



Total mercury and methyl-mercury contents and accumulation in polar microbial mats



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HIGHLIGHTS

- Microbial mats from both polar regions were analyzed for mercury and methyl-mercury.
- Mercury and methyl-mercury concentrations were low in most of the mats.
- Experimental spiking with Hg demonstrated Hg accumulation in the mats but not the transformation of Hg to MeHg.

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ABSTRACT

Although polar regions are considered isolated and pristine areas, the organisms that inhabit these zones are exposed to global pollution. Heavy metals, such as mercury, are global pollutants and can reach almost any location on Earth. Mercury may come from natural, volcanic or geological sources, or result from anthropogenic sources, in particular industrial or mining activities. In this study, we have investigated one of the most prominent biological non-marine communities in both polar regions, microbial mats, in terms of their Hg and methyl-mercury (MeHg) concentrations and accumulation capacities. The main hypotheses posed argued on the importance of different factors, and to test them, we have measured Hg concentrations in microbial mats that were collected from 6 locations in different ecological situations. For this purpose, the direct anthropogenic impacts, volcanic influences, proximity to the seashore, latitudinal gradients and C contents were investigated. Our results show that, other than the direct anthropogenic influence, none of the other hypotheses alone satisfactorily explains the Hg content in microbial mats. In contrast, the MeHg contents were noticeably different between the investigated locations, with a higher proportion of MeHg on the McMurdo Ice Shelf (Antarctica) and a lower proportion on Ward Hunt Island (High Arctic). Furthermore, our results from *in situ* experiments indicated that the microbial mats from South Shetland Islands could quickly accumulate (48 h) Hg when Hg dissolved salts were supplied. Over short-term periods, these mats do not transform Hg into MeHg under field conditions.

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1. Introduction

Despite their remoteness, polar regions are exposed to different sources of natural and anthropogenic pollution from volcanic activity, atmospheric deposition, fuel spills, waste disposal and fuel combustion (Mao de Ferro et al., 2014). The residence time of gaseous elemental mercury in the troposphere facilitates its long-distance transport before it becomes incorporated into ecosystems through atmospheric deposition (Bargagli et al., 2007). High-latitude areas are known to experience atmospheric mercury deposition on the snow during atmospheric mercury

depletion events (AMDEs), which were discovered in Nunavut in 1995 by Schroeder et al. (1998). In addition, it has been suggested that AMDEs are responsible for remarkable increases in the total Hg contents in the Antarctic snow pack (Brooks et al., 2008). Thus, organisms could be exposed to the deposited metals after snow thaws. The Hg concentrations in ecosystems result from a dynamic process in which deposition and re-emission into the atmosphere are the key players (Bargagli et al., 2007). A fraction of the deposited Hg can be biologically transformed during methylation, the process that transforms inorganic mercury into methyl-mercury (MeHg), which is more toxic to organisms (Mergler et al., 2007). In polar regions, vegetation such as lichens and mosses, as well as microbial mats, which are the most abundant components of these

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biological communities, are likely the main sinks for Hg when the snow melts during the warm season. Previous exploration (e.g., Bargagli et al., 1993) of the accumulation of mercury in polar vegetation (i.e., mosses and lichens) has indicated that both Arctic and Antarctic vegetation can accumulate considerable concentrations of Hg and MeHg (Lindberg et al., 2002; Mao de Ferro et al., 2014). Furthermore, previous studies have suggested that microbial mats, which cover vast surfaces in the polar areas, could be important for metal accumulation in non-marine polar ecosystems (Bargagli et al., 2007). However, only 4 microbial mats from Antarctica (Terranova Bay) and none from the Arctic, have been investigated in this regard (Bargagli et al., 2007).

Microbial mats are thin (from mm to a few cm) laminated microbial communities that form vertically stratified layers of interdependent microorganisms on the surface of sediments (Camacho and de Wit, 2003). Microbial mats can colonize a variety of different environments, including several extreme areas on Earth. In cold environments, such as the Arctic and Antarctica, microbial mats mainly live in freshwaters and account for most of the biomass productivity (Vincent, 2000). Microbial mats are ecologically relevant in some polar regions, particularly in the Antarctic Peninsula region in which microbial mats cover nearly the same amount of surface as terrestrial mosses (Velázquez et al., 2013), and are even more important in harsher Antarctic locations, such as the McMurdo Ice Shelf (Vincent, 2000). Along with their biological component, an inorganic matrix composed of geologic and biogenic minerals and small rocks is the other component of such microbial ecosystems (De los Ríos et al., 2004). These multilayered communities are composed of different microorganisms, with a dominance of cyanobacteria. However, other organisms, such as other autotrophic and heterotrophic bacteria, green algae, diatoms, fungi, and different metazoans, also inhabit these ecosystems. In the Arctic, microbial mats have been found to serve as a food source for some aquatic invertebrates (Rautio and Vincent, 2006); thus, bioaccumulation could occur through the relatively simple freshwater food webs of these polar ecosystems. The organisms within the microbial mats are placed at different positions, with some organisms near the upper surface where light is available and others near the sediment in the aphotic zone. This distribution creates a biogeochemical gradient in which the surface layer is supersaturated in oxygen during the daytime and the bottom is anoxic and allows for sulfide and methane production. This chemical gradient provides a complete range of possibilities for the interactions of chemicals, such as metals. In fact, the chemical characteristics of the overlying water are typically quite different from those of the interstitial water (Vincent and Quesada, 2012). The structure of the mats includes a complex matrix of the microorganisms themselves, inorganic materials and extracellular polysaccharides (EPS; De los Ríos et al., 2004). Extracellular polysaccharides are able to accumulate positively charged metallic ions due to their negative charge (Kumar and Gaur, 2012). In fact, a number of studies have reported that bacterial biofilms and microbial mats, especially the latter, present dense EPS covers and are able to react with heavy metals. For example, bacterial biofilms can remove heavy metal ions from wastewater and could be used in remediation strategies for polluted areas (Ferris et al., 1989; Canstein et al., 1999). Furthermore, these types of biofilms can react by reducing divalent mercury to elemental mercury (Brunke et al., 1993), and some biofilms can accumulate Hg in their mucilaginous cell covers (Wagner-Döbler et al., 2000). In addition, some Hg can return to the atmosphere (King et al., 2002). Regarding cyanobacteria, the main components of the microbial mats in the polar areas, the negatively charged cyanobacterial sheaths and the cell walls can interact with divalent cations in a bioaccumulation process that is coupled with the accumulation of exopolysaccharides in the sheaths (Pereira et al., 2011). Although it is known that some of the organisms from the epilithon and periphyton of temperate lakes are responsible for the transformation of Hg to MeHg (Desrosiers et al., 2006a; Hamelin et al., 2011), the role of microbial mats in the transformation of Hg to MeHg remains unknown.

Despite extensive information regarding heavy metal concentrations in polar environments, very little information is known about

the potential accumulation of metals in the biological assemblages that dominate the polar terrestrial and freshwater ecosystems or the harmful effects of this metal pollution. However, the observations that have been made in polar marine coastal ecosystems do show a progressive increase in Hg concentrations in the food web (Bargagli et al., 1998; Jerez et al., 2013), which demonstrates the need for understanding the mechanisms involved in the incorporation of Hg in primary producers. Among the biota that form the base of terrestrial and freshwater food webs, lichens, mosses and, especially, microbial mats are the most important due to their coverage of vast areas in polar regions.

In this study, we analyzed the total mercury and MeHg in vegetation, including mosses and lichens, and mainly in microbial mats that covered freshwater areas in the Arctic and Antarctica, to provide an overview of the mercury contents in these biological systems. In addition, to initially explore the potential accumulation capacities of microbial mats in polar regions, an experimental setup was performed in which the total mercury and MeHg contents in a representative polar microbial mat that was exposed to increased mercury concentrations over a short period were determined.

2. Methods

2.1. Study area

The samples analyzed in this study were collected from different areas within the polar regions shown in Fig. 1. Antarctic samples were collected from the South Shetland Islands (62°S), from Hope Bay in the Antarctic Peninsula (63°S), and from the McMurdo Sound region (78°S; Table 1). The South Shetland Islands samples were collected from Byers Peninsula on Livingston Island and from Deception Island; both areas have multiple lakes and ponds (Toro et al., 2007) and are located in the less extreme areas of Antarctica where the summer conditions favor the development of biological communities, including extensive microbial mats (Fernández-Valiente et al., 2007; Velázquez et al., 2011). Deception Island is a volcanic island near Livingston Island on which frequent eruptions have occurred, with the most recent eruption occurring in the late 1960s. Ecologically, Deception Island is very different from Livingston Island because the volcanic eruptions altered the surfaces of Deception Island and added large amounts of volcanic scoria and lava. The area sampled in Hope Bay is near the Argentinean scientific station (Esperanza Station) and could be influenced by anthropogenic pollution. The McMurdo Ice Shelf contains hundreds of shallow melt ponds that are chemically different. In most cases, the bottoms of these ponds are carpeted by nearly continuous microbial mats. The microbial communities found in this region are very diverse, and nearby communities can present very different compositions (e.g., Vincent et al., 1993).

The High Arctic samples were collected from Northern Ellesmere Island (Canada), from Ward Hunt Island (83°N) and from Taconite Inlet (82°N; Table 1). No permanent stations are located at these sites, although Ward Hunt Island has a permanent camp with an airstrip that is sporadically used by visitors. Thus, some debris could be present at Ward Hunt Island, where the microbial mat sample was collected from Ward Hunt Lake. Because Taconite Inlet is remote, it is only sporadically visited by low-weight camps and can be considered pristine. The samples from this location were collected from nearby shallow melt water streams near the C1 lake (Van Hove et al., 2006).

Table 1 summarizes the locations and main features and provides descriptions of the potential mercury sources for the samples that were studied at the field sites. In addition, the microbial mats from different locations showed different activity rates. The microbial mats from McMurdo Sound were assumed as slow growing due to the harsher environmental conditions in this region. The microbial mats from the Antarctic Peninsula and the High Arctic were potentially more active and faster growing. In addition, the MU microbial mat is very peculiar because it is not an active mat, it was collected dry and ¹⁴C dating indicated that it had an estimated age of 1000 years (V. Parro, personal

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