of the role of microorganisms in the cycling of Hg in the environment is based on studies that were initiated by the discovery of the toxicity of MeHg to consumers of contaminated fish and shellfish in the 1960s (Westö 1966). Results from environmental, geochemical, microbiological, biochemical, and molecular studies have converged to establish our current view of the Hg biogeochemical cycle (Barkay et al. 2005; Fitzgerald et al. 2007; Selin 2009). Within that paradigm, microbes impact the production of MeHg directly by methylation and demethylation processes, and indirectly by controlling the supply of Hg(II), the substrate for methylation, by carrying out redox transformations that affect transitions between Hg(II), and Hg(0). These transformations and how they are likely to be impacted by the unique conditions of cold environments are discussed below.



**Fig. 2** The number of papers retrieved on 11 October 2010 from the ISI Web of Knowledge database, using the keywords indicated. The search was performed using Boolean operators to avoid references to unrelated topics. The descriptor “microbes” is used for clarity and is based on a search that was performed using the query Microbes OR Bacteria OR Archaea AND all other terms as indicated in the figure.

**Table 1** A summary of the uniqueness of microbial transformations and research questions whose answers would enhance our understanding of Hg biogeochemistry in polar regions.

Microbial transformation	What is unique about this transformation in polar regions	Questions/research needs
Methylation	<ul style="list-style-type: none"> <li>● Presence of diMeHg in coastal water (Pongratz &amp; Heumann 1999; Kirk et al. 2008)</li> <li>● Snow as a matrix for Hg transformations and MeHg transport (Constant et al. 2007).</li> <li>● Marine sources for MeHg deposition in coastal regions (St. Louis et al. 2005; Larose, Dommergue et al. 2010)</li> </ul>	<ul style="list-style-type: none"> <li>● What are the pathways for methylation and what fraction of the deposited Hg is being methylated?</li> <li>● What are the pathways for aerobic Hg methylation?</li> <li>● Who methylates Hg in polar regions?</li> <li>● What is the effect of permafrost thawing on methylation rate and subsequent input of MeHg to polar regions?</li> </ul>
Demethylation	<ul style="list-style-type: none"> <li>● Oxidation of C1 compounds is slow in high latitudes (Hines &amp; Duddleston 2001)</li> <li>● <i>mer</i> gene expression in Arctic biomass (Poulain, Ni Chadhain et al. 2007)</li> <li>● Photoreduction of MeHg in epilimnetic lake water (Hammerschmidt &amp; Fitzgerald 2006)</li> </ul>	<ul style="list-style-type: none"> <li>● What are the pathways for the degradation of MeHg in polar regions?</li> </ul>
Hg(II) reduction	<ul style="list-style-type: none"> <li>● Accumulation of dissolved gaseous Hg under sea ice (Andersson et al. 2008)</li> <li>● Hg-resistant bacteria are common in snowpacks (Møller et al. 2011)</li> <li>● High bioavailability of Hg(II) in freshly deposited snow (Lindberg et al. 2002), Barkay &amp; Kroer (unpubl. data)</li> <li>● Interactions of microbes with Hg in structured environments</li> <li>● <i>mer</i> gene expression in Arctic biomass (Poulain, Ni Chadhain et al. 2007) and its impact on Hg(II) reduction</li> </ul>	<ul style="list-style-type: none"> <li>● Development of psychrophilic Hg biosensors</li> <li>● The interactions of microbes in sea ice with Hg; role of exopolysaccharide production</li> <li>● Measurement of Hg concentrations in the complex sea-ice matrix</li> <li>● Further assess the evolution of Hg resistance in polar areas</li> </ul>
Hg(0) oxidation	<ul style="list-style-type: none"> <li>● High chloride concentrations in coastal marine environments induce abiotic oxidation of Hg(0)</li> </ul>	<ul style="list-style-type: none"> <li>● A better understanding of Hg(0) oxidation in Hg biogeochemistry</li> </ul>

## Hg(II) methylation

Anaerobic microbes have been known for over 40 years to methylate Hg (Jensen & Jernelöv 1969) and for the last 25 years this activity has been attributed to sulfate-reducing bacteria (SRB) in anoxic environments (Compeau & Bartha 1985; Gilmour et al. 1992; King et al. 2000). The mechanism of methylation may (Choi et al. 1994) or may not (Ekstrom et al. 2003) be related to the production of acetyl coenzyme A and methylcobalamine (Ekstrom & Morel 2008). More recently, methylation by some iron-reducing bacteria (FeRB) has been suggested (Fleming et al. 2006; Kerin et al. 2006), although when tested under environmentally relevant conditions, only SRB produced significant amounts of MeHg (Ranchou-Peyruse et al. 2009). Methylation of Hg(II) by abiotic processes (Weber 1993; Siciliano et al. 2005) may be indirectly related to biological

activities because of its dependence on biological products such as dissolved organic matter.

Formation of MeHg in the Arctic has been documented in wetland soils (Loseto, Siciliano et al. 2004; Oiffer & Siciliano 2009) and streams (Loseto, Lean et al. 2004), in snow (Constant et al. 2007), in freshwater ponds (St. Louis et al. 2005), in the marine water column (Kirk et al. 2008), and in lakes and tundra watersheds (Hammerschmidt et al. 2006). Based on several considerations we suggest that at least four different methylation pathways contribute to MeHg formation and accumulation in polar regions. These considerations include: (1) the distribution of MeHg and microbial communities in various compartments of the cryosphere; (2) the unique physical properties of polar environments; (3) advances in elucidating the microbial cold way of life using genomic approaches (Methe et al. 2005); and

(4) knowledge of the biochemistry and physiology of microbial transmethylation reactions. With the exception of methylation by SRB and FeRB, evidence for the proposed pathways is lacking. They are highlighted here because their occurrence in polar environments is plausible when available data from polar regions are synthesized with our current understanding of the chemistry and biochemistry of Hg methylation.

### Methylation by SRB and FeRB

The large component of coastal shelves in the Arctic Ocean (Macdonald & Loseto 2010) and the high summer productivity of coastal lagoons (Galand et al. 2008) highlight the likely importance of methylation by SRB and FeRB in anoxic sediments as a possible source of MeHg (pathway 5 in Fig. 1). However, Loseto, Siciliano et al. (2004), who detected low abundance of SRB and failed to detect *Deltaproteobacteria* and genes encoding for the disulfite reductase enzyme in soil DNA extracts, concluded that methylation was not mediated by SRB. This conclusion may have been premature because if methylating SRB are a minor component in the soil community, the sensitivity of the molecular methods may have not been sufficient to detect them. For example, we were recently able to attribute methylation in an Adirondack wetland to SRB only when experiments with metabolic enhancers and inhibitors and highly sensitive molecular methods were employed (Yu et al. 2010). Therefore, the involvement of SRB in methylation in polar regions, especially in anoxic sediments of coastal environments, where sulfate reduction is likely the dominant respiratory pathway, remains to be examined. This involvement is supported by observations that SRB are abundant in Arctic coastal marine sediments such as in Svalbard, Norway (Ravenschlag et al. 2001), and in Antarctic sediments (Purdy et al. 2003) and that psychrophilic SRB isolated from the same sediments actively reduced sulfate at in situ temperatures (Knoblauch et al. 1999; Bruchert et al. 2001). To the best of our knowledge, the role of FeRB in methylation in polar regions has not been explored though iron, like sulfate, reduction readily occurs in cold environments (Finke et al. 2007).

### Methylation in the marine water column

The production of mono- and dimethylmercury (diMeHg) in the Arctic marine environment (pathway 7 in Fig. 1), recently documented by Kirk et al. (2008) in mid- to bottom depth in the Canadian Arctic Archipelago and

in the Hudson Strait and Hudson Bay, is likely a part of the larger story of MeHg production in the marine water column thought to be associated with the remineralization of particulate organic carbon in oxygen minima zones (Monperrus et al. 2007; Cossa et al. 2009; Sunderland et al. 2009). Which organisms are involved in marine water column methylation is currently not known, but these may not be anaerobic microbes as suggested by the failure to detect such microbes at depth where MeHg accumulated (Malcolm et al. 2010). Methylation by phytoplankton and/or their exudates is a possibility as previously reported in a coastal Antarctic water column (Pongratz & Heumann 1999). A possible mechanism for the phytoplankton-associated methylation was very recently proposed by Larose and co-workers (Larose, Dommergue et al. 2010) implicating transmethylation reactions that are involved in the degradation of the phytoplankton osmolyte dimethylsulfoniopropionate (DMSP) (Bentley & Chasteen 2004). Together, these studies challenge the current paradigm that only anaerobic conditions support significant MeHg build up (or net rates of methylation) and underscores the need for more discovery based fundamental research examining mechanistic aspects of Hg methylation.

### Snowpacks: in-snow methylation vs. transport from marine sources

One unique aspect of MeHg accumulation in coastal Arctic environments is a high concentration of MeHg in meltwater at the initiation of snowmelt (Loseto, Lean et al. 2004; St. Louis et al. 2005) suggesting accumulation of MeHg in snowpacks where anaerobic environments are uncommon (pathway 6 in Fig. 1). Positive correlations between MeHg and chloride or methanesulfonates, a product of DMSP degradation (Bentley & Chasteen 2004), and total Hg and chloride (St. Louis et al. 2007) in snowpacks suggest a marine source for Hg. We can speculate that MeHg and diMeHg produced in the marine water column (Kirk et al. 2008; Cossa et al. 2009) may evade from productive leads and polynyas followed by deposition onto sea-ice and terrestrial systems (St. Louis et al. 2005). The photodegradation of the highly volatile diMeHg to MeHg in the atmosphere (Niki et al. 1983) could be a part of this process.

In-snow methylation of bioavailable Hg(II), however, cannot be ruled out. For example, methylation in tundra snowpacks was suggested by correlations between the proportion of total Hg as MeHg and heterotrophic bacterial counts and concentrations of suspended solids (Constant et al. 2007; Kirk et al. 2008). Experiments

using bioreporters (Selifonova et al. 1993; Golding et al. 2002) suggested that a significant proportion of Hg(II) deposited during MDE in Barrow, Alaska, was bioavailable (Scott 2001; Lindberg et al. 2002). Similarly, five out of 12 surface/top layer snow samples collected during or following a snowstorm at Station Nord, north-east Greenland, in spring 2010, had significant amounts of bioavailable Hg (Barkay & Kroer unpubl. data). Moreover, organic compounds, such as dicarboxylic acids, are present in Arctic snow (Kawamura et al. 1996) and may serve as a carbon and energy source for microorganisms (Amato et al. 2007) that may be involved in methylation processes. Our direct bacterial counts showed  $2 \times 10^5$  cells per ml of melted snow from the Canadian High Arctic and  $1 \times 10^3$  cells per ml of melted snow from north-east Greenland (Møller et al. 2011) while melted snow from Antarctica's dry valleys had 200–5000 cells per ml (Alfreider et al. 1996; Carpenter et al. 2000; Segawa et al. 2005). Amato et al. (2007) reported  $2 \times 10^4$  and  $6 \times 10^4$  cells per ml in snow accumulated over a glacier on Spitsbergen, Svalbard, and in a seasonal snowpack bordering the Arctic Ocean, respectively. Microbes in snow may be metabolically active, as indicated by the reduction of 2-(*p*-iodophenyl)-3-(*p*-nitrophenyl)-5-phenyltetrazolium chloride, a respiratory indicator (Alfreider et al. 1996) and by low, but detectable, levels of protein and nucleic acid synthesis at in situ temperatures (Carpenter et al. 2000). This suggests the possibility that microbes in snow may methylate Hg. This proposition, like methylation in the oxygenated marine column (see above), implies methylation by aerobic microorganisms. Many aerobic microorganisms may methylate Hg, e.g., bacteria belonging to the *Pseudomonas*, *Enterobacter*, *Bacillus*, and *Staphylococci* genera and fungi such as *Aspergillus niger*, *Scopulariopsis brevicattlis* and *Saccharomyces cerevisiae* (Vonk & Sijpesteijn 1973), and the activity of these microbes may be environmentally relevant but remains to be demonstrated.

### Photomethylation

It has long been known that MeHg may be formed in solutions containing various organic molecules in response to light (Hayashi et al. 1977) and more recently Siciliano et al. (2005) showed that photomethylation in northern temperate ecosystems depended on the presence and size of dissolved organic matter. This process may affect MeHg formation in snow (pathway 6 in Fig. 1) and other cold environments where biological processes produce dissolved organic matter (Calace et al. 2005).

As has been the case with studies of methylation in temperate regions, direct experimentation using pure cultures of active microbes (Choi et al. 1994), laboratory incubations (Yu et al. 2010), and testing in intact and/or manipulated environmental incubations (Hammerschmidt et al. 2006; Monperrus et al. 2007) are needed to distinguish the relative importance of the four proposed methylation pathways to the accumulation of MeHg in polar regions. This research will benefit greatly from the availability of the sequenced genomes of psychrophilic microbes (Methe et al. 2005) and the metagenomes of microbial communities from cold environments (Larose, Berger et al. 2010). We hypothesize that methylation by anaerobic bacteria is prominent considering the large magnitude of coastal shelves and inputs from river discharge to the high Arctic (Macdonald & Loseto 2010). Yet, considering that both poles, the Arctic in particular, are highly influenced by processes in the marine environment, methylation in water column, and by aerobic microbes, may be a significant contributor to the MeHg pool in polar regions.

### Methylmercury degradation

Because they consume MeHg, demethylation reactions impact net methylation rates and thus the net production of this neurotoxic substance. Three demethylation processes—photodegradation (Sellers et al. 1996) and two microbially mediated processes (Schaefer et al. 2004; Barkay et al. 2005)—are known. Photodegradation, a process mediated by ultraviolet radiation (Lehnherr & St. Louis 2009) and enhanced by the presence of organic ligands (Zhang & Hsu-Kim 2010), is the dominant mechanism for demethylation in surface water. It has been invoked as the sole process responsible for the degradation of MeHg in the epilimnetic water of a highly oligotrophic freshwater Arctic lake (Hammerschmidt & Fitzgerald 2006). To the best of our knowledge, MeHg degradation has not been examined in the euphotic zone of sediments or samples from coastal marine environments in polar regions.

Microbial pathways for the degradation of MeHg are distinguished by the redox state of the gaseous carbon products of demethylation. In reductive demethylation, methane is produced and in the oxidative process the product is both carbon dioxide and methane. We (Schaefer et al. 2004) and others (Marvin-Dipasquale et al. 2000; Gray et al. 2004) have shown that the choice between these processes is to a large extent controlled by environmental factors. Reductive demethylation is mediated by the organomercury lyase enzyme, which is a part of the Hg resistance (*mer*) system in

bacteria (see below). This process is favoured at a high redox potential and high concentrations of Hg since expression of *mer* operon genes is induced by inorganic divalent Hg (Schaefer et al. 2004; Barkay et al. 2010). Oxidative demethylation is favored at low redox potentials and at a broad range of Hg concentrations and is most likely related to C1-pathways in anaerobic prokaryotes (Marvin-Dipasquale & Oremland 1998). The occurrence and rates of C1 metabolism in microbes from cold environments have been getting a lot of attention due to anticipated effects of global warming on the release of carbon from large frozen reservoirs in permafrost and polar tundra. While methanogenesis (Rivkina et al. 2004; Berestovskaya et al. 2005) and methanotrophy (Berestovskaya et al. 2005) were detected in permafrost, rates were drastically impacted by a drop in the incubation temperature. Moreover, degradation of C1 compounds such as methylbromide or acetate, common in temperate soils (Hines et al. 1998), is rarely observed at high latitudes proximal to polar areas (Hines & Duddleston 2001). Based on these observations the likelihood for oxidative MeHg degradation in polar regions is currently low but may increase should the carbon cycle be altered by warmer conditions. Nevertheless, demethylation plays an important role in determining MeHg production and availability to food chains and its occurrence and mechanisms in cold environments need to be addressed.

### Redox transformations of inorganic Hg

Redox transformations between the ionic and elemental Hg forms affect MeHg production by controlling the amount of the substrate that is available for methylation (Fitzgerald et al. 1991). Among the reduction processes, photoreduction dominates in surface water (Krabbenhoft et al. 1998; Amyot et al. 2004; O'Driscoll et al. 2004; Poulain, Amyot et al. 2004; Garcia, Amyot et al. 2005; Zhang et al. 2006) and snow (Lalonde et al. 2002; Lalonde et al. 2003) and is thought to result in the evasion of most of the Hg that is deposited onto snow (Lindberg et al. 2002; Dommergue et al. 2003) or condensed into frost flowers (Douglas et al. 2008). The impact of photoreduction on Hg that is deposited during springtime MDE was recently confirmed by showing a large negative mass-independent fractionation of Hg isotopes (Sherman et al. 2010) thought to be exclusively induced by light mediated reactions (Bergquist & Blum 2007; Kritee et al. 2009).

There are several microbial Hg reduction processes and chief among them is mediated by the inducible Hg resistance (*mer*) operon in Hg-resistant bacteria,

which impacts the partition of Hg into the gaseous phase in some environments (Barkay 1987; Barkay et al. 2005). The enzyme mercuric reductase, MerA, encoded by the *merA* gene, is the core function of the *mer* operon, which also encodes for Hg transport and for an elaborate system that regulates expression of the operon. Some operons also encode for the organomercury lyase and microbes carrying such *mer* operons reductively degrade MeHg (see above). The *mer* operon is broadly distributed among Bacteria (Barkay et al. 2010) and Archaea (Simbahan et al. 2005) from diverse environments (Osborn et al. 1997; Barkay et al. 2010). The presence of Hg resistant bacteria in samples from polar environments (Møller et al. 2011) and the demonstration of *merA* gene expression in samples from the High Arctic (Poulain, Ni Chadhain et al. 2007) suggest that Hg resistant microbes may be endemic and active in cold regions, a conclusion that is also supported by the presence of *mer* gene homologs in the genomes of several psychrophilic bacteria from polar environments (Barkay et al. 2010). Resistant bacteria accounted for 0–31% of the total number of the cultured bacteria in High Arctic snow and for approximately 2% in sea-ice brine and freshwater (Møller et al. 2011) and for up to 3% in permafrost sediments (Petrova et al. 2002; Mindlin et al. 2005), and for 1–68% in Antarctic seawater (De Souza et al. 2006; Miller et al. 2009).

The regulator of *mer* expression, MerR, plays a critical role in determining where and under which conditions Hg(II) reduction by MerA occurs. Expression of the *mer*-operon is repressed in the absence of Hg and is quantitatively induced in its presence (Summers 1992; Brown et al. 2003). Because of this requirement for induction, MerA-mediated reduction has been considered of little relevance to transformations of Hg in natural environments (Morel et al. 1998). Indeed, a series of studies, performed in several environments that were impacted by various sources of Hg, showed mRNA transcripts of the *merA* gene in highly contaminated environments, whereas microbial biomass from environments with low levels of contamination contained low to non-detectable levels of these transcripts (Nazaret et al. 1994; Hines et al. 2000; Poulain, Amyot et al. 2004; Schaefer et al. 2004). Based on these observations one would not expect *merA* expression and reduction of Hg(II) by polar microbial communities where Hg concentrations are in the pM range during most times of the year (Steffen et al. 2002; St. Louis et al. 2005). We were, therefore, surprised when *merA* transcripts were detected in microbial biomass associated with algae that were collected in a coastal lagoon and a sea-ice lead in the Canadian High Arctic in the

summer of 2005 where total Hg concentrations were ca. 10 pM (Poulain, Ni Chadhain et al. 2007). Numerous reasons may account for this apparent discrepancy. The absolute Hg concentrations required for *mer* induction depend on the complicated issue of bioavailability and how it is impacted by interactions with ligands in the environment (Barkay et al. 1997; Crespo-Medina et al. 2009). In environments with low concentrations of ligands, induction may take place at very low Hg concentrations. For example, induction of the *mer-lux* bioreporter in laboratory incubations was documented at sub-pM Hg concentrations when “clean conditions” were employed (Kelly et al. 2003). The slow rates of transcript degradation in cold environments (Vlassov et al. 2005), might furthermore explain the detection of *merA* transcripts in polar microbiota.

Alternatively, the highly heterogeneous nature of microbial habitats in polar regions may lead to locally high concentrations of Hg in micro-niches where *mer* induction may take place. The effect of heterogeneous micro-environments on the distribution of Hg and on selection of resistant bacteria was recently demonstrated (Slater et al. 2008); selection extended to a distance of <500  $\mu\text{m}$  from Hg foci created by the impregnation of fiber with Hg chloride (Slater et al. 2010). Sea ice, the habitat for most of the microbial biomass in coastal polar environments, may contain niches where both Hg and microorganisms are concentrated. It is likely that Hg, like other solutes in sea ice (Eicken 2003), is highly concentrated in brine channels where actively metabolizing microorganisms were documented (Deming 2002; Junge et al. 2004). Our hypothesis on the localized proximity of microbes to Hg in brine channels is also supported by the observations that microbes in brine channels during winter are associated with particles (Junge et al. 2004), that a significant fraction of atmospherically derived Hg is bound to particles (Schroeder & Munthe 1998), and that Hg in snow—especially in marine environments—is almost exclusively associated with particles (Poulain, Garcia et al. 2007). However, the discovery of copious production of exopolysaccharides by microbes in sea ice (Krembs & Deming 2008), proposed as a cryoprotection mechanism (Marx et al. 2009), may suggest an alternative mechanism for Hg tolerance whereby Hg is sequestered extracellularly as has been shown for other metals in other environments (Teitzel & Parsek 2003). The possibility that resistance to Hg among sea-ice bacteria in brine channels is not mediated by *mer* systems is supported by a low number of Hg resistant culturable bacterial counts in brine samples extracted

from sea ice at Station Nord in north-east Greenland (Møller et al. 2011).

Bioreduction of Hg, unrelated to the *mer* system, may be associated with the activity of microorganisms in fresh and salt waters via pathways still to be determined. These could be related to both heterotrophic and/or phototrophic activities (Ben-Bassat & Mayer 1978; Mason et al. 1995; Poulain, Amyot et al. 2004; Rolfhus & Fitzgerald 2004; Wiatrowski et al. 2006; Wiatrowski et al. 2009).

How significant is microbial reduction of Hg(II) in Hg geochemistry in polar regions? Numbers of *merA* transcripts in Arctic microbial biomass (Poulain, Ni Chadhain et al. 2007) and numbers of Hg resistant bacteria in snowpacks (Møller et al. 2011) were used to answer this question. Using Acuchem modeling software (Braun et al. 1988) and a custom-designed kinetic code, Poulain, Ni Chadhain et al. (2007) showed that at equilibrium and when 5% of bacterial cells were considered active 65% of the elemental Hg (Hg[0]) was biogenic at the surface of the Arctic ocean while at a depth of 10 m with diminishing UVA and UVB radiation this fraction increased to 94%. Likewise, an almost 20-fold increase in the potential reduction rate was predicted in snowpacks at Station Nord with sampling depth increasing from about 83 to 105 cm. Comparison with reduction rates measured in snow from the Canadian High Arctic (Dommergue et al. 2003) suggested that an average of up to 2% of the total reduction could be biological and that bacterial reduction became increasingly important with snow depth (Møller et al. 2011). There is therefore a potential for microbial reduction to affect Hg mobility in the Arctic, especially at depth and under sea ice where light and the flux of dissolved gaseous Hg (DGM) to the atmosphere are limited. This conclusion is consistent with observations of enhanced DGM concentrations recorded underneath sea ice (Andersson et al. 2008). Our results and analyses suggest that most of the DGM pool in the Arctic Ocean could be of a microbial origin. Further studies should expand these preliminary findings.

The microbial oxidation of Hg(0) to Hg(II) is the part of the Hg biogeochemical cycle about which we know the least. To date, most research efforts have examined abiotic mechanisms of light and dark oxidation (Lalonde et al. 2001; Lalonde et al. 2004; Poulain, Lalonde et al. 2004; Raofie & Ariya 2004; Sheu & Mason 2004; Garcia, Poulain et al. 2005; Whalin & Mason 2006). Bacterial enzymes known for their role in the response to oxidative damage, such as catalases and hydroperoxidases, oxidize Hg(0) in organisms that are common in natural waters and soils (Smith et al. 1998). Further-



more, Siciliano et al. (2002) related specific rates of Hg(0) oxidation by lake microbial biomass to variations in DGM concentrations. How these microbially-mediated oxidative processes affect Hg speciation in polar regions, and especially their impact on the fate of DGM, has not been examined.

### Conclusions and future needs

The study of Hg (micro)biogeochemistry in polar environments is at its early stages, but the synthesis of information available from temperate regions together with what we know about the distribution of Hg in polar regions and about microbiology in cold environments points to the uniqueness of Hg cycling in polar regions (Table 1). As in temperate environments, MeHg is accumulated by aquatic food chains but the methylation pathways themselves and the sites where methylation occurs may differ from those in lower latitudes. A particularity of polar ecosystems is the enhanced vulnerability of marine and coastal environments to Hg accumulation due to enhanced deposition during springtime.

Global warming poses a major challenge to the management of Hg contamination in polar regions. Increased temperatures are likely to directly affect Hg biogeochemistry by enhancing the rates of microbial transformations and yearly productivity as polar summers are lengthened. In addition, open waters created with the accelerated melting of sea ice are likely to result in higher inputs of halogen aerosols to the atmosphere and the subsequent enhanced deposition of RGM with precipitation. The impact of these changes on both microbial and abiotic methylation as well as MeHg degradation and redox transformations of inorganic Hg will determine future trends in MeHg accumulation in polar regions.

Thawing permafrost may be an increasing source of MeHg to polar ecosystems. One may expect an increased production of MeHg in polar regions as a consequence of global warming considering the known relationship of enhanced methylation with increased oxidation of organic matter (Kelly et al. 1997; St. Louis et al. 2004) and the increased cycling of carbon (Davidson & Janssens 2006; Heimann & Reichstein 2008) together with the release of Hg from peat (Klaminder et al. 2008) when permafrost thaws. Considering the enormous magnitude of carbon that is sequestered in permafrost and the projection for rapid permafrost thawing (Lawrence & Slater 2005), an evaluation of how this change can affect Hg biogeochemistry is needed.

A better description and understanding of Hg transport and transformations in sea-ice microbial habitats

is warranted. These marine environments are characterized by spatially and temporally fractured unique environments in terms of their physical, chemical, and biological features. These niches may alter, or modulate, the pathways of microbial transformations of Hg relative to their characteristics in temperate environments. Our current state of knowledge provides us with a starting point for studies on Hg transformations in polar regions, and such studies promise to add new dimensions to our perception of the mechanisms and pathways that determine Hg toxicity and facilitate life in its presence.

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