



Effect of penguin and seal excrement on mercury distribution in sediments from the Ross Sea region, East Antarctica

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ABSTRACT

Total mercury (Hg) concentration and several other geochemical parameters were determined for five sediment profiles from the Antarctic Ross Sea region. Our data exhibit significant positive correlations between Hg concentration and total organic carbon (TOC) content in all profiles, suggesting the predominant role of organic matter (OM) as a Hg carrier. The OM in the sediments originates primarily from penguin guano and algae. High Hg content in guano and a positive correlation between Hg and a guano bio-element (phosphorus, P) in the ornithogenic sediment profiles (MB6, BI and CC) indicate that Hg was strongly influenced by guano input. The bottom sediments of MB6 with seal hairs contain relatively high Hg. This increase is attributed to the input of seal excrement, suggesting that sedimentary Hg may be an effective trophic-level indicator from seals to penguins. The enrichment factor (EF) for Hg was calculated and the results indicated apparent Hg enrichment in the sediment profiles from the Ross Sea region caused by bio-vectors such as penguins and seals. Compared with typical sediments from other sites in Antarctica and the SQGs (sediment quality guidelines), the total amount of Hg in our study area is still not considered to be adversely high.

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1. Introduction

Heavy metals and persistent organic pollutants (POPs) are hazardous substances threatening the environment (Kennicutt et al., 2010; Negri et al., 2006). With growing awareness of environmental protection and human health, the source, pathway and final fate of such pollutants are important concerns for both researchers and the public. Mercury (Hg) is a heavy metal with well-known high toxicity. It usually exists in gaseous elemental form (Hg⁰) when released from anthropogenic and natural sources, facilitating its transport over long-distances with a tropospheric residence time of up to 1 year or longer (Fitzgerald et al., 1998; Slemr and Langer, 1992; Sprovieri et al., 2002). Possessing such mobility, the influence of Hg can reach far beyond its source area.

Antarctica is generally thought to be a pristine environment because of its remote location and the protection provided by oceanic and atmospheric circulation around the continent. Until now, investigations on some trace metals and POPs in plants (Bargagli et al., 2000; Grotti et al., 2008), marine organisms (Bargagli et al., 1996; Jost and Zauke, 2008; King and Riddle, 2001), and seabirds (Geisz et al., 2008; Metcheva et al., 2011) have provided valuable information on Antarctic pollutants and indicate that even this remote region is impacted by local and global human contaminants to some extent (Bargagli, 2008). Water, soil, plant and faunal samples have

been widely studied, especially from the perspective of the pathway and fate of Hg in ecosystems (Ancora et al., 2002; Bargagli et al., 1998b, 2005, 2007; Bargagli, 2008; Negri et al., 2006; Riva et al., 2004; Siegel et al., 1980, 1981; Vandal et al., 1998). These investigations have included the history of Hg transportation and deposition in Antarctica by examining marine sediments (Maggi et al., 2009) and ice cores (Schuster et al., 2002; Vandal et al., 1993).

More recently, bio-vectors were recognized as important pollutant accumulators and carriers (Blais et al., 2007). As one of the top predators, seabirds can transfer both nutrients and contaminants from the sea to the terrestrial ecosystem via droppings, feathers, eggshells, and other sources (Blais et al., 2007; Brimble et al., 2009; Choy et al., 2010; Liu et al., 2006; Michelutti et al., 2010; Roosens et al., 2007). In Antarctica, bio-vectors such as penguins and seals are the main accumulators and carriers for trace metals in the ice-free areas where most penguins breed. Seabirds in Antarctica have been identified as under intense exposure to pollutants due to their high trophic-level position and wide foraging range (Corsolini, 2009; Roosens et al., 2007; Sun et al., 2006a). Ornithogenic sediments are a geochemical depository strongly influenced by penguin activities (Heine and Speir, 1989; Sun et al., 2000, 2006a). They serve as a perfect natural archive and provide insight into the transport of pollutants and the interactions between biotic and abiotic components of ecosystems including bio-transportation, bio-magnification and geochemical circulation in selected areas (Bargagli et al., 1998a). However, the effect of bio-transported pollutants on ornithogenic sediments has not been well documented in Antarctica.

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In the Ross Sea region, East Antarctica, large colonies of Adélie penguins (*Pygoscelis adeliae*) have been forming extensive deposits of ornithogenic sediments and soils in ice-free areas. However, to our knowledge these ornithogenic sediments have received very little attention in regard to pollutants, and to date very few studies on the geochemical characteristics of pollutants such as Hg have been conducted. Here, we present five sediment profiles that were excavated from ponds and catchments near penguin colonies in the Ross Sea region. We analyzed Hg, P, total organic carbon (TOC), total nitrogen (TN) and other physical/chemical proxies in the sediments, as well as environmental materials such as soil, fresh guano, and algae. We used these profiles to identify Hg sources and the main factors influencing its distribution in the Ross Sea region.

2. Materials and methods

The Ross Sea is a deep embayment between Cape Adare and Cape Colbeck at the border of West and East Antarctica with an average depth of 500 m. The southern part of the Ross Sea is covered by the Ross Ice Shelf extending from the continent. This region forms a confluence of land, sea and ice shelf, making it sensitive to climate change. The weather there is abrupt and severe due to the conjunction of three different air masses from Victoria Land, the Ross Sea, and the Ross Ice Shelf (Monaghan et al., 2005).

The sampling sites are located mainly on Ross Island and Beaufort Island (Fig. 1). Ross Island (~2460 km²) is a volcanic island on the east side of the southern Ross Sea with McMurdo Station on its southern end. Most parts of Ross Island are covered by ice, leaving only three ice-free areas: Cape Crozier, Cape Bird, and Cape Royds. A large number of Adélie penguins occupy these three areas, collectively forming one of the largest Adélie penguin concentrations in Antarctica (>200,000 nesting pairs). Beaufort Island (~18.4 km²) is 21 km north of Ross Island with Adélie penguins nesting on the eastern and southern beaches. Besides the modern penguin colonies, there are also numerous abandoned penguin colonies in the ice-free areas mentioned above, making them the ideal locations for investigations on the history of penguin ecology (Emslie et al., 2003, 2007). Fresh-water algae are widespread in the ponds and catchments near the active penguin colonies.

MB4, MB6, CL2, and CC were collected at Cape Bird and Cape Crozier, and BI was at Beaufort Island (Fig. 1). The sampling sites of MB4 (42 cm) and CL2 (35 cm) are near abandoned penguin colonies in the middle part of Cape Bird. A small pond is located on the fifth beach ridge above sea level, and CL2 was taken on its northern edge (166° 22' 25.6" E, 77° 14' 35.3" S). Core CL2 consists mostly of fairly

homogeneous, black and gray silts, and its uppermost part is comprised of dark green fresh-water algae residues. MB4 was collected in a small pond between the fourth and fifth beach ridges (166° 22' 25.6" E, 77° 14' 35.3" S). The sediment layer below 15 cm is fine-grained ornithogenic soil with a dark color and rancid smell (typical for a young and developing soil); the sediment unit between 5 and 15 cm is mainly composed of dark-colored coarse sands with little cohesion; the surface layer (between the top and 5 cm) is rich in fine black algae residue. The MB6 profile (38 cm) was collected from the catchment on the second terrace above sea level in the active penguin colony on the north side of Cape Bird (166° 26' 44.4" E, 77° 12' 47.5" S). The sediments below 24 cm are believed to be dark-colored ornithogenic soils, and the remainder consists of brown clay. Seal hairs were found in the sediment layer beneath 32 cm. Core BI (20.5 cm) was excavated from a pond near the modern penguin colony on the southwest side of Beaufort Island (166° 58' 23.6" E, 76° 58' 23.6" S). From the bottom to top, brown clay gradually transitions into black fine-grained ornithogenic soils. Core CC (9.5 cm) was retrieved from a small fecal pond at Cape Crozier (169° 14' 41.3" E, 77° 27' 21.9" S). Large amounts of penguin guano are deposited here, together with many eggshells and downy feathers, and there is no algal influence in this profile. The lithological characteristics of all the sediment profiles are summarized in Fig. 2. For comparison, end-member environmental media samples such as fresh guano, fresh algae and soil (bedrock) were also collected in the study area.

Core CL2, BI and CC were collected in PVC pipes (12 cm diameter), since the ponds are shallow and a gravity sampler is unnecessary. After being transported back to the laboratory, the PVC pipes were cut in halves and the sediments were carefully sectioned at 0.5 cm intervals. Both MB4 and MB6 profiles were collected from the pits dug in the sampling sites and directly sectioned on spot (at 0.8 and 0.6 cm intervals respectively). All the subsamples were kept at -20 °C prior to chemical analysis. All air-dried subsamples of sediments and freeze-dried guano and algae samples were homogenized by grinding after the careful removal of large rock fragments and biological remains such as bone pieces, seal hairs, penguin downy feathers and eggshells, and the final powder samples were passed through a 74 µm mesh sieve.

Total Hg contents were analyzed by atomic fluorescence spectrometry (AFS-930, Titan Instruments Co., Ltd.) with a detection limit of 0.02 ng/g. For Hg, 0.1 g subsamples were precisely weighed and digested (H₂O₂-Fe³⁺ oxidant-HNO₃) in colorimeter tubes with electric heating (see Sun et al., 2006a for detailed methodology). Phosphorus concentrations were analyzed by inductively-coupled plasma-optical emission spectroscopy (ICP-OES, Perkin Elmer 2100DV). For P, 0.25 g subsamples were precisely weighed and acid digested (HNO₃-HF-HClO₄) in Teflon

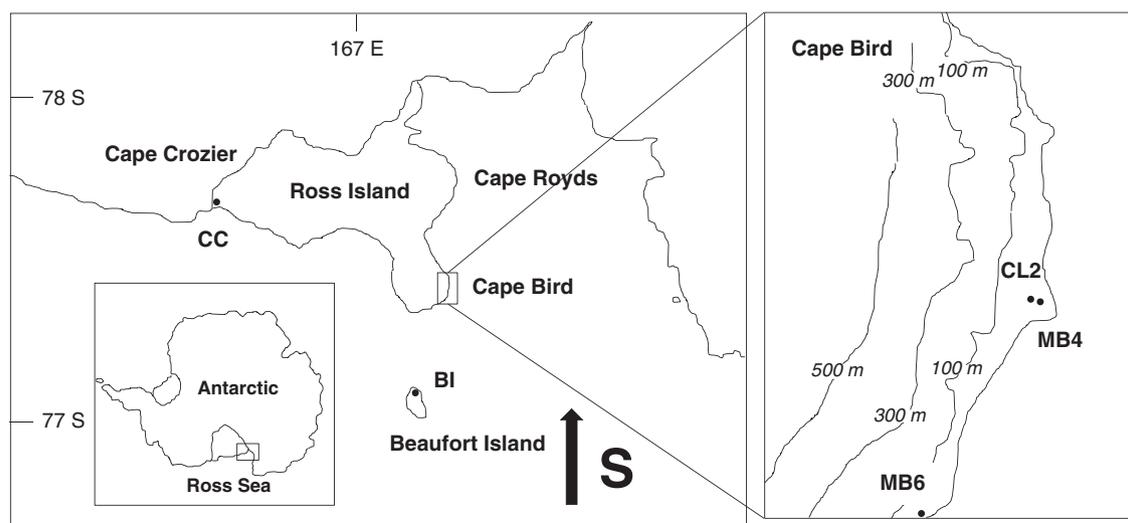


Fig. 1. Map of Ross Sea region showing the sampling sites on Cape Bird, Cape Crozier and Beaufort Island.

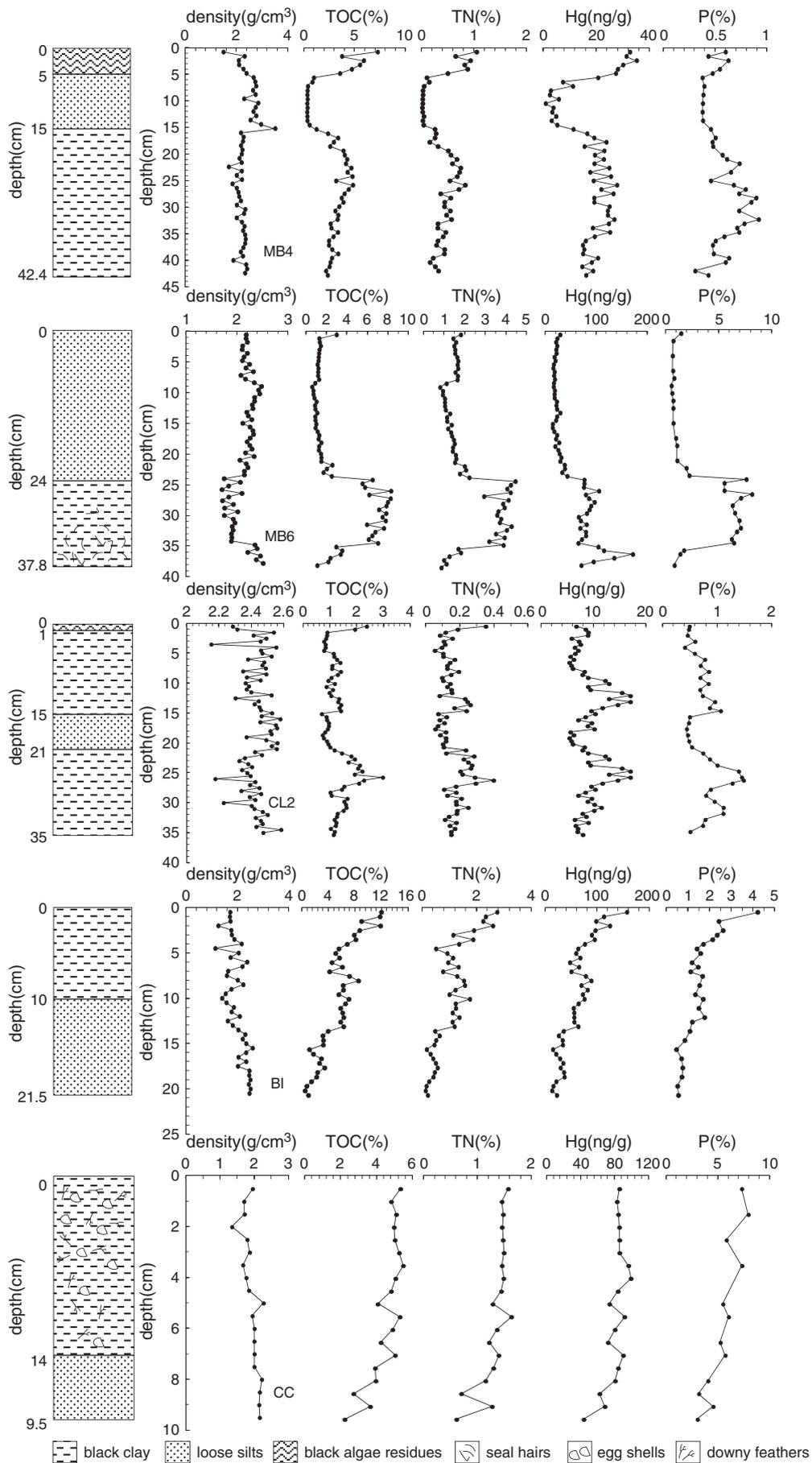


Fig. 2. Variations of dry density, TOC, TN, Hg and P contents in sediment profiles MB4, MB6, CL2, BI and CC versus depth.

tubes with electric heating (Liu et al., 2006). Measurements were conducted at constant solution volume on both AFS and ICP-OES. Nitrogen content analysis was performed on an element analyzer (Vario EL III) with a relative standard deviation (RSD) less than 1%. The chemical volumetric method was employed to measure total organic carbon (TOC) with a relative standard deviation less than 0.5% (Xu et al., 2011). Reagent blanks and standard reference materials (Chinese standard reference material GBW 07403 and 07302 for Hg; GBW 07415 for TOC; high-purity monopotassium phosphate solution for P; Vario EL III build-in standard reference material for TN) were included in every batch of samples for quality control and the results from the analyses were consistent with the reference values with a RSD less than 0.5%. Densities of the profiles were measured by the water displacement method (Cruden and Lu, 1992). Seal hair number was counted according to Hodgson et al. (1998) and Sun et al. (2004): 1 g dried samples were weighed and washed through 125 μm sieve, and then the residues were moved to petri plates and seal hairs were manually counted using a magnifying glass.

3. Results and discussion

3.1. Effect of penguin guano on Hg distribution

Basic physical/chemical proxies including Hg, TOC, TN, P and density for the five ornithogenic sediment profiles are shown in Fig. 2. TN displays the same trends with TOC, indicating its affinity to sedimentary OM, while density curves are generally opposite to that of TOC. To our knowledge, organic matter is lighter than the weathering products of bedrock. Thus, the opposite correlation between density and TOC down the profiles likely reflects the mixture of weathered soil and organic matter in the sediments.

For soil Hg content, local volcanoes are an important natural source that needs to be considered. There are two volcanoes on Ross Island: Mt. Erebus and Mt. Terror. According to Siegel et al. (1980), fallouts from such fumarolic sites can become a steady local gaseous Hg source. Yet the air Hg/soil Hg ratio is much lower at Ross Island (0.67) than that of similar sites such as Iceland (10.8) and Hawaii (6.5), suggesting a poor deposition process of Hg from the air. Their further research (Siegel et al., 1981) found that sediments, clay and rock powders at Ross Island have very high Fe/Hg compared with terrestrial materials from other continents, corroborating the fact that the air Hg in this region mainly disperses into the southern hemisphere air mass. With a low air Hg concentration (about $0.55 \pm 0.28 \text{ ng/m}^3$ at Ross Island, De Mora et al., 1993; $0.9 \pm 0.3 \text{ ng/m}^3$ at Terra Nova Bay, Sprovieri et al., 2002) and a weak deposition of Hg, the volcanoes should have little influence on local sedimentary Hg.

Interestingly, Hg and TOC are found to have similar change trends in the sediment profiles. To better estimate their similarity, correlation analysis was employed. As shown in Fig. 3, MB6 (in this section, we refer only to the upper 35 cm in MB6), BI and CC all show significant positive Hg–TOC correlations ($R > 0.90$, $P < 0.01$), while MB4 is a bit weaker in Hg–TOC correlation with $R = 0.89$, and CL2 even lower at $R = 0.52$. Organic materials in soil and sediments are believed to be an effective sorbent for Hg (Bargagli et al., 1993; He et al., 2007), and positive correlations between TOC and Hg were often found in studies on Hg distribution in fresh water lake and estuarine sediments (Campbell et al., 2003; Ethier et al., 2010; Lindberg and Harris, 1974). It is likely that Hg and OM have similar sources and transport pathways. It has also been recognized that gaseous Hg^0 in the atmosphere can be oxidized to $\text{Hg}(\text{II})$ (mostly by the reactive halogen in the aerosol at the coastal area) and then bond to OM, forming stable complexes (Bargagli et al., 2007; Meili, 1991). Either way, sedimentary Hg and OM should display a strong positive correlation as observed. TOC levels in MB4 and CL2 are much lower than those in the other three profiles. We believe that less OM input leads to weaker Hg absorption in the sediments, and in turn results in less significant Hg–TOC correlation.

Because our sampling sites are located primarily in ponds and catchments near active and abandoned penguin colonies, they are likely influenced by the activities of the penguins via guano input around the sampling sites. Moreover, fresh water algae are widespread in our study area (Broady, 1989), especially in the guano-affected water bodies where nutrient supply is sufficient. Here, the sediments are mainly composed of weathered soil, guano, and algae. Correlations between Hg and TOC have revealed OM as the carrier for Hg, but the relative magnitude of contribution from the three end-members still needs to be determined. For this reason, we analyzed Hg, TOC and P in the end-member environmental media (Fig. 4). The results illustrate that the TOC level of soil is less than 1%, algae has TOC around 10% while guano has about 30%. Apparently TOC in the sediments is derived primarily from guano and algae. In addition, the soil samples have an average Hg concentration as low as 5 ng/g ($\text{SD} = 4.10 \text{ ng/g}$, $n = 7$; Fig. 4), indicating that the high Hg in the sediments originates from exogenous inputs instead of direct influence from atmospheric deposition. Guano and algae have much higher Hg content, up to about 150 ng/g ($\text{SD} = 8.73 \text{ ng/g}$, $n = 3$) and 30 ng/g ($\text{SD} = 14.56 \text{ ng/g}$, $n = 6$), respectively. On a mass basis, a greater influence from guano rather than algae on Hg in the sediments can be expected. Such large differences in Hg concentration between guano and algae result from the distinct Hg enrichment paths. Most Hg that enters into the organisms is assimilated. Due to the bio-magnification, organisms feeding in high trophic levels generally have higher Hg content relative to those feeding at lower trophic levels (Bargagli et al., 1998a). Bargagli et al. (1998b) reported that although the Hg contents in lower trophic organisms are below the global average values, high trophic level animals in Antarctica have Hg contents no different from those in other regions of the world. In Antarctica, penguins are among the top predators and their guano contains relatively high Hg concentrations (Ancora et al., 2002; Choy et al., 2010; McArthur et al., 2003). As an OM source, when the guano is deposited, it could also absorb $\text{Hg}(\text{II})$ from the environment. Therefore, penguin guano is one of the critical factors influencing Hg distribution in Antarctic ornithogenic sediments (Yin et al., 2008). In contrast, Hg in algae is mainly a result of bio-accumulation from direct uptake of $\text{Hg}(\text{II})$ from solution through cellular surfaces and water (Siegel et al., 1980), and is thus much lower than in guano.

Since total Hg contents in guano and algae are obviously different, a proxy capable of distinguishing their contribution of Hg in the sediments is needed. Research on ornithogenic sediments has found that phosphorus (P) is a typical bio-element for penguin guano input (Huang et al., 2009; Liu et al., 2006; Sun et al., 2000; Xu et al., 2011). Analysis on environmental media indicates that guano has P content up to 5.25% ($\text{SD} = 0.28\%$, $n = 3$), while the values in algae and bedrock are one order of magnitude lower (Fig. 4), suggesting that the P level in the ornithogenic sediments is predominantly influenced by the input of guano. Thus, we used P content to represent the amount of guano input into the sediments.

A TOC–P correlation test (Fig. 3) was performed for OM source determination. MB6, BI and CC have a significant positive TOC–P correlation with $R > 0.91$, indicating the dominance of guano in OM. The correlation becomes a little weaker in CL2, but it still has a relatively high correlation coefficient ($R = 0.71$). MB4 has the lowest TOC–P correlation in all five profiles with $R = 0.55$. Average TOC and P contents are plotted in Fig. 5a for comparison. As can be seen, CL2 and MB4 have similarly low P values, but TOC in MB4 is apparently higher than CL2. We suggest that the pond algae likely made a larger contribution to the OM composition in MB4 compared to CL2. In the barren East Antarctic where an oligotrophic environment is natural, guano can serve as the main nutrient source in catchments at our sampling sites. The bio-mass of algae in the sediments is controlled by guano input, and it is reasonable to believe that the algal mass should display the same fluctuation with P throughout the sediment profiles. Under such circumstances, a relatively larger algae proportion in TOC does not affect the positive correlation between TOC and Hg

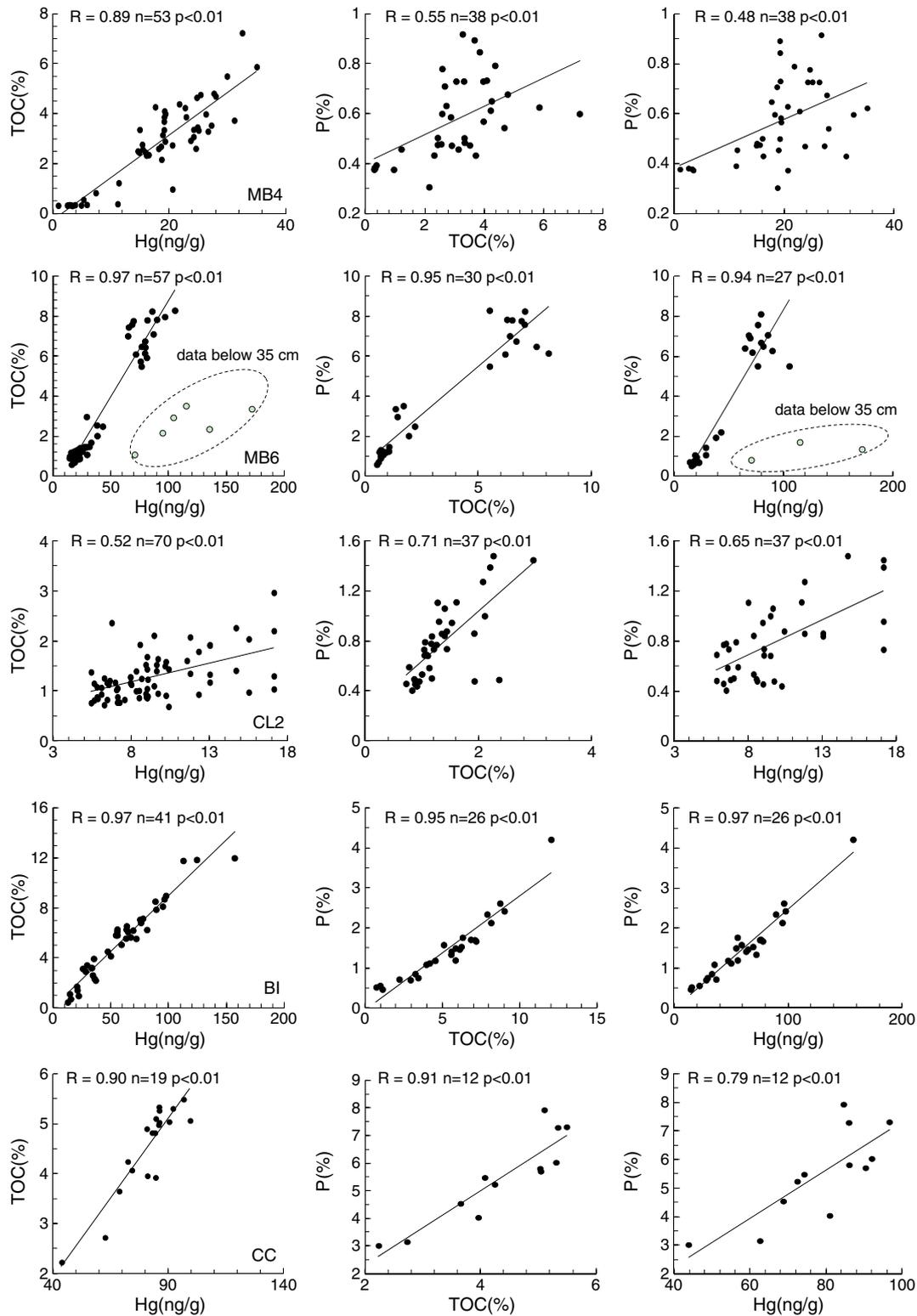


Fig. 3. Correlation tests on TOC–Hg, P–Hg and P–TOC in sediment profiles MB4, MB6, CL2, BI and CC.

($R=0.89$ in MB4). Compared with heavily guano-affected MB6, BI and CC as well as relatively low guano-containing CL2, algae in MB4 has a greater contribution to TOC.

The correlation between P and Hg was evaluated to differentiate between the influence from guano–Hg and algae–Hg. We found that the Hg and P contents in MB6, BI and CC are strongly correlated, with R reaching 0.94, 0.97 and 0.79 respectively, while the Hg–P correlations in MB4 and CL2 are relatively weak, with $R=0.48$ and 0.65,

respectively (Fig. 3). Higher Hg and P contents were observed in MB6, BI and CC (Fig. 5b), consistent with stronger Hg–P correlations. Higher P is indicative of more guano input and greater influence from guano on Hg. In core CL2, relatively low guano input is responsible for the less significant Hg–P correlation. Compared with CL2, higher Hg in MB4 is attributed to the higher algae-derived TOC as discussed above and this further weakens Hg–P correlation, making it lower than CL2. Therefore, Core MB6, BI and CC have high Hg contents which are primarily caused

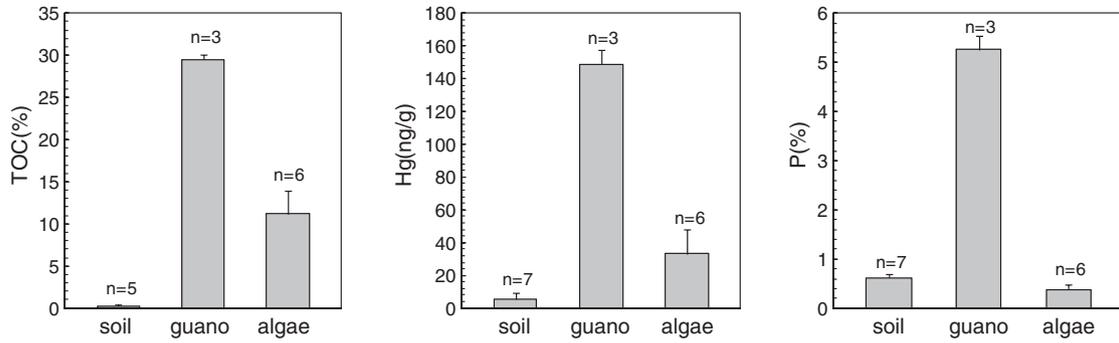


Fig. 4. Levels of Hg, TOC and P in the environmental materials including soil, fresh guano and fresh algae collected from the study area.

by guano input; CL2 and MB4 are low in Hg due to less guano influence; and, relatively larger algae contribution to TOC in MB4 weakens the dominance of guano over Hg.

3.2. Possible effect of seal excrements on Hg distribution

TOC and P in the sediment profile MB6 begin to drop at 35 cm, whereas Hg exhibits a sharp increase and reaches 172 ng/g at 36 cm (Fig. 2). According to the lithological record, well-preserved seal hairs begin to appear below 32 cm, indicating seal influence on the sediments. Seals may feed at the same or higher trophic levels than penguins, so the Hg biomagnification is expected to be equal or greater in seals than in penguins. It has been reported that Hg content in Elephant Seal excreta is 310.7 ± 9.3 ng/g, while that in Adélie penguin guano is 73.3 ± 9.5 ng/g (De Moreno et al., 1997; Bargagli et al., 1998b). Considering its high concentration, the extremely high Hg levels in the bottom section of MB6 might be caused by the input of seal excreta.

To test this hypothesis, two proxies including seal hair number (SHN) and TOC/TN (molar ratio) were employed. SHN in the sediments is directly linked to the former seal population and thus can be used as a

proxy for seal excreta input (Hodgson et al., 1998; Sun et al., 2004). The result (Fig. 6) shows that SHN between 32 and 38 cm follows a similar trend with Hg: SHN is low above 35 cm, but increases quickly and reaches the peak at 36 cm, and then displays a decreasing trend. TOC/TN of seal excreta (about 6) is generally higher than penguin guano (about 2.5; Sun et al., 2006b), thus the dominance of seal instead of penguin in the sampling area could lead to a rise of TOC/TN in the sediments influenced by seal excrements. TOC/TN is also in good correlation with Hg, including the bottom section with $R = 0.92$ ($p < 0.01$; Fig. 6). We suggest that there were once a small number of seals near the sampling site of MB6, just as the bottom section recorded. When the population of seals decreased, a large group of penguins occupied the site and formed their colony there. Due to the difference in population scale, the input of penguin guano is much more than the seal excreta, resulting in the low values of TOC beneath 35 cm. But in spite of its low amount, the high Hg in seal excreta could still cause the Hg peak between 35 and 38 cm. The relatively high Hg in the bottom section of core MB6, therefore, is probably caused by seal excreta, and reveals the potential of sedimentary Hg content as a proxy to trophic level change of the inhabitants in the area.

3.3. Preliminary Hg pollution assessment

Occurrence of Hg in the sediments likely indicates a possible threat of pollution, thus we employed an enrichment factor (EF) to assess the degree of influence that guano and seal excrement may impose upon sedimentary Hg. EF is a useful index to estimate the impact of an exogenous target element by choosing a normalization element to alleviate the variations produced by heterogeneous sediments and other lithogenic effects (Braga Bueno Guerra et al., 2011). Here we chose Ti as the normalization element because of its high concentration and relatively small variability in the sediment profiles. EF is calculated using the following equation:

$$EF = \frac{M_x \times Ti_b}{M_b \times Ti_x}$$

where M_x and M_b are concentrations of Hg in the samples and background references, respectively; Ti_x and Ti_b are concentrations of Ti in the samples and background references, respectively. Previous to the calculation of EF, a proper mercury background reference value needs to be determined. We compared the local background value of this study (Hg content of “soil” constituent = 5.28 ng/g in Fig. 4) with various geological materials, and found it among the lowest ever reported, almost the same as the Hg content determined by Negri et al. (2006) in the uncontaminated nearshore sediments of McMurdo Sound (6 ng/g). It is also consistent with the investigation of metal baseline conducted on basalt-derived soil and scoria (<20 ng/g) from McMurdo Station (Crockett, 1998). Mafic rocks (10 ng/g, Turekian, 1977) overlap with the local background value as well, as most bedrock in our study area consists of “basaltic” volcanic debris (Crockett, 1998; Sun and Hanson, 1975). As for the commonly used average shale (400 ng/g, Turekian and Wedepohl, 1967) and crustal mean values (80 ng/g, Taylor, 1964),

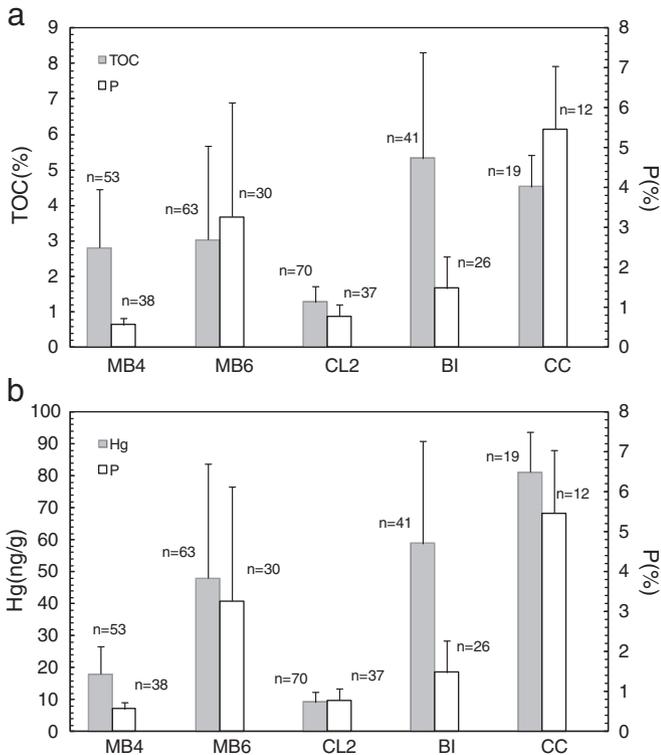


Fig. 5. Comparison of TOC (a) and Hg (b) with P contents in sediment profiles MB4, MB6, CL2, BI and CC.

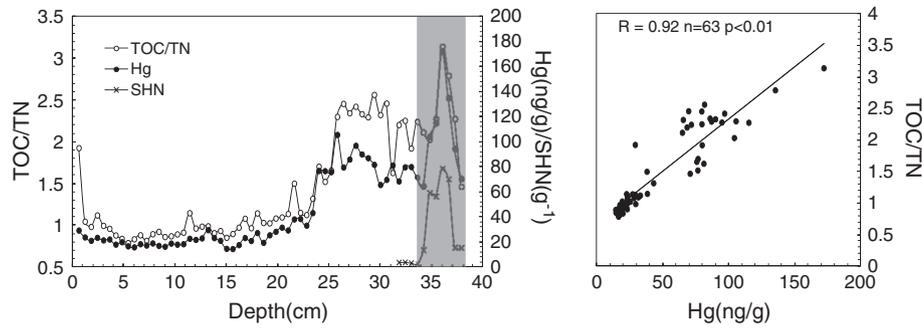


Fig. 6. Changes of Hg, TOC/TN and seal hair number (SHN) in the MB6 sediment profile and their correlation analysis.

they do not seem to be the best option for our study area because of their relatively high value compared with the local background reference. In fact, using world mean values has been criticized due to their failure to function in specific coastal areas (Gibbs, 1993). Local equivalent geo-materials such as sediment and bedrock in a pristine region should provide a more accurate measurement (Rubio et al., 2000).

EF was calculated by local background reference for the five profiles (Fig. 7). As can be seen, the sediment profiles could generally be divided into two groups: MB6, BI and CC, which were strongly influenced by guano input, receive high scores in EF, while MB4 and CL2, with less penguin influence are rather low. This result corroborates our previous perspective that guano is the main source of Hg and ornithogenic sediments in Antarctica are important Hg depositories. Though EF scores in MB6, BI and CC were high, they may only be interpreted as a result of effective Hg enrichment due to the large penguin and seal guano input instead of severe Hg pollution.

To better assess the possible degree of Hg pollution, we compared our data with the Hg concentration of equivalent soil, ornithogenic sediments and marine sediments around Antarctica from the literature (Table 1). This comparison indicates that the data from Antarctica vary due to the geochemical features at different sites, and most of the total Hg content in the present study is comparable to the levels reported at King George Island and the Weddell Sea in West Antarctica, and the Ross Sea region, North Victoria Land, in East Antarctica, suggesting that high EF doesn't necessarily mean extreme Hg content. We also compared our data with several widely used SQGs (sediment quality guidelines) including ERL (150 ng/g) and ERM (710 ng/g), TEL (174 ng/g) and PEL (486 ng/g, Long et al., 1995; MacDonald et al., 1996). SQGs were sets of standards determined by multiple existing data base for eco-toxicological response of benthic organisms, which can serve as warning levels for sedimentary environment (Long and MacDonald, 1998). ERL (effects range-low) and ERM (effects range-medium) stand for the concentration of selected pollutant with 10th and 50th percentile of effect data set (EDS). TEL (threshold effect level) and PEL (probable effect level) are calculated by adding a none effect data set (NEDS) to include extra information in defining the relationship

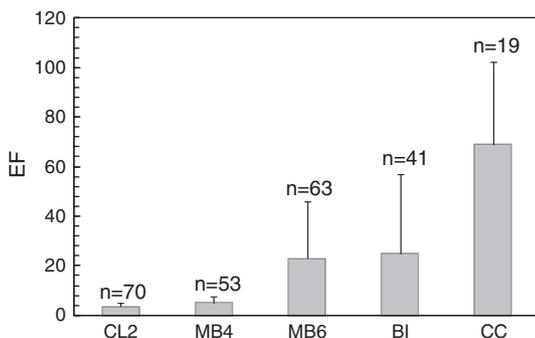


Fig. 7. Enrichment factor (EF) calculated by local background reference in sediment profiles MB4, MB6, CL2, BI and CC.

between pollutants and adverse biological effects. All SQGs mentioned above are used to classify the sediments into three levels: 1) rarely (\leq ERL/TEL), 2) occasionally ($>$ ERL/TEL and \leq ERM/PEL), or 3) frequently ($>$ ERM/PEL) associated with adverse effects. According to the classification standards, only two subsamples in our study exceed ERL (one in MB6 and one in BI with Hg = 172 and 157 ng/g, respectively) in all five profiles. Thus, in spite of high enrichment in Hg caused by guano and seal excreta input, compared to local background values adverse ecological effects on microorganisms or algae seem unlikely in the study area with extremely cold climate. SQGs were only recently applied to sediments from Antarctica (Guerra et al., 2011), and still require optimization to the extreme local environments. Moreover, since krill and fishes in penguin and seal diet and excreta might undergo methylmercury (MeHg, the most toxic organic mercury compounds) bio-magnification in the marine environment, the sediments influenced by penguin guano may have a high MeHg level. However, methylmercury level in the sediments was not determined in the present study. Here the pollution assessment of total Hg by SQGs is only a preliminary result and more data will be needed in future research.

At McMurdo Station, some subsamples of profile MB6, BI and CC contain higher Hg than the sediments with heavy anthropogenic impact from near the station sewage outfall (74 ng/g, Negri et al., 2006), suggesting that the Hg enrichment from bio-vectors in the penguin colonies may have exceeded the effect of human influence in the Ross Sea region. To date, increasing penguin populations have been observed in the Ross Sea region due to the continuous climate warming for the last 50 years (Ainley et al., 2005; Croxall et al., 2002; Wilson, 1990). Should this trend continue, the future threat of heavy metal impact on the terrestrial ecosystem from bio-vectors such as penguins and seals should not be overlooked.

4. Summary and conclusion

Based on our geochemical analyses of five sediment profiles from the Ross Sea region, Hg was found to be closely related to OM input, indicating the role of OM as an Hg carrier. After further comparison with environmental media and correlation tests between P and Hg, guano was then determined as the main factor influencing Hg contents. The larger contribution of algae to OM composition in profile MB4 weakens the P–Hg correlation, indicating the influence of algae on Hg distribution to some extent. The consistent peak values of Hg, TOC/TN and SHN in the bottom layer of MB6 verified seal excreta input, implying the potential of Hg as an index for changes of animal trophic-level in the sedimentary layers. Hg levels in MB6, BI and CC are highly enriched according to EF values, indicative of guano as the controlling factor of Hg deposition. However, analysis of SQGs suggests that the highly enriched Hg is partly due to the very low background values and the present Hg levels seem to have little adverse ecological effect. Our study suggests that in the pristine environment of the Ross Sea region, bio-vectors such as penguins and seals are an important pathway for pollutant transport from marine to terrestrial environments, and this particular

Table 1
Comparison of Hg concentration in carriers from different locations in Antarctica.

Location	Geologic materials	Range/mean (ng/g)	Reference
Admiralty Bay, King George Island	Marine sediments	53–210	Favaro et al. (2004)
Admiralty Bay, King George Island	Soil and costal sediments	16.3–29.9	Dos Santos et al. (2006)
King George Island	Ornithogenic sediments	35.5–100/54.8	Sun et al. (2000)
Weddell Sea shelf	Marine sediments	14–44/22.4	Niemistö and Perttilä (1995)
North Victoria Land	Soil	7–96/34	Bargagli et al. (1993)
Terra Nova Bay	Marine sediments	6–27/12	Bargagli et al. (1998b)
North Victoria Land	Surface soil	12–86/31	Bargagli et al. (2005)
North Victoria Land	Marine sediments (<2000 µm)	11–85/41.86	Riva et al. (2004)
Ross Sea region	Marine sediments	8–34/17.09	Williams et al. (1974)
McMurdo Station Sewage outfall	Costal sediments	63–87/74	Negri et al. (2006)
MB4	Ornithogenic sediments	0.92–35/18.14	This study
MB6	Ornithogenic sediments	14.39–172.06/48.03	This study
CL2	Ornithogenic sediments	5.44–17.09/9.43	This study
BI	Ornithogenic sediments	12.88–157.1/58.88	This study
CC	Ornithogenic sediments	43.83–99.49/81.2	This study

pathway strongly influences the geochemical characteristics of local sediments and pond ecology.

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