Water Air Soil Pollut (2011) 222:91–102
DOI 10.1007/s11270-011-0811-z

Heavy Metals Contamination in Century-Old Manmade Technosols of Hope Bay, Antarctic Peninsula

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Received: 15 November 2010 / Accepted: 4 April 2011 / Published online: 15 April 2011

Abstract Technosols are anthropogenic soils that may be strongly impacted by heavy metal deposition, which have not yet been described in Antarctica. In this paper, we present a chemical study of what is supposedly the oldest manmade soil from Antarctic Peninsula, developed in the vicinity of Trinity House and Nordenskjold Hut at Hope Bay. Chemical and morphological soil attributes indicate that a former ornithogenic site (penguin rookery) was further subjected to human disturbance, following local exploration since 1903. We detected very high amounts of heavy metals such as Cd, Cu, Pb, and Zn. For the most impacted site, pseudototal concentrations of these elements reach 47, 2,082, 19,381, and 5,225 mg kg^{-1}, respectively. Enrichment factors were calculated using Zr as reference element, and high values were found for these contaminated sites, qualifying some of them as extremely polluted. Also, both the mobilizable and mobile fraction of Cd and Pb indicate the need of intervention in the affected area. These findings are all consistent with the human impacts and strong contamination. Strong positive correlation between the pseudototal concentrations of Cd, Cu, Mn, Ni, Pb, and Zn indicates a similar source of pollution. These soils may represent the oldest Technosols in Antarctic Continent.

Keywords Antarctic · X-ray fluorescence · Principal component analysis · Enrichment factors · Bioavailability · Soil pollution

1 Introduction

The first report of human presence in Hope Bay, Antarctic Peninsula, dates back to 1903, when J. Gunnar Andersson, a member of the Swedish expedition to the south pole (1901–1904), carried out the first explorations and mapping. Well-preserved ruins of the stone hut built by the Swedish group can be seen at the harbor entrance of Esperanza station. The UK established the so-called *Base D* at Hope Bay in 1945, as part of the "Tabarin Operation." The British station remained operational until 1964, being transferred to Uruguay in 1997. In 1951, Argentina also established an

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Army station (Esperanza) in the region, with permanent operation to the present day. In the same area and situated approximately 300 m to the northeast of the Uruguayan Base, remains of a former British Base (Trinity House), this burnt down in 1948. The fire left to a widespread mantle of debris in the region, which was subjected to further pedological changes under a cold polar climate (Hattersley-Smith 1991).

The population of breeding birds of Hope Bay is well studied, and a large Adélie penguin (*Pygoscelis adeliae)* colony, numbering around 125,000 pairs, is present at the site near Trinity House (Woehler 1993). Soil morphology such as phosphatic horizons and bleaching as well as terrain characteristics (vegetation development, thick organic horizons) indicate strong ornithogenic influence (Tatur 1989; Simas et al. 2007). Other breeding birds at Hope Bay include gentoo penguins (*Pygoscelis papua*), brown skua (*Catharacta loennbergi*), Antarctic tern (*Sterna vittata*), Wilson's storm petrel (*Oceanites oceanicus*), kelp gull (*Larus dominicanus*), and sheathbill (*Chionis alba).* In Hope Bay, the extension of the penguin rookery appears to have been much larger prior to permanent human settlement, forming the so-called ornithogenic soils (Tatur 1989). On these soils, later human settlement occurred resulting on deposition of all sorts of residues such as metal parts, wood, among others, originating peculiar manmade soils.

The most recent version of the World Reference Base for Soil Resources (IUSS 2006) developed appropriate *taxa* (Anthrosols and Technosols) for soils profoundly affected by human activity in urban/industrial areas (landfills, farming, earth movement, and heavy metal contamination) and agricultural areas (erosion, ripping, and land leveling). Up to this date, we have not found any reference on Technosols in Antarctica, which is regarded as the most pristine and fragile land mass on Earth.

The aim of the present study is to investigate the occurrence and chemical composition of soils under strong cumulative anthropogenic influence at the vicinity of Trinity House, Hope Bay, and observe soil chemical and morphological changes related to the history area occupation. The hypothesis is that cumulative impacts imprint a chemical signature of anthropic pollution not yet described. The studied area possibly represents one of the oldest memories of anthropogenic impact in the Antarctic Continent, with occurrence of Technosols (IUSS 2006).

2 Material and Methods

Figure 1 shows the Antarctic Peninsula highlighting Hope Bay where the Esperanza Station and the Boeckella lake are located.

Soil profiles at selected anthropogenic sites were dug and collected at the vicinity of the Esperanza station, inside the ruins of the British deposit of Trinity House, which was completely burned and destroyed. Its demolition left several materials, such as semi-carbonized wood, bone, charcoal, bricks, charred organic materials, metal parts, and concrete, all distributed randomly at depths between 5 cm down to 30–40 cm.

2.1 Sampling and Preliminary Treatments

A total of eight superficial soil samples (0–10 cm depth) were collected. The characteristics of the studied sites are detailed in Table 1. The majority of the samples presented evidences of contamination with oil, coal, and alloys. Soil samples were oven-dried at 60°C until constant weight, sieved to obtain particles smaller than 212 μm, which were stored in previously decontaminated polyethylene pots.

2.2 Soil Chemical Characterization

The samples were characterized according to three parameters: pH, total organic carbon (TOC), and cation exchange capacity. In the case of pH, 1.0 g of soil was transferred to 50-mL centrifuge tubes, and 10 mL of 0.01 mol L^{-1} $CaCl_2$ were added (Carter and Gregorich 2007). The system was shaken during 30 min in a horizontal shaker (Barnsteady, Iowa, USA). The pH was measured in the supernatant using a pHmeter (PHTEK, PHS-3B). The TOC content was estimated using the Walkley and Black method as described by van Raij et al. (2001). Cation exchange capacity was measured by extraction of 0.5 g soil sample, in triplicates, with 10 mL of $BaCl_2$ 0.1 mol L^{-1} (Carter and Gregorich 2007). After shaken for 2 h, the supernatant was separated by centrifugation. Exchangeable Al, Ca, Fe, K, Mg, Mn, and Na were determined in the extracts by inductively coupled plasma optical emission spectrometry with axially viewed configuration (Vista AX, Varian, Mulgrave, Australia). The operational conditions were those recommended by the manufacturer.

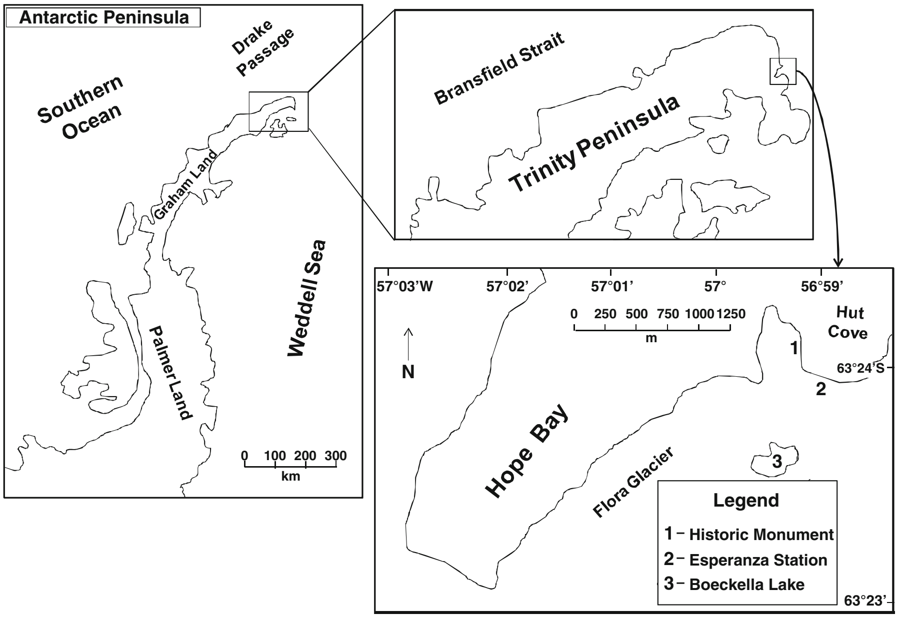

Fig. 1 Map of the Antarctic Peninsula highlighting Hope Bay, Esperanza Station, and the Boeckella Lake

2.2.1 XRF Analysis

An initial soil characterization was made with the help of X-ray fluorescence analysis (XRF). The powdered samples were pressed into pellets at 7 t for 30 s. A certified reference material (CRM), San Joaquin Soil (NIST 2709), was also prepared for XRF analysis using the same procedure of the collected soil samples. The total concentrations of some elements in the certified reference material are: Cu (34.6 mg kg^{-1}), Mn (538 mg kg^{-1}), Pb (18.9 mg kg^{-1}), and Zn (106 mg kg^{-1}). XRF analyses were performed at the National Synchrotron Light Laboratory located at Campinas, São Paulo

Table 1 Description of the sampling points

Identification	Location	Coordinates	Altitude (m)	Remarks
HB1	Harbor point	63°23′44.08″ S/56°59′ 49.15″ W	5	Evident oil contamination
HB2	Behind the Entrance Station building	63°23′43.37″ S/56°59′ 52.01″ W	7	Presence of debris and discreet oil contamination
HB3	Waste pile besides the Dogs House	63°23′58.52″ S/56°59′ 32.73″ W	17	Presence of wastes in the soil profile
HB4	Near the generator	63°23′52.88″ S/56°59′ 52.46″ W	21	Possible, but no apparent contamination
HB5	50 m far from generator	63°23′53.05″ S/56°59′ 52.13″ W	24	Possible, but no apparent contamination
HB6	Inside Trinity House Ruins (THR)	63°23′56.55″ S/56°59′ 33.97″ W	23	Contamination by waste
HB7	THR, near the motor	63°23′56.10″ S/56°59′ 32.35″ W	16	Presence of alloys and coal
HB8	THR, near the ancient buildings	63°23′56.45″ S/56°59′ 33.10″ W	19	Presence of building wastes and coal

State, Brazil. X-ray fluorescence measurement conditions were: beam diameter of 200 μm, three points per sample irradiated with a reading time of 200 s per point, and a Fe filter with 6 mm thickness applied between sample and beam. This Fe filter was used to minimize detector saturation by Fe signal due to the naturally strong presence of this metal in the soil samples. Aiming a better data interpretation and visualization, the obtained XRF spectra were analyzed using principal component analysis (PCA) whose calculi were made with the help of Pirouette 4.0 software (Infometrix, Bothell, USA). Using PCA, the raw data are projected in a smaller dimension named principal components (PC) and separated in two new matrices called scores and loadings. These matrices carry information about the samples (scores) and the variables (loadings) and must be analyzed together aiming a better data interpretation and visualization.

2.2.2 Aqua Regia Extraction

Analytical grade reagents (Merck, Darmstadt, Germany), deionized water, and sub-boiling distilled acids (HCl and HNO_3) were used to prepare all solutions. All flasks and glassware were carefully washed with soap, decontaminated by immersion in HNO_3 10% *v*/*v* during 12 h, and finally rinsed with deionized water. Standard stock solutions of metals (1,000 mg L^{-1}) were used to prepare all analytical curves by successive dilutions.

Extraction with aqua regia was applied to determine the pseudototal content of Cd, Cr, Cu, Mn, Ni, Pb, and Zn in all soil samples. The extraction method was done according to the German Norm (DIN 1983). The extraction procedure was accomplished by weighing 300 mg of dried soil samples. This mass was placed in digester block tubes and 3 mL of aqua regia were added. A pre-digestion step was performed with 12 h reaction without heating. After, the tubes were transferred to a digester block, and a heating step of 3 h at 120°C was done under reflux. Finally, the extracts were transferred to previously decontaminated plastic tubes, and the final volume was completed to 10 mL with deionized water. All samples were analyzed in triplicate. To check the procedure accuracy, a certified reference material, Sewage Sludge from Industrial Origin (BCR 146R), was digested at the same way as the soil samples.

2.2.3 Extraction of Mobile and Mobilisable Metals

Although the pseudototal content provides a good indication of the degree of soil metal contamination, it does not provide enough information about the real environmental impact related to possible anomalous metal contents, since it is observed a poor correlation between this pool of metals and the concentration in the plant tissues. Therefore, in order to evaluate the levels of metals that can be potentially accumulated by organisms, the mobile fraction of metals was determined. The mobile fraction was assessed by an unbuffered salt solution, which simulates the uptake by plants, and it is regarded as an adequate model to simulate raining and flooding conditions (Rao et al. 2008). The mobilizable fraction can be determined by a complexing agent that is a good predictor of the potentially active heavy metals pool in soil. Complexing agents, such as ethylenediaminetetraacetic acid and diethylene triamine pentaacetic acid (DTPA), are capable to extract elements from organic or organometallic complexes and those bounded to inorganic compounds of the soil (Rao et al. 2008). These metal fractions, mainly the mobile ones, are a good approximation for the concentration of metals in the soil solution (Gupta et al. 1996).

In this context, DTPA extraction was used to assess the mobilizable fraction of metals. This solution was prepared with 0.005 mol L^{-1} of DTPA, 0.01 mol L^{-1} $CaCl_2$ buffered at pH=7.30 with triethanolamine (Lindsay and Norvell 1978). The extraction was performed using a soil/solution ratio of 1:5, in a horizontal shaker (Barnsteady, Iowa, USA) by 2 h. The supernatant was separated by centrifugation and transferred to previously decontaminated flasks.

The mobile fraction was evaluated by an unbuffered 0.01 mol L^{-1} $CaCl_2$ extraction solution (Carter and Gregorich 2007). One gram, in triplicate, was placed into centrifuge tubes adding 10 mL of the $CaCl_2$ solution. The extraction was performed in a horizontal shaker for 3 h. The supernatant was separated by centrifugation and transferred to previously decontaminated flasks.

2.3 Spectrometric Determination of the Metallic Elements by AAS

The spectrometric determination of Cd, Cr, Cu, Mn, Ni, Pb, and Zn in aqua regia, DTPA, and $CaCl_2$

extracts was performed by flame atomic absorption spectrometry (FAAS) and slotted tube atom trap (STAT)-FAAS. The most sensitive arrangement, STAT-FAAS (Matusiewicz 1997) was used to reach better power of detection for Cd and Pb quantification. In this scheme, a Ni tube with a 5 cm length slot in its bottom is placed above an air–acetylene flame, after the flame ignition (Watling 1977). All determinations were performed using a flame atomic absorption spectrometer (AA240FS; Varian, Mulgrave, Australia) equipped with a deuterium lamp for background correction. The working parameters: cathode lamp current, spectral resolution, and gas flow rate were those recommended by the manufacturer.

2.4 Enrichment Factors

Enrichment factor (EF) calculi were done in order to assess the degree of heavy metals contamination in the studied soils. In these calculi, it is necessary to selected elements with two characteristics: conservative and not related to anthropogenic inputs. In this case, Zr was selected and determined by X-ray fluorescence. Other elements that can be used for this purpose are Al, Li, Sc, and Ti, because they are practically not associated to human activities (Reimann and Caritat 2000). The equation used for EF calculi was:

$$\mathrm{EF} = \frac{\frac{c_n(\mathrm{sample})}{c_{\mathrm{ref}}(\mathrm{sample})}}{\frac{B_n(\mathrm{crustal})}{B_{\mathrm{ref}}(\mathrm{crustal})}}$$

where c_n (sample) is the concentration of the studied element at the studied site, c_{ref} (sample) is the concentration of the reference element at the studied site, B_n (crustal) is the average concentration in the Earth's crust of the studied element, and B_{ref} (crustal) is the average concentration in the Earth's crust of the reference element. The element chosen as reference was Zr and the crustal average concentrations of all elements, which were used in the equation, can be found in the study proposed by Yaroshevsky (2006). Sutherland (2000) proposed five classes of pollution degree based in the EF calculi:

1. EF<2—Minimal pollution
2. EF between 2 and 5—Moderate pollution
3. EF between 5 and 20—Significant pollution
4. EF between 20 and 40—Very strong pollution
5. EF>40—Extremely polluted

3 Results and Discussion

3.1 SR-XRF

The signal distribution profiles of three selected soil samples are shown in Fig. 2. In this figure, all spectra are in the same scale to facilitate the comparison. In XRF analysis, the concentration of a given element is proportional to its signal intensity, and visual analysis is important to discriminate the soil samples. For example, sample HB5, collected 50 m far from the generator (see details at Table 1), has strong signals of Cu, Pb (both Lα and Lβ), and Zn compared with the CRM. High Cu, Zn, and Pb signals were also detected in sample HB8 by the XRF analyzes. Although the direct comparison of signal intensities can be misleading due to the different matrix effects in the various sample types, it represents a good qualitative indication of metal contamination. Cadmium signals were not observed due to the characteristics lines for this element appears at 23.170 (kα) and 26.091 (kβ).

Nevertheless, this individual analysis of XRF signal profile is very slow, and the use of a chemometric approach such as PCA is appropriate to achieve an exploratory analysis. Therefore, all data obtained by X-ray fluorescence were organized in a matrix with eight rows (eight average spectra of three points per sample) and 2,048 columns (energy intensities ranging from 0.8 to 21.1 keV). This matrix was mean-centered, and the PCA was applied. The scores and loadings of the PCA plot are shown in Fig. 3a and b. The evaluation of the entire XRF profile shows remarkable differences in the chemical composition of the studied soils, especially for Fe contents (see loadings plot, Fig. 3b). Iron loadings were positive and high in the first PC (Fig. 3b) and the samples located at the positive part of scores plot (Fig. 3a) are related to this element. In this first PCA, only the majority elements were visualized (mainly Fe and Ca), and it was not possible to observe the influence of other elements. In this case, another PCA calculation was performed without the most intense and sharp signals (signals related to Ca, Fe, K, and Ti). The scores and loadings plots are presented in Fig. 3c and d, respectively. Thus, a clear separation was obtained for the sampling points, in which the HB7 and HB8 (positive values for PC1, Fig. 3c) points are related to strong signals of Pb and Zn (positive values for PC1, Fig. 3d). This observation is in agreement with that information presented at

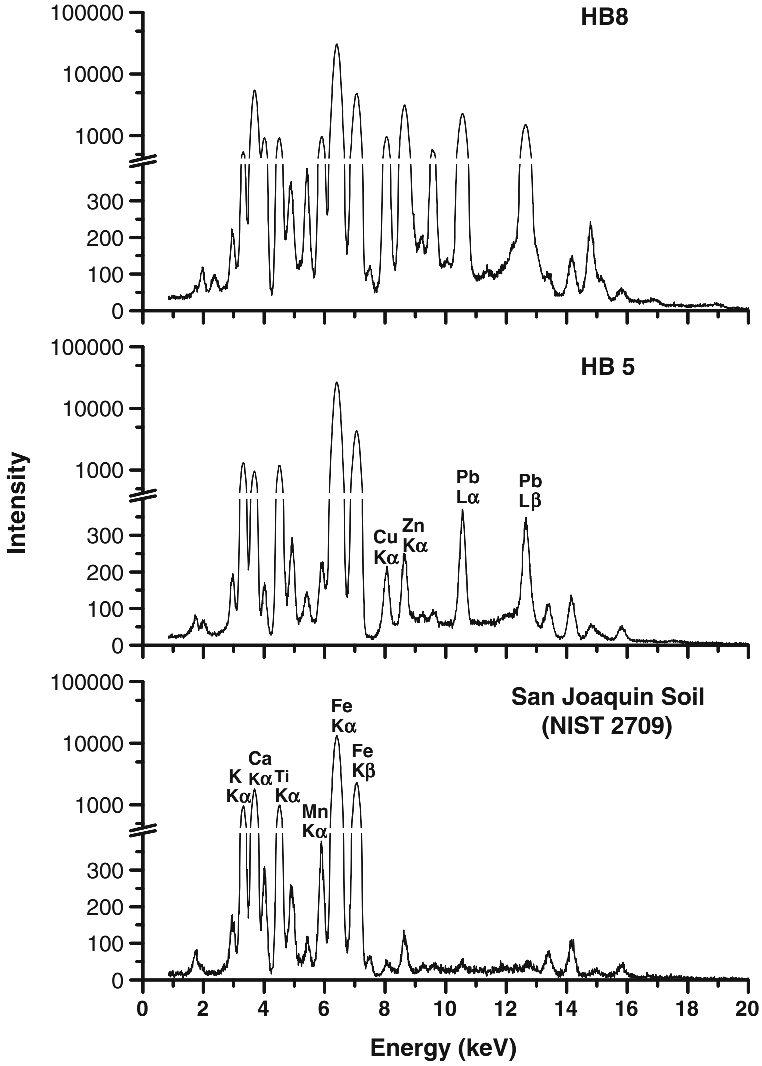

Fig. 2 X-ray fluorescence spectra for three different samples and signal attribution for Ca, Cu, Fe, K, Mn, Ti, Pb, and Zn

Table 1, where these two samples were associated with alloys, building wastes and coal.

3.2 Enrichment Factors

Table 2 presents the enrichment factors for the collected samples. As previously observed with the help of SR-XRF analysis and PCA (Fig. 3c, d), the highest contamination sites were HB7 and HB8. These samples had EFs for Pb ranging from 672 to 768 (average of 720). This average value is 18 times higher than the last class of pollution degree proposed by Sutherland (2000). Cadmium also exhibited elevated EFs values for both sampling points (average of 212), qualifying these sites as extremely polluted (class 5) by both heavy metals as pointed by Sutherland (2000). Similarly to Pb, the XRF analysis combined with PCA was a good predictive tool for Zn, because this element had slightly high EFs (average of 35), indicating a very strong pollution (class 4, Sutherland 2000).

In addition, the EF for Cu (EF=25, in average) was also remarkable for both HB7 and HB8 sites related to a significant pollution (Sutherland 2000). In a general view of the pollution pattern, it is interesting to note the similar values of EFs between these abovementioned points (HB7 and HB8) for the elements Cd, Cu, Pb, and Zn (see Table 2), which

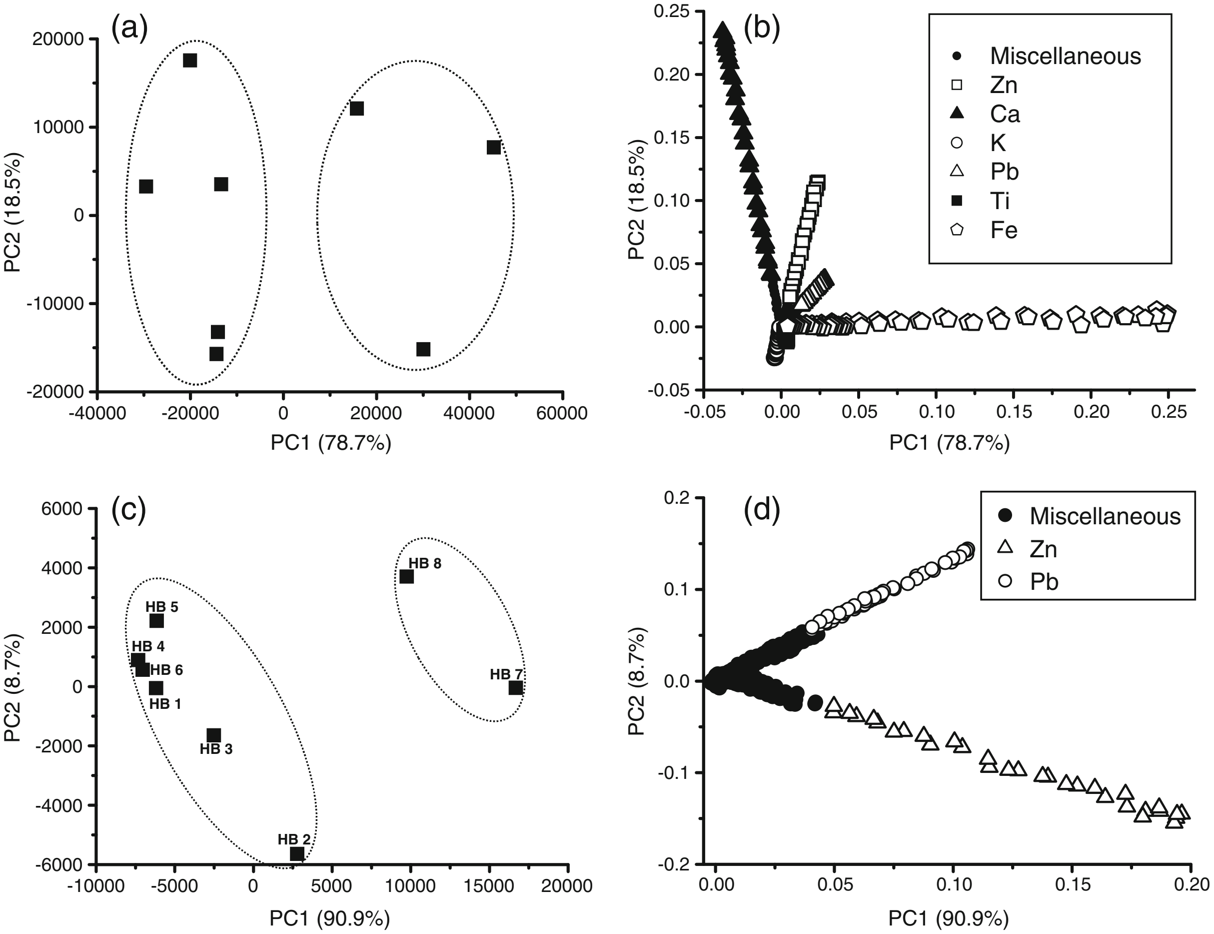

Fig. 3 Scores (**a**) and loadings (**b**) plots using all available data for the eight samples. Scores (**c**) and loadings (**d**) plots after exclusion of Ca, Fe, K, and Ti XRF signals

provide an evidence of same source and load of anthropogenic inputs in these places.

Table 2 EF using Zr as reference element

Sample	Cd	Cr	Cu	Mn	Ni	Pb	Zn
HB1	nc	0.2	1	0.1	0.1	4	3
HB2	59	2.9	4	0.3	1.6	29	45
HB3	18	0.4	7	0.2	0.2	11	11
HB4	nc	0.5	2	0.1	0.1	11	1
HB5	nc	0.6	2	0.1	0.1	11	1
HB6	nc	0.3	3	0.1	0.2	5	2
HB7	211	0.6	26	1.8	3.4	672	36
HB8	213	0.8	25	1.7	3.0	768	34

nc not calculated—element concentration below the limit of detection

The HB2 site showed high EFs for Cd, Pb, and Zn (59, 29, and 45, respectively), and verifying the PCA scores (Fig. 3c), we observed that this sample is positioned in an intermediate location between the lowest (HB1, HB3, and HB4 to HB6) and highest contaminated sites (HB7 and HB8). The remaining studied points, HB1, HB3, and HB4 to HB6 had low EFs for Cd, Cu, Pb, and Zn when compared to the others, although the point HB3 had a significant enrichment by Cd (EF=18). On the other hand, it was not observed evidence of pollution by Cr, Mn, and Ni due to their low EFs (0.2 to 2.9, 0.1 to 1.8, and 0.1 to 3.4 for Cr, Mn, and Ni, respectively) indicating minimal to moderate pollution (Sutherland 2000).

The use of EF may have some flaws (Reimann and Caritat 2000), such as variability of the Earth crust composition and different soil-forming processes that could concentrate metals from parent materials in the soil. However, in the little weathered soils of Antarctica, in areas of similar geochemical characteristics, the EF results provide additional information to infer on the degree of metal pollution.

3.3 Pseudototal Concentrations of Cd, Cr, Cu, Mn, Ni, Pb, and Zn in the Soil Samples

The accuracy of pseudototal extraction procedure was verified using BCR 146R-certified reference material. The recoveries for Cd, Cr, Cu, Ni, Mn, Pb, and Zn ranged from 89% to 102% when compared to the certified concentrations. As the metals concentration in the BCR 146R are in the same range of those found in the Hope Bay soil samples, it is possible to conclude that the procedure did not promote analyte losses during the heating process.

Table 3 shows the pseudototal concentrations of the studied elements. Consistently with SR-XRF, PCA results, and EF calculi, Hope Bay sites HB7 and HB8 have the highest metals concentration, especially for Cd, Pb, and Zn. The average pseudototal concentrations in HB7 and HB8 were 46, 18,993, and 4,823 mg kg^{-1} for Cd, Pb, and Zn, respectively. On the other hand, for the other sites, the average concentrations for these elements are 2.0, 233, and 999 mg kg^{-1}, respectively. These pseudototal contents of heavy metals such as Cd, Cu, Ni, Pb, and Zn are extremely above the limits according to the São Paulo State regulations (CETESB 2005). In addition, taking into account the prevention values for soil-quality preconized by CETESB (2005), pseudototal levels of these elements in samples HB7 and HB8 were 36 (Cd), 35 (Cu), 26 (Ni), 270 (Pb), and 87 (Zn) times higher. This prevention value is related to the concentration of a substance above which may occur detrimental changes to soil quality and groundwater, and it also indicates the quality of a soil able to support its primary function, namely to protect both ecosystem and groundwater. Special and urgent attention must be given to water pumping from the nearby Boeckella Lake (see details at Fig. 1), used as water supply for the Argentinean Base, in view of the imminent risk to human health.

It is important to mention that the deposition of heavy metals in the soil from avifauna excrements cannot be neglected. Otero Pérez (1998) studying soils strongly affected by yellow-ledged gulls in the Cies Islands (Galicia, northwest Spain) found a pattern of Cd, Cr, and Zn deposition well related to the density of these bird species in the region. Nevertheless, the same assumption could not be addressed to Pb that has another major source than gull feces. At the same way, Headley (1996) analyzing peat cores from the high Arctic region identified a markedly increasing trend of metals enrichment (especially for Cu, Pb, and Zn) at the most superficial depths and close to the seabirds' nests.

In this study, the investigated Hope Bay area has a deposition of bird feces mainly from penguin colonies. The heavy metals concentrations (Cd, Hg, and Pb) in stomach content, feathers, and excreta of Antarctic penguins (*P. adeliae*) was already studied by Ancora et al. (2002) and they have shown concentration levels of these metals ranging from 5.5 mg kg^{-1} of Cd (in excrements) to minor than 0.5 mg kg^{-1} for Pb.

In this way, we could assume that the pattern of contamination in the Hope Bay area is systematically linked to anthropogenic inputs (see the most impacted points HB7 and HB8, in the Tables 1 and 3), because Cd and Pb concentrations in these points reach 47 and 19,000 mg kg^{-1}, respectively.

Stark et al. (2008) during an assessment and remediation of a disposal site at the neighboring of the Australian Antarctic Casey Station found contamination by metals in the Thala Valley landfill. Using EDXRF technique, they observed remarkable contamination of Cu, Cr, Mn, Ni, Pb, and Zn in the most polluted site with a total concentration of 2,620, 833, 1,560, 450, 7,190, and 9,010 mg kg^{-1}, respectively. In the quoted study, the authors used the values suggested by the EPA of Tasmania (Australia) to classify the degree of soil pollution. These values are also shown in Table 3 (see more details in Environmental Protection Authority 2009), with classes of soil for disposal based on its total metal concentration. If the content of only one of the metals is greater than a critical concentration level, it is classified at a higher rank. Based on the EPA values for Tasmania, Hope Bay sites HB7 and HB8 are in the highest level of pollution (level 4), because Pb concentration is greater than the level 3 upper limit (3,000 mg kg^{-1}, Table 3). This Australian classification implies that the Antarctic Hope Bay soils are not acceptable for disposal without previous cleaning-up treatment.

Table 3 Comparative table with pseudototal concentrations of Cd, Cr, Cu, Mn, Ni, Pb, and Zn in the soil samples

Sample	Cd (mg kg^{-1})	Cr (mg kg^{-1})	Cu (mg kg^{-1})	Mn (mg kg^{-1})	Ni (mg kg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})
HB1	<LOD (0.04)	34±1	105±2	195±10	10.3±0.2	129±9	405±13
HB2	7.2±2.5	225±7	159±13	326±10	89±7	438±21	3,484±60
HB3	4.1±0.4	60±3	580±37	315±8	17.6±0.7	295±14	1,555±56
HB4	<LOD (0.04)	46±1	104±5	128±8	5.0±0,1	184±8	134±3
HB5	<LOD (0.04)	74±2	150±6	73±2	4.2±0.1	250±7	151±5
HB6	<LOD (0.04)	35±1	195±27	202±10	12.6±0.9	103±4	263±14
HB7	47±11	90±2	2,082±114	3,198±82	336±37	18,606±28	5,225±213
HB8	44±12	99±2	1,836±62	2,661±80	278±28	19,381±120	4,422±145
Tailings from a mine[a]	148.8	Unavailable	2,019	Unavailable	<LOD	20,412	38,076
Shanghai urban soils[b]	3.66	233.26	151.7	Unavailable	65.70	192.4	1,025
Waste disposal site in Antarctica[c]	Unavailable	833	2,620	1,560	450	7,190	9,010
Soils from a 25 years e-waste recycling site[d]	12.5	40.5	1,641.3	Unavailable	68.6	2,374.1	518.7
Lead and Zn smelter[e]	600	1,800	1,700	8,300	600	15,000	27,000
Prevention value[f]	1.3	75	60	Unavailable	30	72	300
Soil contamination (level 1)[g]	3	50	100	500	60	300	200
Soil contamination (level 2)[g]	40	500	2,000	5,000	600	1,200	14,000
Soil contamination (level 3)[g]	400	5,000	7,500	25,000	3,000	3,000	50,000

[a] Maximum reported concentrations (Boularbah et al. 2006)

[b] Maximum reported concentrations (Shi et al. 2008)

[c] Maximum reported concentrations (Stark et al. 2008)

[d] Maximum reported concentrations (Tang et al. 2010)

[e] Maximum reported concentrations (Stafilov et al. 2010)

[f] CETESB 2005

[g] Maximum allowable concentrations (Environmental Protection Authority 2009)

3.4 Mobilizable and Mobile Concentrations of Cd, Cr, Cu, Mn, Ni, Pb, and Zn in the Soil Samples

The mobilizable and mobile concentrations of the investigated metals grouped for each sampling point, and the percentage of these fractions in relation to the pseudototal content was calculated for Cd, Cu, Mn, Ni, Pb, and Zn, respectively (see Table 4). Chromium was not presented because the concentrations of this element were below the limit of detection for both fractions. In addition, Cr was the only element among those determined in this study, which did not present large anomalies in its concentration (Table 3). Generally, mobilizable fractions were higher than the mobile ones for all elements, due to the complexing property of the DTPA extractant. In relation to the mobilizable contents of heavy metals, substantial environmental concern is implied because of large amount of labile Pb reaching 1,817 (for HB7) and 2,094 mg kg^{-1} (for HB8; see Tables 3 and 4).

A Pearson correlation matrix (Table 5) was calculated using the pseudototal and mobilizable concentrations of elements. High correlations were observed between the pseudototal and mobilizable contents for several elements, showing a good selectivity for the DTPA extractant. However, the most important information obtained in this correlation matrix was a high correlation among the

Table 4 Percentage of mobilizable and mobile fraction in relation to the pseudototal content of metals

Sample	Element (%)										
	Cu		Mn		Ni	Pb		Zn		Cd
	Mobilizable	Mobile	Mobilizable	Mobile	Mobilizable	Mobilizable	Mobile	Mobilizable	Mobile	Mobilizable
HB1	15.51	nc	3.09	0.65	nc	nc	nc	4.36	0.08	nc
HB2	13.99	1.23	3.91	0.45	3.19	5.25	nc	13.21	0.11	6.77
HB3	6.08	0.60	2.99	0.87	5.63	2.48	nc	5.40	0.26	11.13
HB4	24.43	1.01	2.99	0.48	nc	0.00	nc	4.58	nc	nc
HB5	20.82	0.58	2.29	1.32	nc	3.12	nc	3.69	1.28	nc
HB6	15.18	0.55	2.78	2.24	9.67	nc	nc	3.79	1.95	nc
HB7	6.50	0.11	0.17	nc	0.50	9.77	0.02	5.77	0.03	4.08
HB8	5.95	0.09	0.19	nc	0.56	10.81	0.01	5.48	0.02	4.62

nc not calculated—concentration of the element below the limit of detection

pseudototal concentrations of Cd, Cu, Mn, Ni, Pb, and Zn, which may indicate the same pollution source.

The results obtained for the mobilizable fraction suggest the apparent order of mobility for the elements under investigation: Cu (14% in average) >> Cd (6.7%)>Pb (6.3%)>Zn (5.8%)>Ni (4.0%)>Mn (2.3%) >>Cr (<1.5%).

Similar results were obtained by Papafilippaki et al. (2007) in agricultural soils (Cu>Pb>Zn>Cr) as well as by Andreu and Gimeno-García (1999), analyzing rice-farming soils in marsh areas (Cu>Cd>Pb >> Zn>Ni>Co). As discussed by these authors, their findings indicate a potential risk of Cd and Pb to living organisms. This mobility order depends on chemical reactions and electrostatic interactions between clay minerals and soil organic matter with metals, and a better understanding of these phenomena will depend on further knowledge of soil characteristics, such as clay content, pH, cation

Table 5 Pearson correlation matrix using mobilizable (DTPA) and pseudototal concentrations

	Cd mo	Ni mo	Pb mo	Cu mo	Mn mo	Zn mo	Cd ps	Ni ps	Pb ps	Cu ps	Mn ps	Zn ps	Cr ps
Cd mo	1	0.39	0.97	0.96	0.02	0.61	0.99	0.98	0.98	0.98	0.98	0.92	0.27
Ni mo	–	1	0.26	0.23	0.72	0.95	0.36	0.49	0.26	0.24	0.30	0.69	0.93
Pb mo	–	–	1	0.96	−0.18	0.46	0.98	0.95	0.99	0.97	0.98	0.83	0.12
Cu mo	–	–	–	1	−0.19	0.44	0.98	0.95	0.98	0.99	0.99	0.83	0.08
Mn mo	–	–	–	–	1	0.65	−0.07	0.03	−0.18	−0.11	−0.12	0.33	0.67
Zn mo	–	–	–	–	–	1	0.57	0.68	0.47	0.47	0.51	0.86	0.90
Cd ps	–	–	–	–	–	–	1	0.99	0.99	0.98	0.99	0.90	0.22
Ni ps	–	–	–	–	–	–	–	1	0.96	0.95	0.98	0.94	0.34
Pb ps	–	–	–	–	–	–	–	–	1	0.98	0.99	0.84	0.13
Cu ps	–	–	–	–	–	–	–	–	–	1	0.99	0.85	0.09
Mn ps	–	–	–	–	–	–	–	–	–	–	1	0.87	0.14
Zn ps	–	–	–	–	–	–	–	–	–	–	–	1	0.58
Cr ps	–	–	–	–	–	–	–	–	–	–	–	–	1

mo mobilizable, *ps* pseudototal

Table 6 Physicochemical characteristics of the soil samples, pH in $CaCl_2$, TOC, and CEC

Variable/Sample	HB1	HB2	HB3	HB4	HB5	HB6	HB7	HB8
pH in $CaCl_2$	6.14	5.95	6.05	6.21	5.90	6.83	5.70	6.07
TOC (g/kg)	141.13	32.19	97.89	41.68	21.43	40.59	50.34	54.81
CEC ($mmol_c$/kg)	15.63	12.95	13.87	16.57	5.80	6.83	18.65	20.71

exchange capacity (CEC), organic matter content, among others.

Table 6 provides some physicochemical characteristics of the soil samples. In relation to pH, no significant difference was observed between the samples (average value of 6.1±0.3). On the other hand, there is a strong linear relationship between CEC and TOC ($R=0.98$) for sites HB2, HB4, HB5, HB7, and HB8. However, when all sites were included, the correlation was considerably depreciated ($R=0.33$). This might be due to the fact that sites HB1, HB3, and HB6 have been affected by organic materials (such as oil and wastes) which have not gone through humification. Although such materials increase the TOC content, they do not contribute to the CEC increment. For those sites with good correlation between CEC and TOC (HB2, HB4, HB5, HB7, and HB8), negative correlation was obtained between these variables and the mobile Cu (except for HB2), Mn, and Zn (see Table 4).

In relation to the mobile fraction of Cu, Pb, and Zn (see Table 7), for HB7 and HB8, the obtained values (concentration in the extracts) indicate substantial presence of these elements in the readily bioavailable pool.

Boularbah et al. 2006 investigated the heavy metal concentration in soils from five mining sites and carried out a toxicity evaluation of soil water extracts, using the MetPAD™ biotest, especially adapted to evaluation of anthropogenic soils. This biotest is specifically designed to detect heavy metal toxicity in environmental samples, based on the percentage of enzyme activity inhibition. When comparing our results with those obtained by Boularbah et al. 2006 (also presented at Table 7), sites HB7 and HB8 would show potential toxicity response in the MetPAD™ biotest, being one additional evidence of the need for remediation in these affected regions.

4 Conclusions and Outlook

Herein, we show the intense contamination degree of soils at the vicinity of Esperanza Station in Hope Bay, Antarctic Peninsula. The high contamination by heavy metals was confirmed by XRF and FAAS determinations. In addition, the EF calculi indicates that pollution pattern is mainly by Cd, Pb, and Zn. Due to the fragile characteristics of the Antarctic ecosystem and the relative simplicity of its food chain, these results are of great environmental concern.

Urgent measures must be taken for treatment and final disposal of contaminated soils at the studied sites in Hope Bay, especially by the strong presence of Cd and Pb, potentially toxic elements. Both the mobiliz-

Table 7 Comparative table with mobile concentrations of Cu, Pb, and Zn and responses of a MetPAD™ biotest

Soil sample	[Cu] ($\mu g\ L^{-1}$)	[Pb] ($\mu g\ L^{-1}$)	[Zn] ($\mu g\ L^{-1}$)	Innibition (%)
HB7[a]	236	348	173	–
HB8[a]	169	238	106	–
Control soil[b]	40	10	300	0
Soil A[c]	80	<LOD	50	20
Soil B[c]	300	<LOD	140	60

[a] This study—mobile concentrations

[b] Water extract of a control soil (Boularbah et al. 2006)

[c] Water extract of soils from a Cu mine (Boularbah et al. 2006)

able and mobile fraction of these elements indicate contamination and the need of intervention at the affected area.

Acknowledgements The authors are grateful to Fundação de Amparo à Pesquisa do Estado de São Paulo (Processes 07/04515-4, 09/09481-6, and 08/08260-3), Conselho Nacional de Desenvolvimento Científico e Tecnológico and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior for financial support; to the Brazilian Navy for the logistic support, and to Dr. Carlos Pérez for the analysis of SR-XRF at Laboratório Nacional de Luz Síncrotron (Processes XRF 7045 and 7046). This work is a contribution of the TERRANTAR laboratory of the INCT Criosfera (CNPq – Brazil). The authors also thank the anonymous reviewers for the contributions.

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