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Mercury accumulation in sediments and seabird feathers from the Antarctic Peninsula

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ABSTRACT

In an effort to assess the impact of mercury in the Antarctic Peninsula, we conducted ecotoxicological research in this region during the summer of 2012 and 2013. The objectives were to assess: (a) mercury levels in sediment samples; (b) mercury accumulation in Antarctic seabird feathers: *Catharacta lonnbergi* (brown skua), *Pygoscelis papua* (gentoo penguin) and *Pygoscelis antarctica* (chinstrap penguin); and (c) biomagnification (BMF predator/prey) and biota sediment accumulation (BSAF skuas/sediment) factors. Mercury concentrations in sediment were relatively low. Mercury concentrations were significantly higher in brown skuas and gentoo penguins than in chinstrap penguins (2012), and significantly higher in brown skuas than in both penguins (2013). BMF indicated 2–7.5 times greater mercury levels in brown skuas than in penguins. BSAF values suggested an apparent temporal decrease of 18.2% of this ratio from 2012 to 2013. Long-range environmental transport is the likely route of entry of mercury into the Antarctic Peninsula.

1. Introduction

The Antarctic continent is one of the few regions on the planet that is still considered a pristine environment; therefore, it is of particular importance to preserve this unique region. However, there are several studies that have given warning signals of possible contamination and degradation of the Antarctic environment by anthropogenic pollutants, including relatively high metal concentrations at various trophic levels of the regional marine food web (Bargagli et al., 1998; Metcheva et al., 2006; Jerez et al., 2011). Other studies have demonstrated that due to its high volatility and long residence time, mercury (Hg) can reach remote areas of the planet through long range atmospheric transport (Nriagu, 1989; Fitzgerald et al., 1998; Lindberg et al., 2007). Atmospheric Hg is predominantly the gaseous elemental form (Hg^0), which can be oxidized to Hg^{II} and then deposited. It is estimated that more than 80% of the Hg deposited in the ocean is re-emitted to the atmosphere as Hg^0, driving the cycle of Hg through biogeochemical reservoirs (Strode et al., 2007). The half-life of atmospheric Hg^0 in polar regions is short (Driscoll et al., 2007), but once Hg^0 is deposited in aquatic ecosystems, it can be methylated by microorganisms to form methylmercury (Me–Hg). Me–Hg is highly toxic and bioaccumulates throughout the food web almost entirely via dietary uptake, reaching the highest concentrations in organisms at the top of the food web (Wiener et al., 2007).

Seabirds have been successfully used worldwide as indicators of environmental contamination (Furness and Camphuysen, 1997; Walsh, 1990) because they exhibit different trophic levels and they have long life spans (Walsh, 1990). Seabirds can accumulate bioavailable forms of contaminants and species at high trophic levels can biomagnify contaminants to concentrations that are several orders of magnitude higher than the concentration in the environment (Burger and Gochfeld, 2000; Roomen et al., 2006). Seabird feathers have been employed as indicators of metal contamination in the environment because metals are sequestered in feathers during the birds' growing phase (Burger, 1993) and seabirds eliminate metals through their feathers during molting (Burger, 1993: Hughes et al., 1997). In the case of Hg, the concentration of Hg in feathers has been shown to correlate with those in internal tissues (Thompson et al., 1990, 1991). Therefore, the use of feathers represents a noninvasive approach for monitoring mercury accumulation in seabirds and the marine environment (Appelquist et al., 1984; Furness et al., 1986; Thompson et al., 1990; Bond and

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Diamond, 2009). Data for mercury in seabird feathers are substantial for the North Pacific, North Atlantic and Arctic regions (Norheim, 1987; Thompson and Furness, 1989a,b; Thompson et al., 1990; Thompson et al., 1998a,b; Bearhop et al., 2000; Savinov et al., 2003; Burger et al., 2007; Bond and Diamond, 2009). Data on mercury in seabirds from the Southern Ocean and Antarctica like Antarctic penguins, brown skuas and albatrosses (Norheim et al., 1982; Thompson and Furness, 1989a,b; Ancora et al., 2002; Becker et al., 2002; Metcheva et al., 2006; Jerez et al., 2011; Blevin et al., 2013), and for seabirds from the Chilean and Argentinean coasts (Ochoa-Acuña et al., 2002; Frias et al., 2012) are gradually emerging.

The aim of the present study was to assess ambient Hg levels and Hg bioaccumulation in seabirds in the Antarctic Peninsula. Specifically, this study aimed to: (a) determine concentrations of mercury in sediment and in feathers samples of the Greenwich and Barrientos Islands; and, (b) assess mercury accumulation in feathers of Antarctic seabirds, including penguins (*Pygoscelis papua* and *P. antarctica*) and brown skuas (*Catharacta lonnbergi*). Sampling for this study was done during the XVI and XVII Ecuadorian-Antarctic expeditions to Ecuador's Scientific Station "Pedro Vicente Maldonado" at the Antarctic Peninsula carried out by the Ecuadorian Antarctic Institute (INAE).

2. Materials and methods

2.1. Study area

The study area encompasses the Greenwich and Barrientos Islands of the Antarctic Peninsula. Greenwich Island is located at 62°31′S, 59°46′O and harbors the Ecuadorian Research Station "Pedro Vicente Maldonado" (i.e. Punta Fort Williams). Sampling was conducted around the station using three tracks established by the Ecuadorian Station to access the coastline of Punta Fort Williams, which enclose two sampling sites: Ensenada Guayaquil and Bahia Chile. This sector of the island is used only by the technical and military personnel that work at the Station and visiting scientists that come to the island for research purposes. Barrientos Island is located at 62°42′S, 59°47′O, and is used principally as a tourist stopover for cruise ships where tourists land and walk around the island for birdwatching. Sampling at this island was deployed around its coastline (Fig. 1). All sampling was done during the Antarctic summer and seabird breeding seasons of 2012 and 2013. A total of eleven sampling sites were surveyed for Punta Fort Williams and seven sites for Barrientos Island (Fig. 1).

2.2. Samples collection

Samples of sediment were collected from eighteen locations in the Antarctic Peninsula including Ensenada Guayaquil ($n = 6$ sites) and Bahia Chile ($n = 5$ sites) of Greenwich Island and seven sampling sites of Barrientos Island (Fig. 1). Sediment samples (~5 cm deep) were collected using a small plastic shovel and placed in Ziploc-type plastic bags. Sediment was stored at 4 °C until transportation to the laboratory in Ecuador for about one month. Once in the laboratory each sediment sample was homogenized and dried using a conventional oven at 70 °C for 48 h. Dried sediment samples (~40 g) were pulverized using clean acid washed mortar and pestle. Pulverized sediment samples were stored in the desiccator until total mercury analysis.

Three species of seabirds, gentoo penguins (*P. papua*), chinstrap penguins (*P. antarctica*) and brown skuas (*C. lonnbergi*), that inhabit the Antarctic Peninsula were identified as potential bio-indicators of Hg contamination. Hg binds strongly to the sulphydryl groups of feathers' keratin (i.e. a high molecular weight fibrous, structural protein), within which organic mercury (i.e. Me–Hg) is highly stable and resistant to environment factors such as ultraviolet light, heat, freezing and weathering (Appelquist et al., 1984). Molted feathers were collected randomly in and around nests and colonies of penguins aggregated on Barrientos Island and skuas from Punta Fort Williams. While collected feathers for skuas (i.e. primary feathers) were from adult individuals, molted feathers for penguins were from chicks. Samples were brought to the laboratory of Maldonado Station and rinsed with pure acetone, followed by a generous rinse with deionized water (Burger and Gochfeld, 2000). Feathers were air dried at 20 °C, after which they were wrapped in acetone-rinsed aluminum foil and stored in the freezer (−18 °C) until analysis.

While the major purpose of the analysis was to measure the whole feather, we also investigated whether concentrations of Hg exhibit variation along the feather's length. Therefore, three feathers from brown skuas (Feather 1: 33 cm; Feather 2: 22.5 cm; Feather 3: 18.0 cm) collected in 2013 where cut and analyzed in four sections from the calamus or quill (region 1) located at the base of the feather, through regions 2 and 3, to the tip of the feather rachis (region 4), as illustrated in Fig. 2.

2.3. Mercury analysis

Total mercury in sediment and seabird feathers of the Antarctic Peninsula was determined via atomic absorption spectrophotometry using a Direct Mercury Analyzer (DMA-80). The advantage of using this equipment is that the instrument does not require acid digestion of the sample or other pretreatment. Because great amount of mercury in feathers is present in the form of Me–Hg, a measurement of total mercury concentration was used as a proxy of this bioavailable form (Thompson and Furness, 1989a, 1989b). The limit of detection of the equipment was 0.005 ng. Quality control and assurance was performed by analyzing the concentration of the standard reference material (SRM)-1646a Estuarine Sediment (NIST) and procedural blanks in each set of sediment and feathers samples analyzed. SRM recoveries were >94% for the 2012 samples and >93% for the 2013 samples (Table 1). For sediment samples, blanks had mean concentrations ranging from 0.0008 to 0.0015 mg/kg dw, while mean concentrations for blanks run with feathers ranged from 0.0010 to 0.0015 mg/kg dw (Table 1). All mercury concentrations are expressed as dry weight (mg/kg dw) (See Table 2).

2.4. Data treatment and statistical analysis

Concentrations of mercury measured were blank-corrected using the method detection limit (i.e. MDL), defined here as the mean response of concentrations measured in $n = 3$ and $n = 5$ procedural blanks analyzed in the same run as the sediment and seabird feather samples, respectively. Most mercury concentration data were normally distributed as tested by the Shapiro–Wilk W test ($p > 0.05$), except for concentrations observed in skua feathers collected in 2012 and sediments from Bahia Chile collected in 2013, which were not normally distributed (Shapiro–Wilk W test, $p < 0.05$). Differences in contaminant concentrations among sites and seabird species were evaluated using analysis of variance (ANOVA) when variances among sites or seabird species were equal (i.e. homoscedastic as tested by the Bartlett test, $p > 0.05$), or Welch ANOVA when variances were unequal (i.e. heteroscedastic; Bartlett test, $p < 0.05$) for normally distributed data. These statistical comparisons were followed by a Tukey–Kramer honestly significant difference (HSD) multiple comparison test, which is a *post hoc* method recommended to test differences between pairs of means among groups that contain unequal sample sizes (Zar, 1999). Alternatively, a nonparametric test (Kruskal–Wallis test)