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Pathways and speciation of mercury in the environmental compartments of Deception Island, Antarctica

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HIGHLIGHTS

- We report the first integrated mercury study in Deception Island, Antarctica.
- Several samples of sediment, water, ice, snow and vegetation were collected.
- Volcanic activity should be the main source of Hg in Deception Island.
- A high proportion of methylmercury was found in the saline water of Foster bay.
- The results point to the existence of a MeHg poll available for aquatic organisms.

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ABSTRACT

This work reports the first integrated mercury study in an Antarctic ecosystem. Sample collection took place in Deception Island, an active volcano in the South Shetland Islands, in several environmental compartments (water, snow, sediments and vegetation) and different locations, during December 2011. The results suggest that volcanic activity is the most important Hg source. Mercury levels in water and sediments sampled at two fumaroles were up to 10,000 times higher than in the other sampling sites. Dissolved methylmercury (MeHg) is below the detection limit in those samples, probably due to the very high temperature found in fumaroles (above 80 °C). On the other hand MeHg accounted for, on average, 23% of total dissolved Hg in the saline waters of Foster bay, which suggests exceptional conditions for Hg methylation. Combined with the high residence time of the water in Foster bay, the results point to the existence of a MeHg pool available for aquatic living organisms.

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1. Introduction

Antarctica is seen as a remote and hostile place, symbol of a pristine environment untouched by human disturbances. However, the development of Antarctic research especially after the International Geophysical Year (1957–58) and tourism have resulted in a sharp increase of pressure from human activities, leading to several pollution problems, mainly near scientific stations (Bargagli, 2008; Braun et al., 2012).

Studies in King George Island (Santos et al., 2005; Lu et al., 2011) and Ross Island (Claridge et al., 1995; Sheppard et al., 2000), indicate that the main sources of anthropogenic trace elements are due to fuel spills, waste disposal sites, sewage, paint residues and exhaust gases. However, there are important natural sources in Antarctica that have been also considered, namely in what concerns mercury (Hg). Siegel et al. (1980) showed that Hg content in air samples collected in Mt. Erebus (the second highest volcano in Antarctica, located in Ross island, near Victoria Land) were similar to that of volcanic sites in Iceland and Hawaii. Despite the volcanic Hg input in Victoria Land, low Hg concentrations were confirmed in several abiotic compartments of this region, such as sediments (Matsumoto et al., 1983; Bargagli et al., 1993), snow (Dick et al., 1990; Sheppard et al., 1991) and air (de Mora et al., 1993). Surprisingly, these data clearly contrast with the results of lichen and moss biomonitoring. In fact, Hg content in moss and lichen samples collected in Victoria Land were similar to other temperate urban and industrial areas of the Northern hemisphere (Bargagli et al., 1993).

More recently, Bargagli et al. (1998) determined total Hg concentrations in marine sediments and biota in Terra Nova bay. They found that Hg levels in marine sediment were the lowest ever reported for coastal marine environments, although a progressive increase of total Hg was notice along the different trophic levels. As suggested by Cossa et al. (2011), inorganic Hg must be converted to methylmercury (MeHg) and bioconcentrated by phyto and zooplankton in order to be magnified in fish and sea-birds. Apparently, there seems to exist in Antarctica a unique combination of atmosphere, ocean and sea ice processes that could explain the elevated concentrations of MeHg in the Antarctic

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waters. The presence of halogens in the atmosphere promotes oxidation and deposition of atmospheric mercury Hg^0 in the water column; scavenging of inorganic Hg by the phytoplankton in superficial waters and consequent sink in the hypoxic zone, richer in organic matter, supply methylation bacteria as substrate, and finally upwelling of deep waters increases MeHg concentrations (Cossa et al., 2011). In consequence, the remote Antarctic waters exhibit some of the highest MeHg concentrations observed in open waters, exposing marine organisms to a higher level of this important neurotoxin (Cossa et al., 2011). Biotic factors such as decreasing metabolic rate with lower temperatures could also have an important key role (Bargagli et al., 1998). Accordingly to Trudel and Rasmussen (1997), the uptake of MeHg in fish is up to 10 times higher than Hg, but the excretion processes of MeHg is slower by 3-fold. Moreover, MeHg elimination was significantly correlated to water temperature (Trudel and Rasmussen, 1997), which suggests that in Antarctic waters its excretion is inhibited.

Comparatively to other locations in Antarctica, environmental studies in Deception Island are scarce and are of great interest since it has potential sources of trace element related to the volcanic activity, as well as anthropogenic input due to its history, tourism and two scientific stations. Although Hg levels in Deception were previously analysed in lichen specie *Usnea Antarctica* by Bargagli et al. (1993), to the best of our knowledge this is the first integrated mercury study held in this volcanic island, in order to define sources and pathways of mercury in this ecosystem. We also intend to investigate the speciation of Hg regarding one of its most important methylated form, MeHg, and to assess the role of particulate organic matter as well as the geochemistry nature of the sediment in the cycle of this important contaminant. Thus, Hg and MeHg concentrations were determined in different environmental compartments: snow ($n = 18$), fresh ($n = 31$) and saline ($n = 13$) waters, sediment ($n = 26$), Moss ($n = 4$) and Lichen ($n = 2$), collected in different locations of the island, from 1 to 20th of December 2011.

2. Materials and methods

2.1. Study area

Deception Island (DI), one of the most active volcanoes in Antarctica, is located in the South Shetland Islands, which are separated from the Antarctic Peninsula by the Brandsfield Strait (Rey et al., 1995), Fig. 1. DI has a large flooded caldera named Port Foster or Foster bay. Its geographical position as well as its unique shelter offered by the interior harbour made it the centre of the earliest fur seals hunting commercial activity in Antarctica during 19th century. Nearly a century later, it was the most extensive anchorage used by the non-pelagic whale processing ship factories and later on housed the Hektor wailing station, the only land based commercial activity in Antarctic History, which operated in Whalers Bay from 1912 until 1931 (Dibbern, 2009). Currently, there are two 'summer only' scientific stations operating in DI: Decepción (Argentina) and Gabriel de Castilla (Spain) were established in 1948 and 1989, respectively, to support topographic and research works as well as to observe volcanic activity. More recently, DI became a regular stop for the growing Antarctic tourism cruise industry (Dibbern, 2009).

2.2. Sampling sites

Sampling sites in Deception Island are presented in Fig. 1. Sampling took place in three main areas of DI: A – Vicinity of Gabriel de Castilla (GC) station, B – Fumarole bay and Murature beach, C – Colatina beach.

2.2.1. Area A: Vicinity of GC station

GC station is located 50 m from the Mecon river mouth. Fresh water samples were collected during 8 consecutive days (d1–d8) in 3 stations of Mecon river, denominated R1, R2 and R3, and located at 20 m from the river mouth, middle course and headwaters of Mecon, respectively. In those 3 stations (R1, R2 and R3), and accordingly to the fresh water sampling days, sediment samples were collected in days d1, d4 and d8, while snow samples were collected in days d2 and d8. Sample stations I1 to I5 were located in Mt. Irizar, positioned south and upstream of Mecon river. Fresh water samples at I1–I5 stations were collected in or nearby water springs. Port Foster saline water samples were collected in sample stations B5 to B9, located near GC station. During the campaign snow precipitation occurred and fresh snow was immediately sampled in stations FS1–FS6, dispersed over several sites. Sediment samples were also collected in B1–B3 sites, relatively near to the GC station. Lichen (V1 and V6) and Moss (V2–V5) samples were collected in different sites of area A.

2.2.2. Area B: Fumarole bay and Murature beach

Fumarole bay is located north of Argentina station (Fig. 1). During the campaign two Fumaroles were active, named Fumarole1 (F1) and Fumarole2 (F2). Two sediment samples were collected in each fumarole. The samples F1A/F2A correspond to the sampling in the centre of both fumaroles, respectively, while samples F1B/F2B were collected at 3 m away. Fumarole1 was located in the shoreline, and was periodically submerged by Port Foster water due to tides. One saline water sample was collected in F1 and another at 15 m away (B4) in Foster bay.

Additionally, sediment and saline water samples were collected in 3 stations (M1, M2 and M3) at Murature beach and a snow sample was also collected in station M2.

2.2.3. Area C: Colatina beach

This site is located southeast of GC station near the narrow entrance of Port Foster. Sediment and saline water samples were collected in 3 stations (C1, C2 and C3). Snow samples were also collected in stations C1 and C3.

2.3. Sampling

Sampling was carried out with ultra-clean protocol techniques, using acid decontaminated material and wearing latex gloves.

Fresh water samples were collected into acid decontaminated 50 mL Falcon tubes that were submerge facing upstream. Snow samples were collected in similar 50 mL Falcon tubes, using decontaminated spatulas after removing the first layers to avoid accumulated deposit particles. Water samples were immediately filtered to decontaminated PTFA Nalgen Flaks using an acid decontaminated 60 mL HSW syringe through a 0.45 μm filter (Whatman Fp 30). After filtration samples were acidified with HCl (Merck, Hg free) to a final concentration of 0.5% (v/v). For snow samples the same procedure was carried out after the snow melt.

Lichen and Moss were removed using a decontaminated tweezer from the volcanic sediment of Deception and stored in zip sealed plastic bags. At the laboratory they were washed with ultra pure Milli-Q water to remove dust and sediment, and then oven dried at 40 °C. Sediment samples were collected with a decontaminated plastic spatula, stored in zip sealed plastic bags and also dried at 40 °C. After dried, sediments where sieved and only the fraction <2 mm were used for analyses, to avoid the dilution of contents by coarse material (Loring et al., 1992).

Finally, sediment and biological samples were homogenized and pulverized in a decontaminated agate mortar.

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