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Hg distribution and speciation in Antarctic soils of the Fildes and Ardley peninsulas, King George Island

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Abstract: Data on the content and speciation of mercury (Hg) in the soils of Antarctica are scarce and vary greatly between the regions studied, but overall Hg concentrations found were generally very low. We investigated the Hg quantity and speciation by solid-phase Hg pyrolysis and chemical fractionation in selected maritime Antarctic soils, comparing ornithogenic and non-ornithogenic areas of the Fildes and Ardley peninsulas of King George Island. The total Hg contents ranged from 4.3–256 ng g^{-1}, and values for ornithogenic soils were the highest recorded for Antarctic soils. A close correlation between Hg and organic matter was observed in the ornithogenic soils, with levels decreasing with depth. In the non-ornithogenic soils, a correlation between Hg content and soil depth was also observed, but the values were found to increase with depth. Thermograms showed that all Hg was in the 2^+ oxidation state and was predominantly linked to organic matter, corroborating the chemical fractionation results for the ornithogenic soils. These results show the need for further refined studies about the interactions of Hg with organic matter in order to better understand the biogeochemistry of this metal in the Antarctic environment.

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Key words: direct mercury analyser, Hg contamination, ornithogenic soils, soil analysis, total mercury

Introduction

Environmental sources of mercury (Hg) can be either natural or anthropogenic. The natural concentration of Hg in rocks, sediments and soils varies between 0.08 to 0.4 mg kg^{-1} (Gu *et al*. 1998). Elemental Hg is rare in nature, although there are several Hg-containing minerals, cinnabar (mercuric sulphide) being the most common in the terrestrial crust (Bowen 1979). Burning fossil fuels is the main anthropogenic source of Hg in the atmosphere (Lacerda 1997).

Although Antarctica is the most isolated continent, it is not free of contamination from human activities. The contribution of anthropogenic Hg to the continent may originate from distant sources through atmospheric transport across low latitudes or by ocean currents. Some sources of Hg may also arise from human occupation of the continent by incineration of garbage from scientific stations as well as from paints, fuels and sewage (Santos *et al*. 2005).

There are few studies concerning the presence of Hg in the Antarctic, with most related to atmospheric transport and its environmental fate (Vandal *et al*. 1993, Bargagli *et al*. 2007). Springtime Hg depletion events, first observed in the Arctic, were also proven to happen in Antarctica. During these events, elemental Hg, the main species present and transported in the atmosphere, is photochemically oxidized by reactive halogens in the Polar Regions, after which enhanced deposition as ionic Hg species takes place (Ebinghaus *et al*. 2002, Witherow & Lyons 2008, Nguyen *et al*. 2009).

Hg and other metals have been extensively studied in biological matrices of marine organisms, but little data from terrestrial Antarctic environments are available. Santos *et al*. (2006) quantified the total Hg (HgT) in soils and sediments on King George Island and found very low values, in the range of 15–30 μg kg^{-1}. Crockett (1998), studying red and gley soils around McMurdo Station (Hut Point Peninsula) reported background levels of Hg < 40 μg kg^{-1}. Sun *et al*. (2006) also quantified HgT in seal hair from a lake core and proposed that the accumulation of Hg in this material is related to the five main periods of global gold mining in the last two thousand years.

It is well known that the determination of HgT is insufficient for understanding its biogeochemical cycle, whereas research on the environmental risks and on Hg speciation in different matrices is extensive. Sequential chemical extractions, X-ray atomic absorption (Sladek *et al*. 2002, Kim *et al*. 2003) and liquid or gas chromatography coupled with many techniques of detection (e.g. mass spectrometry, solid-phase Hg pyrolysis and Cold Vapour Atomic Absorption Spectrometry (CV-AAS)) are examples

of techniques currently used to investigate Hg speciation. The identification of elemental Hg by X-ray absorption spectroscopy is difficult (Vandal *et al*. 1993), as its detection limit is too high (Kim *et al*. 2003). Techniques for determining the specific short-chain organomercury compounds usually involve many steps and sophisticated equipment. According to Sladek *et al*. (2002), solid-phase Hg pyrolysis and CV-AAS is the most appropriate technique for identifying elemental Hg as well as for differentiating it from ionic Hg bound in solid matrices. This technique identifies Hg species by controlled heating and comparison with thermodesorption patterns of known Hg substances and has been commonly used to investigate Hg phases in soils and sediments (Windmöller *et al*. 1996, Biester & Zimmer 1998, Biester *et al*. 2000).

This study aims to provide information about the presence of Hg in soils from Maritime Antarctica. This was accomplished by the determination of HgT in different soil types from the Fildes and Ardley peninsulas (King George Island) and correlating these data with physical and chemical characteristics of the soils. We also studied the metal speciation using solid-phase Hg pyrolysis and CV-AAS, as well as by chemical fractionation.

Materials and methods

Soil sampling and preparation

Eighty-six soil samples (ranging from 0–80 cm in depth) were collected on the Fildes (F samples) and Ardley (A samples) peninsulas on King George Island, South Shetland Islands. Most profiles were collected up to 50 cm due to shallow permafrost occurrence below this depth. The soil was collected and stored in plastic bags at -5°C.

Ornithogenic ecosystems are observed in many areas of the Ardley Peninsula. They are formed by deposition and accumulation of bird excreta, mostly by penguins, known as guano (Simas *et al*. 2007). In these soils, we also find penguin remains including bones, feathers, and decomposing bodies. Hence, ornithogenic soils have high organic matter (OM) content, high phosphate concentrations and show formation of secondary phosphates with metals released from the weathering rock matrix (Kuo 1996, Simas *et al*. 2007, 2008). Biogenic soils here refers to soils under the influence of other marine animals, such as seals (elephant seals, Weddell seals, crabeaters, fur seals).

The non-ornithogenic soils considered in this study are mainly composed of decomposition products of basalt and andesite-basalt mineral rocks with no apparent contribution of organic matter from birds or marine animals, but show development of mosses on the soil surface.

For comparison, we collected 20 ornithogenic soil profiles, one biogenic soil profile and nine non-ornithogenic soil profiles, as shown in Appendix A. The geographical location of soil profiles are also presented in the same appendix.

Soil samples were air-dried, sieved through a 2 mm sieve and ground in a tungsten mill to produce a sample with < 200 mesh particle size, used for all subsequent analysis. The samples were taken at a depth where it was possible to sample "soil", below these depths, only fragments of rock or permafrost were present. This is why different sample depths had to be acquired for the profiles. Because it was not possible to visually differentiate the horizons in the soil, we established equal (20 cm) intervals of depth to test, as defined in Appendix B by the letters, a, b, c, d and so on, to ensure the observation of gradual changes within the soil profile.

Soil characterization analysis: total phosphorus, available phosphate and carbon, hydrogen and nitrogen determination

These analyses were performed in all samples. Total phosphorus (P_{total}) was determined by X-ray fluorescence spectrometry using an EDX 720 instrument (Shimadzu, Japan). A certified reference material, GBW07408 (soil), was also analysed to evaluate the accuracy. The experimental result was $P_{total} = 0.18\%$ ($n = 1$), and the certified values is ($P_{total} = 0.18 \pm 0.01\%$). Available phosphate ($P_{available}$) was extracted using a Mehlich-1 solution (H_2SO_4 0.05 mol l^{-1} + HCl 0.05 mol l^{-1}) and was quantified by the ascorbic acid method, according to Kuo (1996). Total C, H and N (CHN) content were determined using a Perkin-Elmer CHNS/O model 2400 CHNS. All results obtained for the measured cystine standard were between 98.9 and 106.73%, showing good accuracy for this method.

HgT determination

The determination of HgT was performed on all collected samples by direct analysis using a Milestone Direct Mercury Analyser (DMA-80). The sample masses ranged between 100 and 300 mg. The sample was subjected to a heating program with the following steps: drying at 200°C, pyrolysis at 650°C where the sample matrix burned and the released Hg is carried by a stream of O_2 and retained in a gold trap. Finally the gold trap is heated and the Hg is released into an atomic absorption cell. The great advantage of this equipment is that it precludes a sample extraction step, resulting in less possibility for sample contamination. The reference materials GBW-08301 (river sediment) and IAEA-336 (trace elements in lichens) with Hg concentrations 220 ± 40 ng g^{-1} and 200 ± 40 ng g^{-1}, respectively, were used to evaluate the accuracy of the method. The certified reference material IAEA-336 was used because we have some soil samples with large amounts of algae and lichens, observed during sample collection. Examples are samples A2a, A2e, and A11a.

The detection limit (LOD) was calculated according to IUPAC (International Union of Pure and Applied Chemistry) recommendation, by taking three times the ratio of the

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standard deviation of ten independent blanks and the slope of analytical curve. For the quantification limit (LOQ), the same ratio was multiplied by ten. The results of LOD and LOQ were, respectively, 1.04 and 4.32 ng g^{-1}.

The analytical technique used enable differentiation of the different sample types. The equipment used has three cells with different optical paths for readings at different concentration ranges. Therefore it provides three analytical curves, cell 0, cell 1 and cell 2. The data curves were for cell 0, concentration range 0–12 ng, 7 points, equation curve $Y = -0.0026\ X^2 + 0.0907\ X + 0.0008$ and $r^2 = 0.9999$; for cell 1, concentration range 0–20 ng, 10 points, equation curve $Y = -0.0006\ X^2 + 0.0421\ X - 0.0025$ and $r^2 = 0.9962$; and for cell 2, concentration range 50–1000 ng, 5 points, equation curve $Y = -0.0000002\ X^2 + 0.0008\ X + 0.0018$ and $r^2 = 1$. Since the adjustment is not linear the number of points is large enough that the value of r^2 is suitable for quantitative analysis (at least two nines), as can be seen. Virtually all the readings of the samples fell into the equations of cell 0 and cell 1, only the readings of the samples of seal hair fell into the cell 2. For the calculation of LOD and LOQ was made linear fit of the lowest points of the curve of the cell 0, whose slope was 0.07542. Results of recovery for reference materials varied from 99–104%, with an average precision of 4%. The results of the two reference materials were as follows: GBW-08301 (river sediment), certified value 220 ± 40 ng g^{-1}, experimental value 223 ± 4 ng g^{-1} ($n = 3$); and IAEA336 (trace elements in lichens) certified value 200 ± 40 ng g^{-1}, experimental value 210 ± 6 ng g^{-1} ($n = 3$). The precision obtained was good, the relative standard deviation of all results (Appendix B) were in the range of 0.17–11%, with a mean value of 4.2%.

Statistical data analysis

Data were analysed using STATISTICA, version 6.0, for linear correlations (Pearson correlation) between the studied physico-chemical parameters and Hg contents (variables). Multivariate analysis through hierarchical cluster analysis (HCA) was performed by MINITAB, version 14, to classify the samples according to the values of a set of variables and to generate dendrograms. Ward's linkage method and Euclidean distance were used. The data were mean centered and autoscaled to a variance of 1. Only the samples with all parameters analysed were included in the statistical analysis.

Hg chemical fractionation

Chemical fractionation of Hg was performed on a subset of samples with expressive Hg content: F9a, F11b (also analysed by solid-phase Hg pyrolysis), A28d and A28a, which corresponds to the surface and subsurface layers, primarily consisting of penguin guano. The F11b sample was analysed in two ways: i) fresh, or ii) only seal hair present in the sample. This method, proposed by Bloom *et al*. (2003), was developed specifically to analyse the mobility of Hg in matrices of soils and sediments. The following extractors were used: (S1) deionized water (30 ml), (S2) 0.1 M CH_3COOH + 0.01 M HCl (40 ml), (S3) 1 M KOH (40 ml), (S4) 12 M HNO_3 (40 ml) and (S5) aqua regia (1 HNO_3: 3 HCl) (10 ml).

An initial sample mass of 3.0 g was used. It was shaken for 18 ± 4 hours in a shaker at a speed of 30 rpm, with each extractant. Each extractation step was centrifuged for 20 mins at 3000 rpm, and the supernatant liquid was analysed by a Direct Mercury Analyser (DMA). The solid residue remaining from each step was washed twice with deionized water before the addition of the next extractant.

It was not possible to analyse samples with Hg low levels (< 100 ng g^{-1}) because the extracts obtained in the fractions showed Hg concentrations below the detection limit for our instruments.

Hg species determination by solid-phase Hg pyrolysis and CV-AAS

The samples were analysed by a solid-phase Hg pyrolysis and CV-AAS system described in previous works (Valle *et al*. 2005, 2006). Sample F9a, (collected at the soil surface) with ornithogenic influence, and sample F11b, a surface A horizon of a profile collected on a marine terrace and containing a visible abundance of seal hair, were chosen because of their high Hg concentrations (215 ± 4 and 256 ± 4 ng g^{-1}, respectively). Sample F11b was analysed in three ways: i) fresh, ii) free of seal hair, and iii) only seal hair. Separation of the seal hair was performed manually with tweezers. An atomic absorption spectrometer (CG Analytica, GBC Model 380) coupled to a thermodesorption furnace was used to evaluate the Hg phases present in the matrix. This system heats the sample from ambient temperature to about 600°C at a constant heating rate (33°C min^{-1}) (Windmöller *et al*. 1996, Valle *et al*. 2005). The vapours released are brought to a cell of an atomic absorption detector by a nitrogen stream. The graphics obtained in units of absorbance as a function of temperature are called thermograms. Sample masses up to 3 g were used in the analysis with at least three replicates of each sample. The differentiation between Hg^0 and Hg^{2+} present in the samples was made by comparison of these profiles with others from previous studies using the same equipment and the same analytical conditions (Valle *et al*. 2006).

Results and discussion

Soil characterization

The soil samples contained total C, H, N content ranging from 0.09–23.23%, 0.23–6.15% and 0.05–9.12%, respectively. The ornithogenic soil profiles showed the highest C and N values (Appendix B), as expected from previous studies (Michel *et al*. 2006, Simas *et al*. 2007). The heavy use of the terrestrial environment by penguins every year results in high

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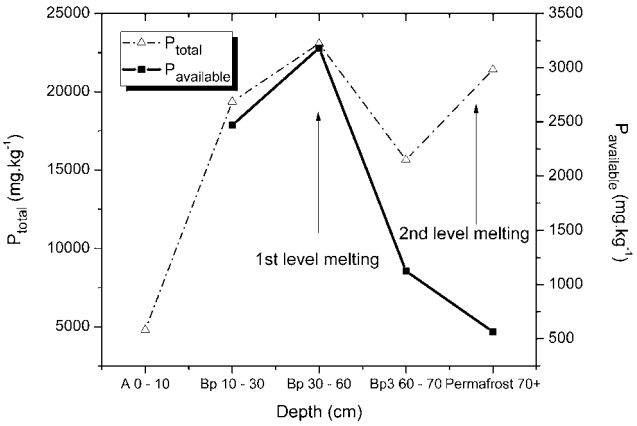

Fig. 1. Concentrations of P_{total} and $P_{available}$ in the profile for sample A2.

deposition of organic material and nutrients (guano and bird remains) containing especially C, P and N. The total P content can be used to indicate the degree of ornithogenic influence in the local soil environment. In the studied soils, the total P content ranged from 249–89 461 mg kg^{-1} which reflects soil development, especially with regards to phosphatization (Simas *et al*. 2008).The other soil samples, with less ornithogenic influence, showed much lower C, N and P contents, as expected.

The organic matter derived from penguin guano is rich in phosphates and goes through a process of mineralization, enhancing the chemical weathering process by acidic reaction with the underlying rock, resulting in the formation of secondary phosphate minerals (struvite, NH_4-taranakite for example) (Simas *et al*. 2007).

The $P_{available}$ contents ranged from 0.2–3182 mg kg^{-1} (Appendix B). This large variation is due to several factors including ornithogenic composition, type of P-mineral constituents and local soil drainage conditions. The highest $P_{available}$ value found in non-ornithogenic soils was 111.2 mg kg^{-1} (sample F5b). This value is much lower than values obtained for the ornithogenic profiles and is indicative of decreased phosphorous availability due to low P_{total} content

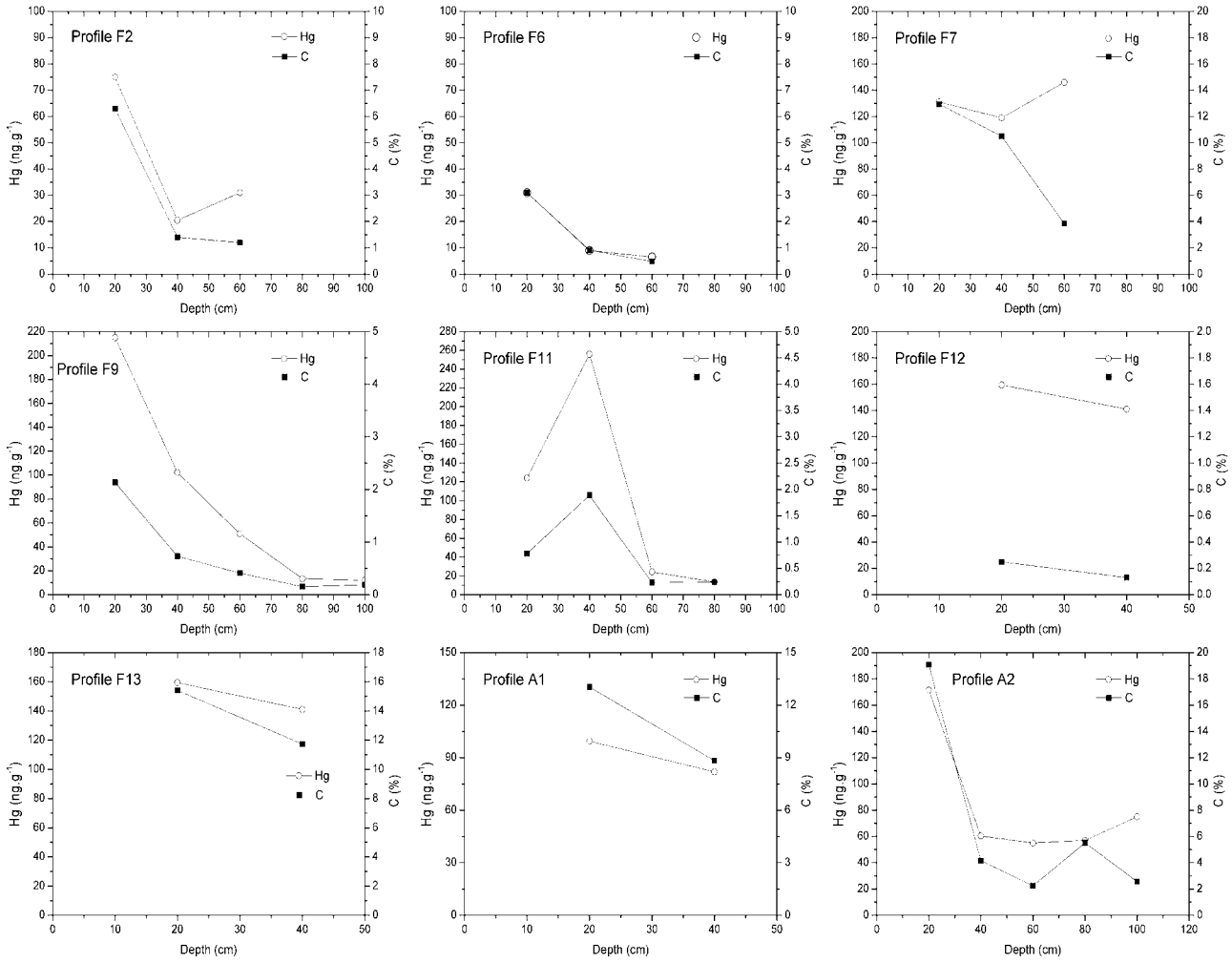

Fig. 2. Mercury and organic carbon concentrations as a function of depth in all ornithogenic profiles and one biogenic profile.

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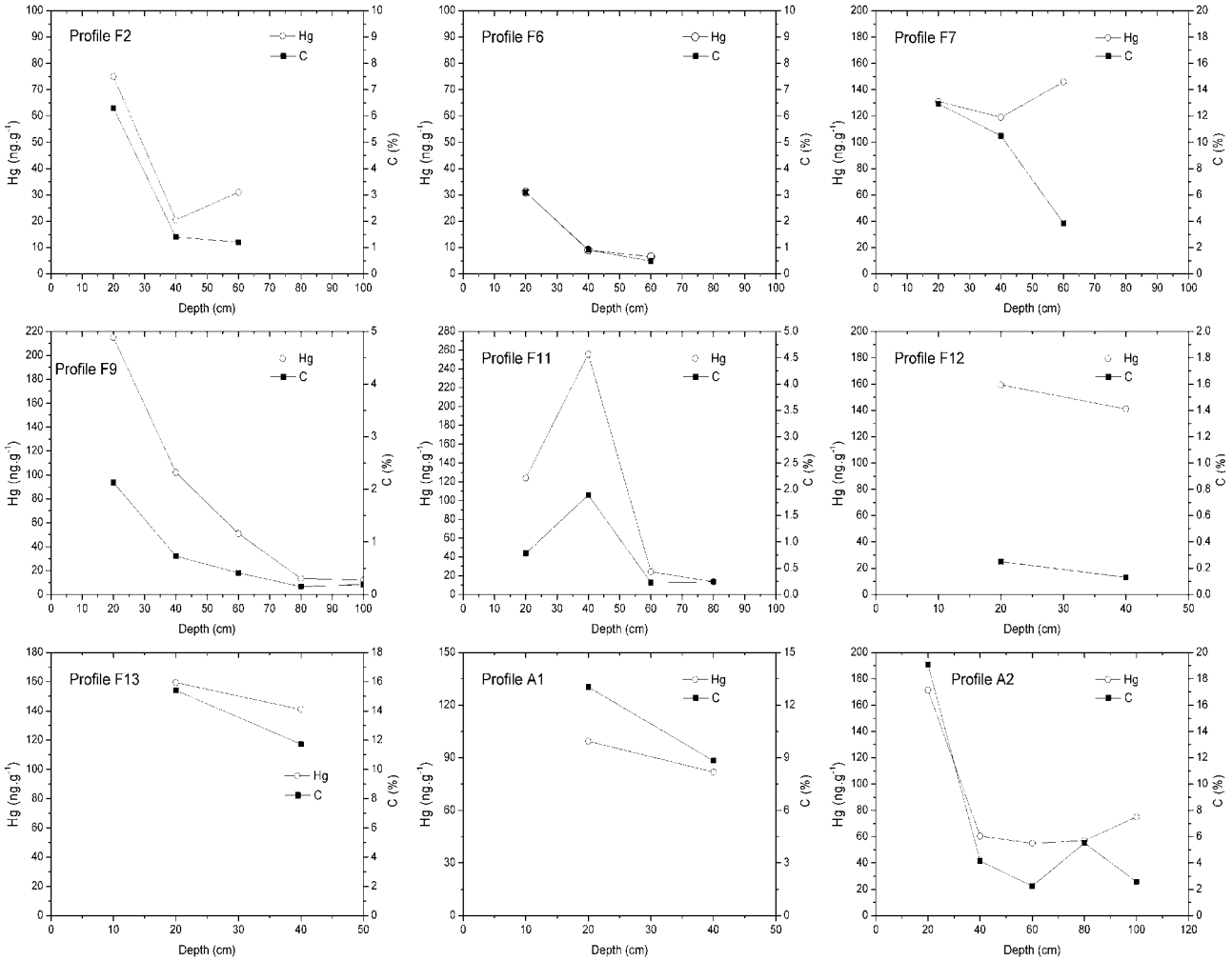

Fig. 2. Continued.

in the soils. In the ornithogenic soils, high levels of P are able to leach into deep layers due to dissolution of primary bone apatite in the topsoil and re-precipitation (Simas *et al*. 2008). The degree of P availability also depends on the soil pH and redox potential because NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+} and Fe^{3+} phosphates have very different solubility constants, with lower solubility following the order presented. Greater P availability can suggest the presence of NH_4^+. The local drainage is also an important factor in P content, as secondary phosphates are usually concentrated above the permafrost table, which prevents further downward leaching. This phenomenon can be observed in the profiles for samples F13, A2 and A9 (Appendix B). Similar behaviour can be observed at intermediate depths in sample A2 (P_{total} and $P_{available}$) due to movement of the impermeable ice layer during the thawing season (Fig. 1).

Pearson correlation analysis of data from Appendix B showed no significant correlation between P_{total} and N (0.16, $P < 0.05$ and $n = 72$), as expected, because the guano present in ornithogenic soils is the main source of the two elements, suggesting that the loss of NH_4^+ should be more intense than PO_4^{3-}, which forms insoluble compounds with Al^{3+} or Fe^{3+}. The low correlation of C with P_{total} (0.43, $P < 0.05$ and $n = 72$) suggests an additional input of organic carbon from plant material in addition to the decomposition of dead animals. In some soils (samples F6, F9, A1, A2, A4 and A13) the presence of non-decomposed mosses corroborates input of organic matter from plant sources. Wang *et al*. (2007) reported that the three major types of vegetation on Ardley Island, namely coprophilic algae, moss and lichen, showed variations in relative abundance according to fluctuations in the penguin populations. A moderate penguin population was observed to be favourable for algae and moss growth, while lichen populations were found to decrease whenever penguin population increased, and *vice versa*.

HgT determination

The Hg content in soils varied between 4.3 ± 0.2 and 256 ± 4 ng g^{-1} (Appendix B). These values are considered

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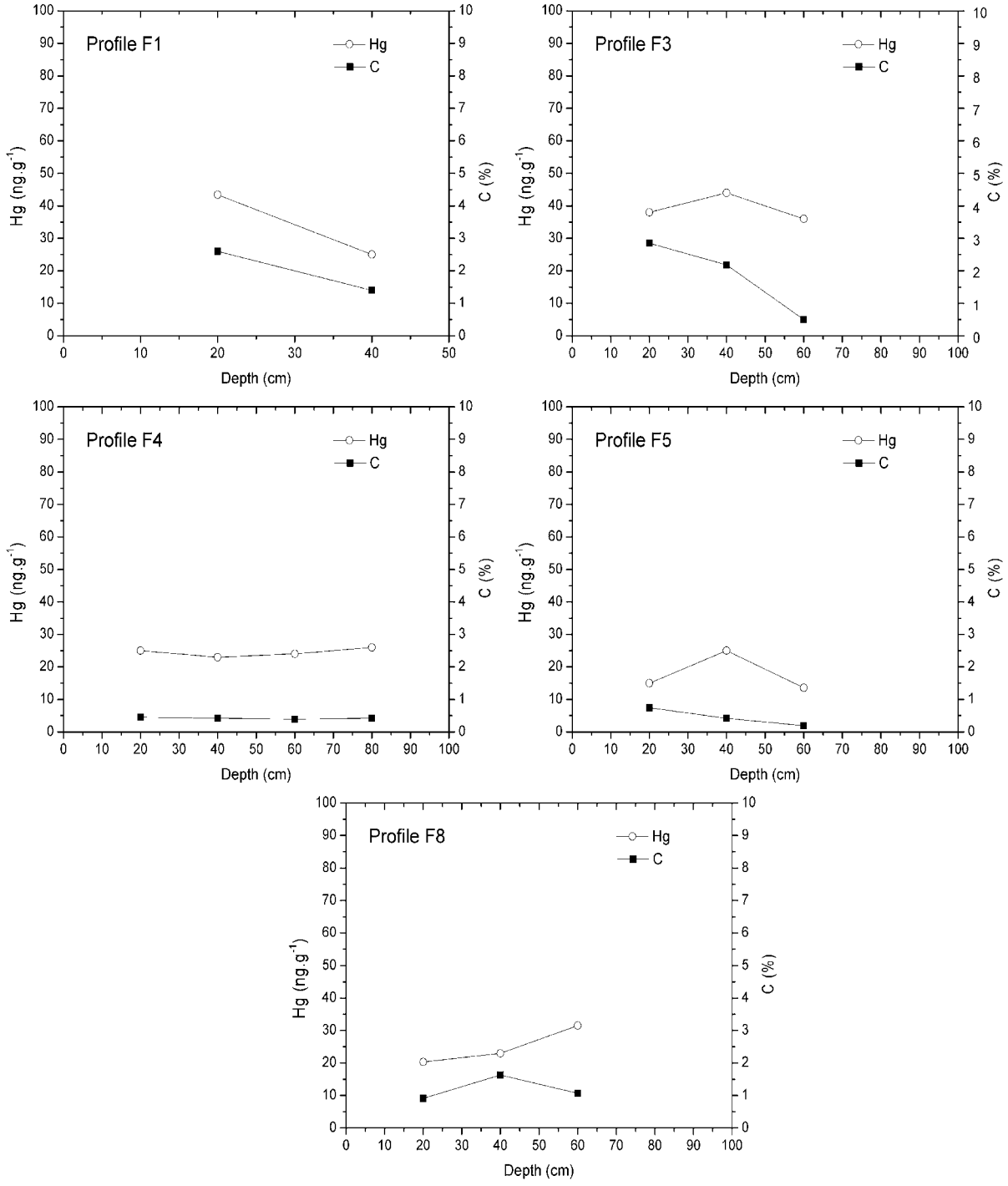

Fig. 3. Mercury and organic carbon concentrations as a function of depth in non-ornithogenic profiles.

normal relative to average levels for uncontaminated global soils (200 ng g^{-1}) (Horvat 1996), but they are the highest reported in the literature for soils in Antarctica to date. Siegel *et al*. (1980) reported values for Hg concentration in soils from Ross Island, Antarctica, from 3.1–7.1 ng g^{-1}. In 2005, Bargagli *et al.* reported values of Hg content in soils from Victoria Land, Antarctica, in the range of 12–86 (soil fraction $<$ 0.25 mm), and in 2007, they reported values in the range of 3.7–22 ng g^{-1} (soil fraction $<$ 2 mm). In 2005, Santos *et al.* reported Hg concentrations in soils from Admiralty Bay, King George Island, close to the levels found in the lower crust (21 ng g^{-1}). However, there has not been a large amount of research measuring Hg concentrations in large numbers of soil samples from

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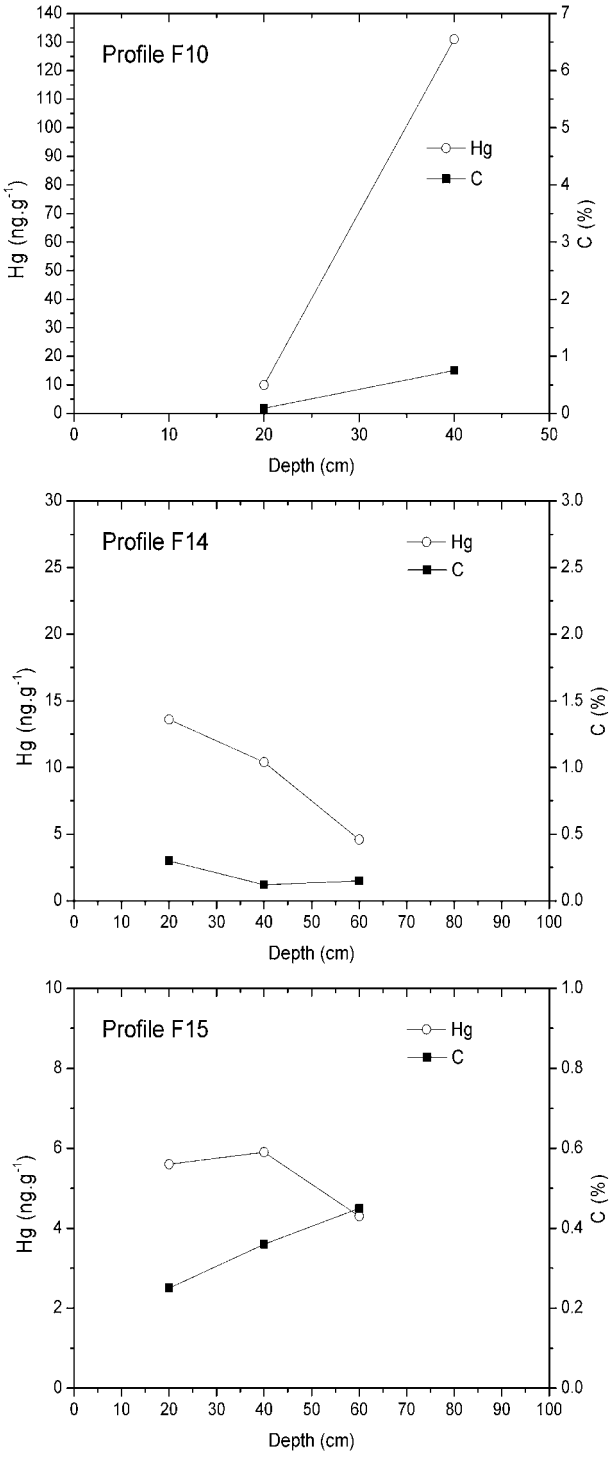

Fig. 3. Continued.

Antarctica. Our results may represent a preliminary assessment of natural values for volcanic soils with and without ornithogenic influence in Maritime Antarctica.

The ornithogenic profiles showed a clear trend of higher Hg values (from 6.3 ± 0.4 to 215 ± 4 ng g^{-1}), which may be due to a variety of sources: i) the excreta of seabirds, which feed on fish and krill that bioaccumulate the metal, ii) the decomposition of dead birds, releasing bioaccumulated Hg to the soil, and iii) the atmospheric deposition of Hg transported by air currents from lower latitudes, where the largest anthropogenic emissions occur (springtime depletion events, Schuster 1991, Ebinghaus *et al*. 2002, Bargagli *et al*. 2007, Witherow & Lyons 2008, Nguyen *et al*. 2009). Bargagli *et al*. (2007) analysed sediment cores and did not observe an increase in concentrations of Hg in recent surface sediments from ice-free areas of Victoria Land, which represents deposited Hg from anthropogenic and natural emissions from lower latitudes.

Regardless of the source, the ornithogenic soils contain large amounts of organic carbon, which can complex Hg and lead to its accumulation. The ability of organic matter to complex Hg in soils and sediments is already known and has been observed in many ecosystems (Schuster 1991). This affinity for complexation with OM of both animal and vegetable origin is due to the presence of carbonyl groups and protein-derived material containing nitrogen and sulfur, all of which can bind with the metal.This Hg-OM bond has been considered one of the most important in the case of soils and sediments, especially where clay minerals are present, as they are known to be metal and organic matter retainers (Bloom *et al*. 2003).

Conversely, non-ornithogenic profiles showed lower Hg content (from 4.3 ± 0.2 to 43 ± 3 ng g^{-1}), when compared with global Clarke values of Hg (86 ng g^{-1}) (Ronov & Yaroshevsky 1972) and average values for the continental crust (40 ng g^{-1}) (Wedepohl 1995), indicating that there has been no contamination in these soils. The lowest Hg values (4.3 ± 0.2 ng g^{-1}) were found in the shallow lithic soils in samples F12, F14, and F15, all of which are characterized by a very limited degree of weathering.

The exception to the above conclusion is the profile for sample F10, which is not ornithogenic, but contains high organic matter content from seal (elephant seals, Weddell seals, fur seals) excreta and hair. The Hg contents in F11 were the highest value found in all the soils studied (256 ± 4 ng g^{-1}).

Santos *et al*. (2006) studied the Hg distribution in different materials from the nearby Keller Peninsula (King George Island) and found low levels of Hg (15–30 ng g^{-1}) in soil and sediments, with very low Hg content in vegetation, invertebrates and fish. The only high Hg concentrations (2060 ng g^{-1}) were found in feathers and mammal hair, indicating biomagnification in the Antarctic ecosystem. These materials have been suggested as possible biomonitors for that region (Santos *et al*. 2006).

The Pearson correlation between HgT and C was found to be significant but moderate (0.57, $P < 0.05$ and $n = 72$), but the graphics in Fig. 2 clearly shows that the profile of Hg and organic matter content is very similar in the ornithogenic soils studied. This correlation is clear in all profiles (except F7) and especially in the profiles with the largest number of samples, such as F9, F11, A2, A6 and

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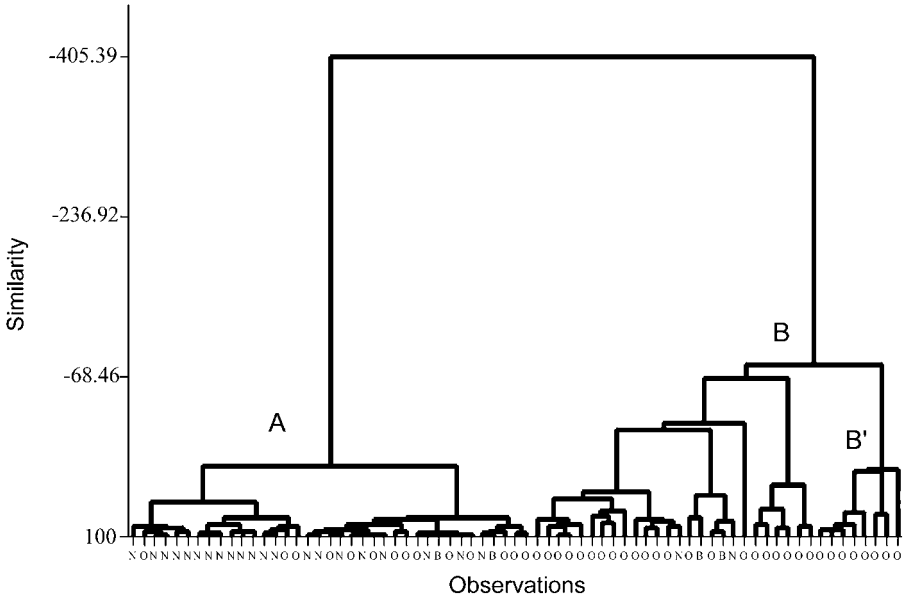

Fig. 4. Dendrogram of data (samples) from Appendix B.

A8. For these soils, one can see a decrease in Hg content with increasing depth; when there is a sharp decline in carbon content, there is also a sharp drop in the amount of the metal. The presence of greater amounts of Hg at the surface of ornithogenic soils indicates a recent deposition of the metal, probably from the contribution of guano and from the remains of dead animals that bioaccumulate the metal.

This reduction in Hg content with increasing depth was not observed in the non-ornithogenic soils as shown in Fig. 3. In most of these cases, there was an increase in element content with increasing depth, suggesting that the Hg deposited on the surface was leached to deeper soil layers. One cannot exclude that Hg in surface soil is partly released as gaseous Hg. As described by Simas *et al*. (2008), these basaltic or andesitic soils are in general poorly developed, but may be covered by mosses and lichens, which are a source of organic matter, allowing for A horizon formation. Figure 3 shows the correlation of Hg content with organic matter, although the trend is not as clear as was seen for the ornithogenic soils.

The high correlation observed in ornithogenic soils between Hg and OM indicates that bioaccumulation of Hg in marine animals is probably the main source of Hg in these terrestrial ecosystems. This means that the metal concentration found in these soils indirectly depends on the processes of oxidation from Hg^0 to Hg^{2+}, including methylation of the metal in the environment. In the case of ornithogenic soils, this contribution obviously is high, but in non-ornithogenic soils this seems likely to be the predominant Hg source. The contribution due to atmospheric deposition cannot be discounted, but it is a more important contributor in non-ornithogenic soils.

The analysis of seal hair showed a high Hg content of $1795 \pm 56\,ng\,g^{-1}$, in agreement with values reported by several authors. Santos *et al*. (2006), for example, found $2060\,ng\,g^{-1}$ of Hg in seal hairs from the Keller Peninsula, and Sun *et al*. (2006) found $1740\,ng\,g^{-1}$ of Hg in the same matrix from the Fildes and Ardley peninsulas. Both attributed these high values to biomagnification.

The statistical analysis of all variables (presented in Appendix B by HCA), using ward linkage and Euclidean distance, showed the formation of two large groups of samples, the non-ornithogenic soils (group A, Fig. 4) and ornithogenic soils (group B, Fig. 4). The branch B' shown in Fig. 4 grouped ornithogenic soil samples with the highest concentrations of Hg, C and H. These results made clear the importance of physical and chemical processes related to the sea-land transfers promoted by marine animals (penguin and seals) to the geochemistry of Hg in this region.

The Polar Regions are recognized as important sinks for the long-range transport of Hg derived from natural and anthropogenic sources at low latitudes. Bargagli *et al*. (2007) studied Antarctic ecosystems and suggested that Hg brought from low latitudes is deposited at the poles and accumulates in soils, mosses and lichens in ice-free areas of

Table I. Results of Hg ($\mu g\,kg^{-1}$) sequential extraction of the samples F9a, F11b, A12a, A12d and seal hair.

Step	Samples				
	F9a	F11b	A12a	A12d	Seal hair
S1	0.58	2.47	4.69	1.45	< LQ
S2	< LQ	< LQ	4.43	< LQ	< LQ
S3	162.44	225.45	23.29	13.80	1841.82
S4	73.21	30.26	23.13	32.67	< LQ
S5	8.99	0.74	5.12	0.98	< LQ
Σ Steps	245.22	258.93	60.65	48.89	1841.82
HgT (DMA)	214.74	259.2	82.96	48.69	1795.18
Recovery (%)	114.19	99.89	73.12	100.41	102.59

LQ = quantification limit; detection limit = $1.04\,ng\,g^{-1}$.

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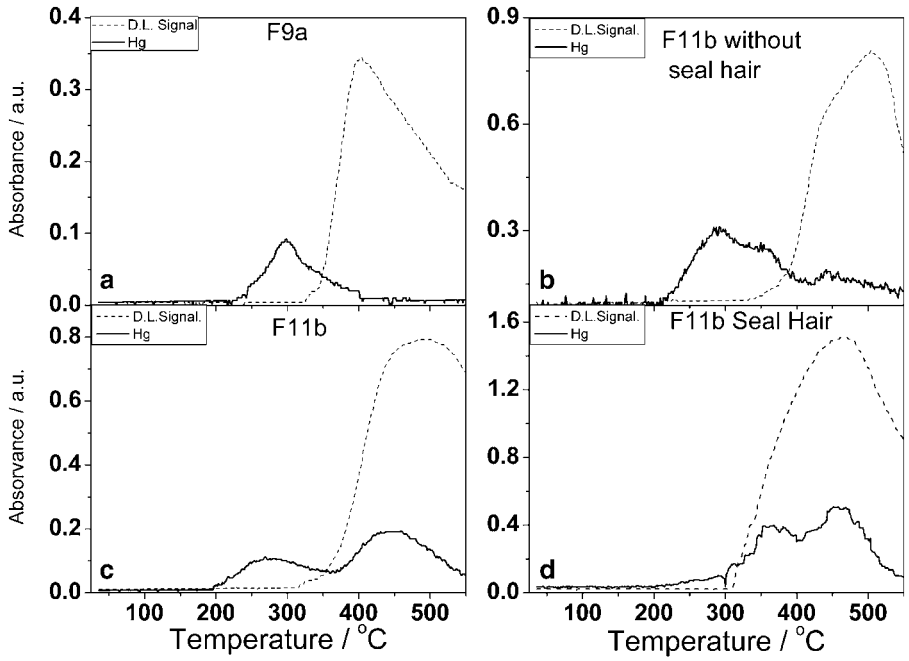

Fig. 5. a. Thermogram of profile F9a. **b.** Thermogram of profile F11b seal hair. **c.** Thermogram of profile F11b. **d.** Thermogram of the profile F11b without seal hair.

the Antarctic continent. In the same study the authors reported that due to melting in the summer, the metal is released from the crystalline lattice of ice and interacts in plankton, benthic mats, cyanobacteria and soil OM, resulting in high correlations between Hg and organic carbon.

Hg chemical fractionation in soil and seal hair samples

Results from chemical fractionation can provide information about the availability of Hg to the environment. Extraction of labile phases S1 and S2, which solubilize Hg weakly bound in the matrix, showed low values (< LQ to 4.69 ng g^{-1}), with only one sample (A12a) containing an environmentally significant value over the two phases (15%). A12a is a guano-rich surface sample, in which not enough time had elapsed for complexation and retention of Hg with insoluble OM. Other ornithogenic soils with a greater degree of OM mineralization (F9a) show a greater interaction of Hg with OM (higher Hg extraction in S3, Table I).

Sequential extraction applied to seal hair samples confirms that the method is effective for the extraction of Hg bound to OM (step S3) because 100% of the Hg was extracted (Table I). The highest percentage of Hg bound to OM was found in the marine terrace soil F11b (88%) because this sample was richest in seal hair, as seals breed at this site during the summer. We believe that OM from seal hair is more difficult to break down and mineralize than that derived from faunal excreta. The mineralized excreta easily reacts with the bedrock, forming insoluble secondary minerals such as Al/Fe phosphate, which

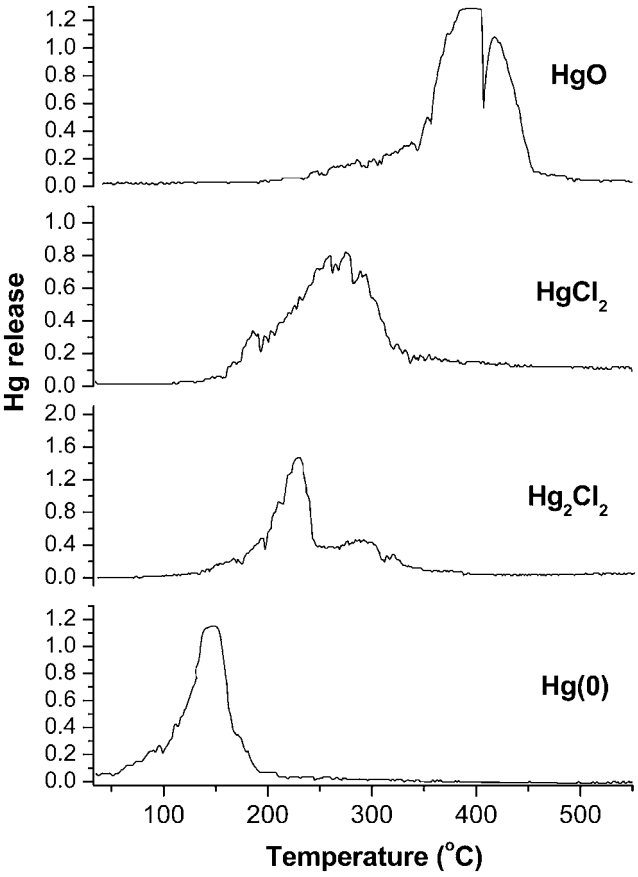

Fig. 6. Thermograms for standard samples of Hg compounds (from Valle *et al*. 2006).

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probably incorporate Hg into their structures. This phase is well represented by extracting step S4, in which HNO_3 solubilizes phosphates. For samples A12a and A12d, deeper layers showed a greater amount of Hg retained in the S4 extract, indicating the formation of insoluble materials that retain Hg in those soils. No sample showed large amounts of residual Hg (S5).

Solid-phase Hg pyrolysis and CV-AAS

The results of solid-phase Hg pyrolysis and CV-AAS (Fig. 5) show that all Hg is present in the form of Hg^{2+} because the absorbance peaks appeared only above 200°C. Studies with standards of Hg^0, Hg_2^{2+} and Hg^{2+} salts, with the same equipment and under the same analytical conditions described here, showed Hg^0 release in the range of 20–100°C and Hg_2^{2+} release as a narrow peak close to 130°C, whereas other species of Hg^{2+} release at temperatures higher than 200°C (Fig. 6). It has been found that Hg bound to OM usually releases at higher temperatures (Valle *et al*. 2005). Other authors also found similar results under experimental conditions differing from those used here (Biester & Scholz 1997). We observed the presence of more than one absorption band in our samples (Fig. 5), indicating at least two types of complexes of Hg with the matrix.

Sample F9a shows the presence of weakly bound Hg compared with sample F11b, which has visible fragments of seal hair. We observed a stronger Hg-OM interaction, as the profile from the deuterium lamp, which is sensitive to gases produced by OM decomposition, follows the profile of the Hg spectrum of the hollow cathode lamp. Sample F11b, containing no seal hair, showed a similar thermogram (Fig. 5b) to sample F9a (Fig. 5a). This indicates a weaker Hg-matrix interaction (temperature release between 220 and 320°C), probably due to Hg bound to highly mineralized OM. A stronger interaction is observed at temperatures from 320–500°C, following the release of Hg bound to OM from the seal hair. These results are in agreement with the results obtained by sequential extraction, with Hg present mainly in association with OM. Thermograms were conducted with larger masses of samples to check for the loss of Hg at low temperatures, characteristics of Hg^0, and it was not observed.

Conclusions

The Hg content in soils of the Fildes and Ardley peninsulas in Maritime Antarctica ranged from 4.3 ± 0.2 to 256 ± 4 ng g^{-1}, with higher contents observed for ornithogenic or seal-affected soils. The values found were the highest reported in Antarctic soils to date. The analytical procedure used had an appropriate quantification limit for analysis, as well as good precision and accuracy. There was a clear correlation between Hg and OM associated with nesting birds and breeding seals. Ornithogenic soils showed declining Hg concentrations in deeper soil layers, whereas in non-ornithogenic soils the opposite trend was observed. It can be argued that in the ornithogenic soils the interaction of Hg with OM is dominant over other types of interactions. The possibility that a portion of the Hg present may be derived from atmospheric deposition (springtime depletion events) followed by OM complexation should also be considered, mainly in the non-ornithogenic soils.

The large variation in P_{total} and $P_{available}$ is probably due to varying levels of ornithogenic influence, the types of phosphate minerals present and the conditions of solubilization and local drainage patterns.

All Hg found was in the form of Hg^{2+} and mainly associated with organic matter, as confirmed by the results of solid-phase Hg pyrolysis coupled to CV-AAS and sequential extraction.

Statistical analysis of all variables made clear the importance of physical and chemical processes related to sea-land transfers promoted by marine animals (penguins, seals) to the geochemistry of Hg in this region. The close correlation observed between Hg and OM in the ornithogenic soils motivates the need for more detailed studies to elucidate these interactions in order to understand the biogeochemistry of Hg in the Antarctic environment.

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Appendix A. Geographical co-ordinates (UTM) of the sampling points (F = Fildes and A = Ardley).

Perfil	Location	Latitude	Longitude	Origin
F1	Fildes Peninsula	396.900.671	3.099.979.071	non-ornithogenic
F2	Fildes Peninsula	397.972.644	3.101.573.474	ornithogenic
F3	Fildes Peninsula	398.311.966	3.099.343.223	non-ornithogenic
F4	Fildes Peninsula	397.682.551	3.099.753.826	non-ornithogenic
F5	Fildes Peninsula	397.531.930	3.100.544.839	non-ornithogenic
F6	Fildes Peninsula	397.901.036	3.100.774.069	ornithogenic
F7	Fildes Peninsula	397.772.411	3.101.124.119	ornithogenic
F8	Fildes Peninsula	398.019.298	3.101.592.639	non-ornithogenic
F9	Fildes Peninsula	396.596.943	3.102.149.643	ornithogenic
F10	Fildes Peninsula	396.585.267	3.102.038.658	non-ornithogenic
F11	Fildes Peninsula	396.214.221	3.102.042.795	biogenic
F12	Fildes Peninsula	395.956.840	3.101.920.640	ornithogenic
F13	Fildes Peninsula	399.707.675	3.100.523.968	ornithogenic
F14	Fildes Peninsula	395.960.226	3.099.263.302	non-ornithogenic
F15	Fildes Peninsula	396.245.985	3.100.087.774	non-ornithogenic
A1	Ardley Island	399.670.205	3.100.507.296	ornithogenic
A2	Ardley Island	400.035.848	3.100.509.203	ornithogenic
A3	Ardley Island	400.085.867	3.100.498.131	ornithogenic
A4	Ardley Island	399.511.932	3.100.881.084	ornithogenic
A5	Ardley Island	399.543.513	3.100.870.665	ornithogenic
A6	Ardley Island	399.493.117	3.100.912.812	ornithogenic
A7	Ardley Island	398.723.086	3.100.684.946	ornithogenic
A8	Ardley Island	398.758.804	3.100.693.925	ornithogenic
A9	Ardley Island	398.787.926	3.100.738.311	ornithogenic
A10	Ardley Island	399.256.900	3.100.480.528	ornithogenic
A11	Ardley Island	399.297.536	3.100.361.955	ornithogenic
A12	Ardley Island	400.219.479	3.100.714.507	ornithogenic
A13	Ardley Island	399.693.397	3.100.927.978	ornithogenic
A14	Ardley Island	399.200.273	3.100.687.288	ornithogenic
A15	Ardley Island	399.378.477	3.100.605.223	non-ornithogenic

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Appendix B. Contents of C, H, N, P_{total}, $P_{available}$ and HgT in soil samples from the Fildes (F) and Ardley (A) peninsulas.

Profile*	C %	H %	N %	P_{total} mg kg^{-1}	$P_{available}$ mg kg^{-1}	HgT ± s** μg kg^{-1}	Profile*	C %	H %	N %	P_{total} mg kg^{-1}	$P_{available}$ mg kg^{-1}	HgT μg kg^{-1}
F1a	2.56	1.14	0.38	435	15	43 ± 3	F15b	0.36	0.97	1.04	271	41.6	5.9 ± 0.4
F1b	1.43	0.72	0.96	496	33	25 ± 2	F15c	0.45	0.98	0.77	384	53.6	4.3 ± 0.2
F2a	6.26	1.53	1.73	2476	60	75 ± 5	A1a	13.03	2.55	1.11	6051	380.7	99 ± 3
F2b	1.37	0.94	0.67	1615	128	20.5 ± 0.7	A1b	8.83	1.99	0.9	9205	***un	81.8 ± 0.1
F2c	1.21	0.69	0.66	1049	***un	31 ± 2	A2a	19.08	2.59	2.14	4803	***un	171 ± 6
F3a	2.85	0.55	1.57	686	33	37 ± 2	A2b	4.16	1.07	0.76	19359	2469	60.4 ± 0.8
F3b	2.18	0.69	1.2	250	46	44.1 ± 0.8	A2c	2.24	1.33	0.89	23078	3182	55 ± 3
F3c	0.5	0.53	0.93	647	24	36 ± 4	A2d	5.51	1.27	0.8	15646	1126	57 ± 4
F4a	0.45	0.65	0.24	312	24	25 ± 2	A2e	2.57	0.77	0.7	21419	564	74 ± 2
F4b	0.42	0.63	0.25	419	***un	23.2 ± 0.3	A3a	9.36	1.64	0.98	9267	511	63 ± 3
F4c	0.39	0.75	0.24	386	28	24 ± 1	A3b	6.73	1.47	0.71	8890	524	54 ± 5
F4d	0.42	0.65	0.74	395	49	26 ± 1	A3c	3.38	1.04	9.12	14981	108	48 ± 0.6
F5a	0.74	0.23	1.16	503	18	15.0 ± 0.3	A3d	2.65	0.86	7.32	10059	***un	39.8 ± 0.1
F5b	0.42	1.1	0.16	427	111	25 ± 2	A4a	2.39	0.42	0.29	1718	196	29 ± 2
F5c	0.19	0.29	1.71	474	93	14 ± 0.1	A5a	2.62	0.36	0.3	1517	414	33 ± 2
F6a	3.10	0.43	2.14	1097	41	31 ± 2	A5b	0.56	0.65	0.11	928	502	9.6 ± 0.3
F6b	0.91	0.51	0.34	615	54	8.7 ± 0.3	A6a	11.19	1.87	1.1	7567	715	133 ± 1
F6c	0.48	0.76	0.11	488	86	6.5 ± 0.2	A6b	2.36	1.9	1.4	14508	***un	49 ± 2
F7a	12.93	2.03	1.14	8373	422	131 ± 7	A6c	1.81	1.18	0.45	22728	***un	37 ± 3
F7b	10.49	2.12	0.96	7274	317	119 ± 6	A6d	0.74	0.26	0.18	16421	183	22.0 ± 0.4
F7c	3.84	1.78	0.53	14827	525	146 ± 6	A6e	0.77	0.55	0.36	13538	***un	29 ± 2
F8a	0.91	0.63	1.55	483	96	20.3 ± 0.2	A6f	0.61	0.54	0.32	8029	***un	25.1 ± 0.4
F8b	1.63	0.67	0.2	871	93	23.1 ± 0.3	A7a	12.45	6.15	0.66	5351	399	103 ± 1
F8c	1.07	0.41	0.14	851	81	31 ± 2	A7b	5.72	1.31	2.97	15552	382	54 ± 1
F9a	2.13	0.61	2.19	3823	766	215 ± 4	A8a	6.19	1.37	0.66	9244	568	60 ± 1
F9b	0.73	0.48	0.19	3335	267	102 ± 1	A8b	7.60	1.26	5.8	4220	***un	60.0 ± 0.1
F9c	0.41	0.46	0.12	1998	142	51 ± 3	A8c	3.17	1.01	1.18	11717	34	33.8 ± 0.8
F9d	0.15	0.52	0.05	1959	201	13 ± 1	A8d	3.14	0.99	1.21	2299	251	38 ± 5
F9e	0.19	0.79	0.03	1468	133	11.9 ± 0.2	A9a	8.99	2.9	0.78	5366	727	192 ± 1
F10a	0.09	0.37	0.05	587	75	9.9 ± 0.7	A9b	5.16	1.8	0.24	31774	1998	63 ± 2
F10b	0.75	0.33	1.57	787	67	131 ± 1	A10a	4.27	1.08	0.32	35613	1676	54 ± 2
F11a	0.78	0.63	0.17	830	116	124 ± 1	A10b	3.77	0.96	0.13	7064	2832	36.7 ± 0.3
F11b	1.89	0.72	0.39	702	46	256 ± 4	A10c	4.45	0.9	0.54	14757	66	49 ± 1
F11c	0.23	0.4	0.04	672	85	24.2 ± 0.4	A11a	23.29	3.54	1.47	6149	***un	147 ± 2
F11d	0.24	0.38	0.07	611	105	13.5 ± 0.5	A12a	9.6	3.61	4	89461	***un	82 ± 2
F12a	0.25	0.49	0.08	759	77	6.3 ± 0.4	A12b	8.86	2.07	2.72	89638	***un	77 ± 3
F12b	0.13	0.27	0.04	718	62	7.1 ± 0.8	A12c	8.51	1.82	2.29	68354	***un	62 ± 2
F13a	15.41	2.12	1.57	13543	2219	159 ± 3	A12d	8.12	1.71	2.01	65275	***un	49 ± 6
F13b	11.73	2.5	1.28	27968	2749	141.0 ± 0.6	A13a	4.24	1.11	0.56	7679	2284	59.0 ± 0.7
F14a	0.30	0.66	0.11	730	32	17 ± 1	A13b	1.25	0.98	0.32	1662	448	11.5 ± 0.9
F14b	0.12	0.33	0.12	720	21	10.4 ± 0.6	A14a	5.34	1.78	0.32	5791	195	62 ± 3
F14c	0.15	0.72	0.19	699	156	4.59 ± 0.04	A14b	2.05	1.76	0.42	7456	254	15.3 ± 0.2
F15a	0.25	1.33	0.43	394	26	5.6 ± 0.6	A15a	2.35	0.97	0.21	9672	0.2	14.9 ± 0.7

*the letters a, b, c, d, e and f indicate increasing depth.
**standard deviation, $n = 3$.
***unspecified.

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