

## Heavy metal contamination in coastal sediments and soils near the Brazilian Antarctic Station, King George Island

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### Abstract

This paper investigates the natural and anthropogenic processes controlling sediment chemistry in Admiralty Bay, King George Island, Antarctica, emphasizing the area affected by the Brazilian Antarctic Station Comandante Ferraz (Ferraz). Total and bioavailable concentrations of sixteen elements were determined in 32 sediment and 14 soils samples. Factor analysis allowed us to distinguish three groups of samples: (1) Ferraz sediments, with higher content of total trace metals and organic matter; (2) control sediments, with intermediate characteristics; (3) Ferraz soils, with higher bioavailability of most metals due to its oxidizing condition and low organic matter content. Major elements such as Fe, Al, Ca and Ti presented similar levels in all three groups. Enrichment factor calculations showed that paints, sewage and petroleum contamination enhanced metal concentrations in Ferraz surface sediments as follows: B, Mo, and Pb (>90%); V and Zn (70–80%); Ni, Cu, Mg, and Mn (30–40%). Despite evidence of contamination in these sediments, the low bioavailability, probably caused by iron-sulfide, indicates small environmental risks.

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### 1. Introduction

Despite being the most isolated continent, Antarctica is not free from deleterious human impacts. Anthropogenic pollution can reach the polar regions through atmosphere circulation, e.g., organochlorines and metals such as Pb and Hg; and sea currents, e.g., plastic (Santos et al., 2004). Increasing human activities in Antarctica after the International Geophysical Year (1957–58) has caused several pollution problems, mainly near scientific stations. These problems have led to the implementation of strict environmental protocols, with the aim of preventing pollution.

Antarctic ecosystem is particularly sensitive to anthropogenic modifications. Ice-free land occupies <2% of the continent, but most of the human and terrestrial biological activities are concentrated in these areas (Campbell and Claridge, 1987). Furthermore, natural environmental stresses and some characteristics of Antarctic marine biota, such as low capacity of larval dispersion, narrow reproductive season, low fecundity, and low growth rates during crucial developmental stages (King and Riddle, 2001; Smith and Simpson, 1995), make it highly susceptible to human impact and sensitive to environmental contamination.

Heavy metals naturally occur in the earth crust. However human activities have introduced high loads of these elements in the environment, making the differentiation of natural and anthropogenic contributions

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difficult. Sediments provide a temporally integrated indication of the aquatic environment condition and act as a major reservoir for metals (Caccia et al., 2003), though some sediments can also act as a source of contaminants (Adams et al., 1992; Burton Jr. and Scott, 1992). Furthermore, sediments have high physical-chemical stability and their characteristics usually represent the average condition of the system, often being representative of the average water quality (Forstner and Wittman, 1983; Salomons and Förstner, 1984). Soils, along with rocks, are the terrigenous sources of elements to adjacent sediments and can indicate local hot spots.

The Protocol to the Antarctic Treaty on Environmental Protection recognizes the importance of scientific monitoring and continuous assessment of the impacts of ongoing activities in Antarctica (Champ et al., 1992). Yet, these kinds of studies are still incipient in most scientific bases. The understanding of local pollution processes concerning heavy metals in soils and sediments is particularly scarce in Antarctica (Ciaralli et al., 1998; Claridge et al., 1995; Kennicutt et al., 1995; Lenihan, 1992; Lenihan et al., 1990; Merlin et al., 1989; Sheppard et al., 2000; Webster et al., 2003). The only study on heavy metals in sediments of Admiralty Bay showed no evidence of pollution due to the human presence in this region (Gomes, 1999), but sampling was small. The aim of this paper is to investigate the naturally and anthropogenic processes controlling sediment chemistry in Admiralty Bay (AB), King George Island (KGI), Antarctica. Emphasis is given on heavy metal contamination in the region affected by Brazilian research and logistical activities in Keller Peninsula.

## 2. Materials and methods

### 2.1. Site description

The Brazilian Antarctic Station Comandante Ferraz (hereafter called just Ferraz) started operating in 1984. Nowadays, it shelter nearly 15 people during the winter months (March–November) and up to 48 people during the summer season, when research activities are intensified. At Ferraz Station, the organic matter is removed from the sewage (secondary treatment) and all environmental regulations of the Madrid Protocol (such as environmental monitoring and garbage disposal) are respected.

Admiralty Bay is a fjord in the King George Island, which is located approximately at 63°S in the South Shetlands Islands. This bay has an area of 131 km<sup>2</sup> and maximum depth of 530 m (Rakusa-Suszczewski, 1980). The South Shetlands Islands expose volcanic and plutonic rocks of Early Cretaceous to Early Miocene age, which are related to the subduction of the SE-Pacific oceanic crust underneath the Antarctic Con-

tinental. Mafic volcanic rocks (i.e. basalts, basalt-andesites and andesites) are the dominant lithologies. Rhyolite and dacite are less abundant (Groeneweg and Beunk, 1992; Machado et al., 1998, 2001; Pride et al., 1990; Schaefer et al., 2004).

### 2.2. Sampling

Surface sediment samples (top 2 cm) and soil (top 10 cm) were collected during the summer of 2002/2003, in the 21st Brazilian Antarctic Expedition. Surface soil samples ( $n = 14$ ) were collected in the marine terrace in front of the Ferraz Station. Coastal sediment samples ( $n = 32$ ) were collected with a Van Veen grab in transects (Fig. 1) normal to the coast at depths of 20, 30 and 60 m as follows: CF 1 (in front of Ferraz fuel tanks); CF 2 (in front of Ferraz helicopter landing area and sewage outfall); CF 3 (in front of Ferraz Chemical module); MP (in front of the Peruvian Machu Picchu Station); HE (at Hennequin Point). Two additional sediment samples were collected at Botany Point (BP) at 18.5 m depth. Samples were collected at the beginning (November and December of 2002) and at the end of summer season (January and February of 2003) in order to evaluate possible temporal variability caused by the increase in research and logistical activities at the Brazilian Antarctic Station during the summer.

### 2.3. Analysis

In the laboratory, samples were dried (<40°C) and ground for chemical analysis. Organic matter (OM) was determined by calcination (450°C, 24 h). Total metals were extracted with an adaptation of methods extensively used in literature (Bettinelli et al., 2000; Windom et al., 1989). Approximately 1 g of each sample was digested with aqua-regia and hydrofluoric acid in a Teflon bomb during 1 h at 120°C. After cooling, bombs were opened and heated again until almost dry. Extract recuperation was done with HCl 0.5 M. The samples were then analysed by ICP-OES (Perkin-Elmer), some in triplicate. All reagents used were Suprapur Merck® and water was Milli-Q. International Certified Reference Material (Estuarine sediment—NIST 1646a) and blanks were included in the set of samples to check the precision and accuracy of the analysis. Results of certified sediment analysis showed satisfactory analytical accuracy, varying between 85% for Ni and 104% for Ba. The precision of the analytical procedures (calculated as standard deviations of triplicates) were better than 8%, with the exception of Pb (11%) and Ni (12%), all considered satisfactory.

In order to quantify the labile or bioavailable forms of metals in relation to total metals, 1 g of the sediment sample was extracted for 2 h with 10 ml of 1 M HCl (Luoma and Bryan, 1981; Szefer et al., 1998). This tech-

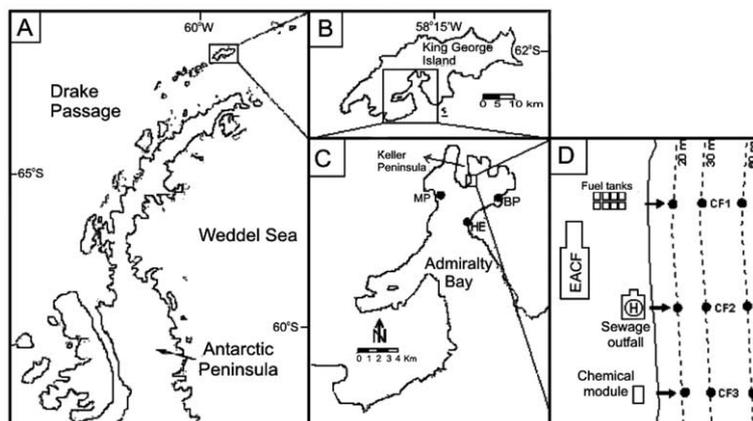


Fig. 1. Study area. (A) Antarctic Peninsula; (B) King George island; (C) Admiralty Bay; and (D) detail of coastal sediment sampling points in Keller peninsula near Ferraz Station.

nique determines the fraction of metals associated to Fe- and Mn-oxides and therefore allows measurement of bioavailable forms of metals in sediments. This extraction procedure has been extensively used because high correlations between metals in benthic organisms and 1 M HCl extracted metals in surface sediments are often found (Bryan and Langston, 1992).

Since there are no important point contaminant sources for the sediments collected in BP, MP, and HE, these points were called controls. In this paper, the concentrations of the variables under study were compared in sediments theoretically contaminated (in front of Ferraz) with control sites through *t*-test for independent samples. Outlier values were identified throughout test of Grubbs (Sokal and Rohlf, 1981). Here, the outlying values were deleted and then replaced by the highest values in datasets after deletion (Zhang et al., 1998). After outlier replacement, all variables passed in the normality test of Kolmogorov–Smirnov. Pearson's correlation coefficients were used for testing dependency between two variables. A significance level of  $p < 0.01$  was used throughout the study. Principal Component Analysis followed traditional methods (Wenchuan et al., 2001).

### 3. Results and discussion

#### 3.1. Heavy metal distribution

Table 1 shows the average concentrations of total metals in soils and coastal sediments in comparison with several reference values. No important temporal (beginning and end of summer) and depth-related variability of metal concentrations in sediments were observed, therefore data presented is a mean of the two temporal samplings. In comparison with the earth crust (Wedepohl, 1995), the high levels of copper, in the studied

soils and sediments, is of major environmental concern. It is related to the widespread mineralization of calcopirite in the volcanic rocks of the area (Machado et al., 2001), and not necessarily related to anthropogenic contamination. Cr and Fe concentrations were higher than sediments of Collins Harbour, KGI (Ahn et al., 1996), though extraction techniques were different.

In relation to local rocks (Groeneweg and Beunk, 1992; Machado et al., 1998, 2001) concentrations of most elements were similar, with the exception of Sr, Mg, Ca, and Ba, which are higher in rocks probably due to the dissolution processes in subaqueous sediments. The heavy metal contents indicate the influences from the geochemical weathering of terrigenous sources on Admiralty Bay rocks. The results of the only previous study on Admiralty Bay sediments (Gomes, 1999) were also similar to the results presented here, with the exception of Ni.

Principal Component Analysis (PCA) was applied for evaluating the hypothesis of a geographical separation of sampling points. Three groups of samples with different physical-chemical properties and geographical distribution were clearly separated (Fig. 2). Group 1 is formed by sediment samples collected in front of Ferraz Station. These samples had higher OM and trace elements content. In Group 2 control sediment samples were fitted, characterized by lower content of total trace elements and fine-grained sediments. Group 3 was formed by CF soil samples, having coarser grains and less organic matter compared with the other groups.

In fact, total B, Cu, Pb, V, Zn, OM and fine-grained sediments presented higher content in CF sediments (*t*-test;  $p < 0.01$ ). Sr was the only element with higher values in the control sediment samples (Table 1 and Fig. 3). For the major elements Al, Fe, Ca, and Ti there were no differences between Ferraz and the control sediment sampling points. Titanium, probably as ilmenite, is one of the most stable elements in the aquatic environment

Table 1

Average content of metals in studied soils and sediments in comparison with results of other studies

Matrice (local)	Al	B	Ba	Ca	Cr	Cu	Fe	Mg	Mn	Mo	Ni	Pb	Sr	Ti	V	Zn
Ferraz sediments (AB, KGI) <sup>a</sup>	3.16	243	41	0.58	31	92	6.47	0.14	624	1.5	10.1	10.5	63	0.58	204	89
Control sediments (AB, KGI) <sup>a</sup>	3.02	136	75	0.68	35	67	6.88	0.11	527	0.7	7.9	5.5	121	0.58	127	52
Ferraz soils (AB, KGI) <sup>a</sup>	3.44	89	109	0.48	40	44	6.15	0.12	442	2.1	5.1	11.5	118	0.58	91	52
Sediments (Collins Harbour, KGI) <sup>b</sup>					7.6	77	2.42		640		15.4	8.7				69
Sediments (McMurdo Station) <sup>c</sup>						11					68.0	7.0				32
Sediments (AB, KGI) <sup>d</sup>	5.44					68	6.28				41.3	14.9				60
Sediments (Intertidal area, KGI) <sup>e</sup>			28		2.6	52	2.37		280	46.2	11.5	121.0	344	0.04	82	47
Sediments (Ross Sea) <sup>f</sup>					47.0	25					23.0	15.0			49	50
Soils (near Lake Vanda) <sup>g</sup>						28	1.00		104		11.2	3.9				24
Sediments (Terra Nova Bay) <sup>h</sup>	5.61				20.3		1.64		359		6.3	20.7				42
Vulcanic Rocks (KGI) <sup>i</sup>	5.18		198	7.27			2.92	2.65	1100		60.7		542	0.56		
Vulcanic Rocks (AB, KGI) <sup>j</sup>	4.77		333	5.72		111	2.79	2.20	1500		12.5	7.7	583	0.64	107	66
Rocks (Global average) <sup>k</sup>	7.96	11	584	3.85	126	25	4.32	2.20	716	1.1	56.0	14.8	333	0.4	98	65

Values in mg/Kg, except Al, Ca, Mg, Fe and Ti, in %.

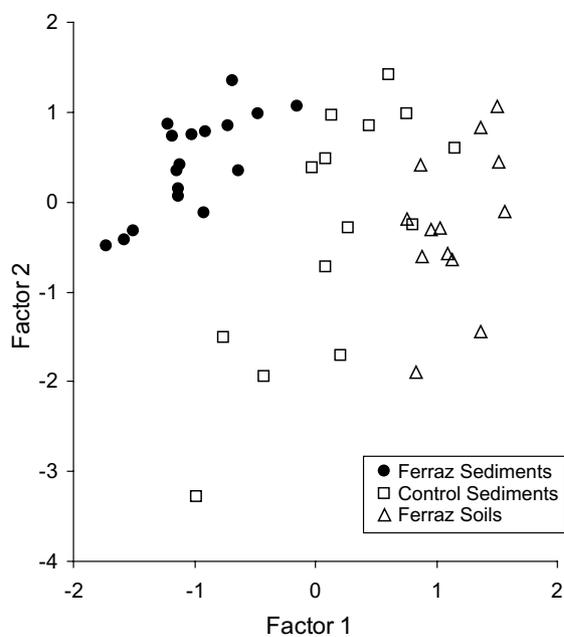
<sup>a</sup> This Study.<sup>b</sup> Ahn et al. (1996)<sup>c</sup> Lenihan et al. (1990).<sup>d</sup> Gomes (1999).<sup>e</sup> Alam and Sadiq (1993).<sup>f</sup> Merlin et al. (1989).<sup>g</sup> Webster et al. (2003).<sup>h</sup> Ciaralli et al. (1998).<sup>i</sup> Machado et al. (2001).<sup>j</sup> Groeneweg and Beunk (1992).<sup>k</sup> Wedepohl (1995).

Fig. 2. Factor scores obtained from principal component analysis.

and together with Al represent the most important indicators of detrital origin (Karageorgis et al., 1998). Thus, little variation in Al and Ti among the different sampling groups indicates that lithological sources are basically the same, and different loads of most trace metals cannot be explained solely by natural geochemical signatures.

### 3.2. Geochemical carrier

In the absence of a sequential extraction of metals in sediments, statistical procedures can be used for making inferences on the most important geochemical carrier. Organic matter, sulfide, carbonate, iron oxyhydroxide and fine-grained sediments have been considered the main metallic scavenger and/or geochemical carriers in sediments (Salomons and Förstner, 1984). Pearson's correlation coefficients were calculated for evaluating the dependency of metals in relation to Al, Fe, Ca, OM, and grain size for the three groups of samples (Table 2). Pearson's correlations for all samples could not be calculated because scatter plots (Fig. 3) and PCA (Fig. 2) clearly formed different populations of samples, which would lead to inconsistent interpretation.

With the exception of the strong relationships between Zn, Pb and fine-grained sediments in Ferraz soils, Pearson's coefficients did not show good correlations between metals and OM and fine-grained sediments (<0.062). This was unexpected, since trace element concentrations usually increase as grain size decreases, due to the higher ability of the fine particles to collect both transition and heavy metals. Fine-grained sediments have a greater surface area and provide a more efficient environment for the adsorption of metals. Organic matter is also considered a good metallic scavenger (Wasserman et al., 1998).

Although elemental correlations are different between sampling groups, it is possible to identify two main cat-

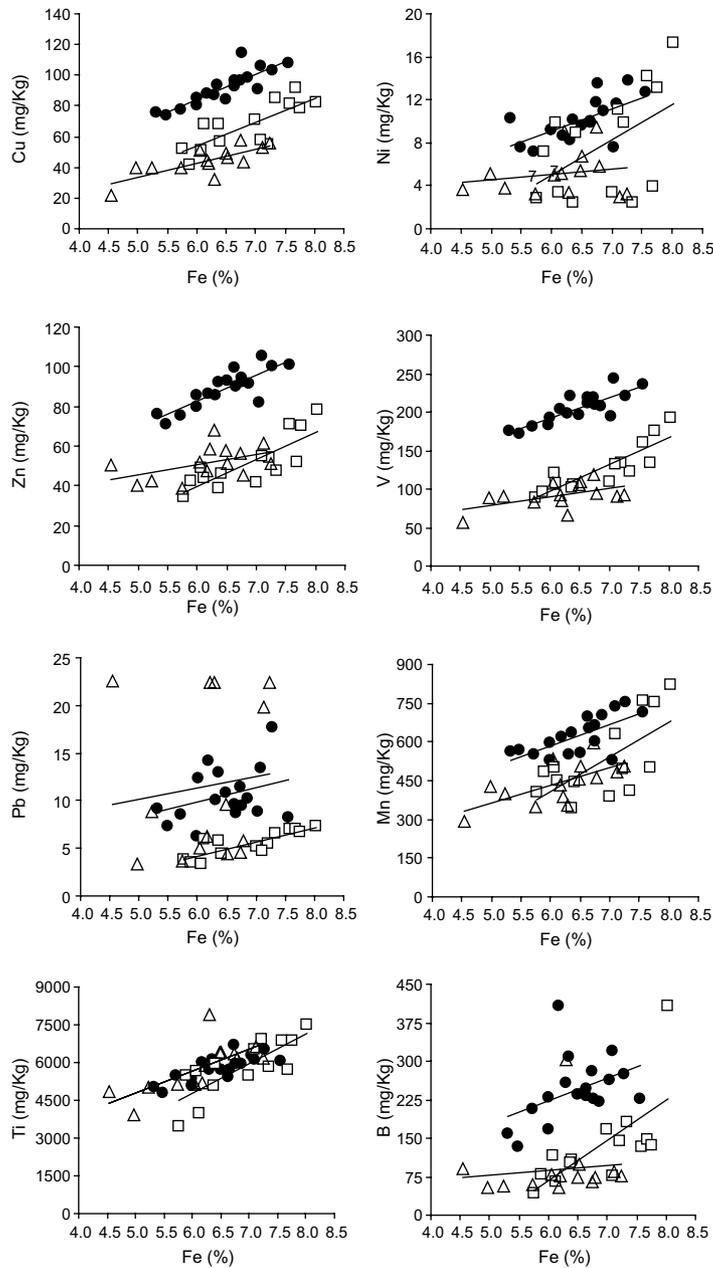


Fig. 3. Scatter plots of iron and other metals. Circles—Ferraz sediments; Squares—Control sediments; Triangles—Ferraz soils.

egories of elements with similar behaviour. The first category was clearly composed by Fe and metals such Cu, B, Ti, Pb, V, and Zn. These elements showed high positive correlation with Fe mainly in the Ferraz sediments, indicating the existence of a FeMn oxyhydroxide and/or an iron sulfide factors (depending on the prevailing redox conditions), which attracts a substantial part of trace elements. Concentrations of Mn, Ni, Cr, and Ba depend either on iron or calcium. In Ferraz sediments, these metals had stronger correlations with iron, while in control sediments Cr, Mn and Ni correlated better with calcium (Table 2).

The adsorption of metals in Fe–Mn oxyhydroxides is a common phenomenon in marine sediments (Calvert, 1976). The oxides are observed either as coatings on the clay-minerals or as individual particles. However, this behaviour is normally observed in very weathered environments, whilst trace metals entering Admiralty Bay will probably be removed as sulfides in the coastal anoxic sediments, likewise in other Antarctic ecosystems (Green et al., 1989; Webster et al., 2003). This hypothesis is supported by prevalence of reducing conditions in sediments (authors unpublished data), abundance of iron-sulfide minerals (pyrite/calcopyrite; Pride et al.,

Table 2  
Pearson correlation coefficients between variables for Ferraz sediment samples ( $n = 18$ ); control sediments ( $n = 14$ ); and Ferraz soils ( $n = 14$ )

	Ferraz sediments ( $n = 18$ )					Control sediments ( $n = 14$ )					Ferraz soils ( $n = 14$ )				
	Al	Ca	Fe	OM	<0.062mm	Al	Ca	Fe	OM	<0.062mm	Al	Ca	Fe	OM	<0.062mm
Al		0.60 <sup>***</sup>	0.45 <sup>*</sup>									0.61 <sup>**</sup>			
B			0.42 <sup>*</sup>					0.69 <sup>***</sup>							
Ba							0.51 <sup>*</sup>	0.55 <sup>**</sup>			0.51 <sup>*</sup>				
Ca	0.60 <sup>***</sup>		0.48 <sup>**</sup>								0.61 <sup>**</sup>				-0.54 <sup>**</sup>
Cr		0.46 <sup>*</sup>	0.60 <sup>***</sup>			-0.47 <sup>*</sup>	0.88 <sup>***</sup>	0.58 <sup>**</sup>							
Cu	0.52 <sup>**</sup>	0.48 <sup>**</sup>	0.87 <sup>***</sup>					0.79 <sup>***</sup>		0.60 <sup>**</sup>			0.77 <sup>***</sup>	0.57 <sup>**</sup>	
Fe	0.45 <sup>*</sup>	0.48 <sup>**</sup>													
Mg					0.42 <sup>*</sup>					-0.49 <sup>*</sup>	0.75 <sup>***</sup>	0.75 <sup>***</sup>			
Mn	0.58 <sup>**</sup>	0.52 <sup>**</sup>	0.68 <sup>***</sup>				0.84 <sup>***</sup>	0.67 <sup>**</sup>				0.56 <sup>**</sup>	0.65 <sup>**</sup>	-0.52 <sup>*</sup>	
Mo					-0.54 <sup>**</sup>		-0.57 <sup>**</sup>								
Ni	0.43 <sup>*</sup>	0.58 <sup>**</sup>	0.63 <sup>***</sup>			-0.53 <sup>*</sup>	0.91 <sup>***</sup>	0.51 <sup>*</sup>				0.54 <sup>**</sup>			
Pb								0.84 <sup>***</sup>				-0.76 <sup>***</sup>		0.48 <sup>*</sup>	0.79 <sup>***</sup>
Sr	0.74 <sup>***</sup>	0.49 <sup>**</sup>					0.88 <sup>***</sup>	0.49 <sup>*</sup>			0.59 <sup>**</sup>	0.91 <sup>***</sup>		-0.50 <sup>*</sup>	-0.54 <sup>**</sup>
Ti			0.79 <sup>***</sup>			-0.59 <sup>**</sup>	0.55 <sup>**</sup>	0.79 <sup>***</sup>					0.72 <sup>***</sup>		
V	0.55 <sup>**</sup>	0.46 <sup>*</sup>	0.84 <sup>***</sup>				0.60 <sup>**</sup>	0.87 <sup>***</sup>				0.63 <sup>**</sup>	0.54 <sup>**</sup>	-0.61 <sup>**</sup>	
Zn	0.50 <sup>**</sup>	0.50 <sup>**</sup>	0.84 <sup>***</sup>				0.70 <sup>***</sup>	0.81 <sup>***</sup>					0.48 <sup>*</sup>		0.48 <sup>*</sup>
OM					0.42 <sup>*</sup>					0.64 <sup>**</sup>					0.49 <sup>*</sup>

\*  $p < 0.1$ .

\*\*  $p < 0.05$ .

\*\*\*  $p < 0.01$ .

1990; Schaefer et al., 2004) in local rocks and higher organic content in sediments in front of Ferraz Station, which favors iron sulfides formation to the detriment of Fe–Mn oxyhydroxides. Furthermore, predominance of physical weathering in the Antarctic environment do not favor the formation of secondary minerals, like clays (Campbell and Claridge, 1987), decreasing relative importance of aluminum on controlling heavy metals distribution patterns.

The second category of elements was formed by Al, Ca, Sr, and Mg. These elements have strong interdependency in Ferraz soils and sediments, indicating a common lithogenic source and the occurrence of Ca–Al minerals, like plagioclases (Machado et al., 2001). Molybdenum is the only element without any strong ( $p < 0.01$ ) correlation with other elements in Ferraz soils and sediments and has a higher enrichment factor indicating that anthropogenic inputs control its distribution, rather than natural inputs, as described ahead.

### 3.3. Heavy metal bioavailability

Ratios between 1M HCl extracted metals and total concentrations (hereafter called bioavailable:total ratio) are presented in Fig. 4. Results clearly show an increase of bioavailability of heavy metals in soils in comparison to sediments. This could be explained by possible different redox properties of soils and sediments. Soils are oxidizing environments, favoring the occurrence of Fe–Mn oxides in relation to iron sulfides, therefore increasing the relative contribution of easily extractable metals. Sediments, on the other hand, are probably more reduced and iron occurs predominantly as sulfide complexes, decreasing its bioavailability and, consequently, the efficiency of the 1M HCl extraction procedure. In fact, metal sulfide complexes have low solubility in natural waters and their formation is very important to metal bioavailability/toxicity reduction in the aquatic environment (Clark et al., 1998; Fernandes, 1997).

Sulfur and iron cycling in surface sediments is largely influenced by sedimentation rates, organic matter supply, availability of sulfate and reactive iron, and oxygen concentrations in the bottom waters (Billon et al., 2001;

Wijsman et al., 2002). With increasing concentrations of organic matter in the sediment, the relative importance of sulfate reduction usually increases (Clark et al., 1998; Wijsman et al., 2001). Hence, the observed higher organic content of Ferraz sediments favors the occurrence of reducing environments and sulfide formation, decreasing bioavailability of metals.

The percentages of easily extractable metals in Admiralty Bay sediments are usually low in comparison with other environments, with the exception of Aluminum. In sediments of the Baltic Sea, for example, Cd, Pb and Zn (>70%) were efficiently leached out with HCl 1M; Cu, Cr, Mn, Ca, Sr and Mg were less efficiently leached (~60%); and Al poorly leached (4%) (Szefer et al., 1995). The only previous study on ratios between total and easily extractable metals for Antarctica was conducted in Terra Nova Bay (Ciaralli et al., 1998). These authors extracted with 0.5N HCl 3.5% (Fe) to 35.4% (Zn) of total metals, but these results are not comparable due to different extraction techniques employed.

### 3.4. Contamination processes

The possibility of sediment contamination was assessed through the calculation of the metal enrichment factor (EF), which is the observed metal/normalizer ratio in the sample divided by the metal/normalizer ratio reported for a reference material (Salomons and Förstner, 1984; Zhang, 1995). Metals such as Al, Li and Fe have been largely used as geochemical normalizers (Daskalakis and O'Connor, 1995; Niencheski et al., 2002). In this work, Fe and Al were tested as normalizers and the earth crust average as reference value (Wedepohl, 1995).

In relation to Aluminum, the use of iron as geochemical normalizer seems to be more adequate because (1) it shows better correlation with most elements (Table 2), suggesting that iron is the main geochemical carrier in the studied sediments; (2) the common disadvantages of using iron as normalizer probably do not occur in the studied surface sediments; and (3) aluminum occurs at lower levels in the studied sediments in relation to earth crust values, generating unrealistic enrichment factors. The main limitation of using iron as a geochemical normalizer is the possibility of anthropogenic input of this element (Niencheski et al., 2002), as well as its redox sensitivity, which is a limiting factor for its application in sediment cores (Wasserman et al., 2001). The use of statistical procedures for determining the main geochemical carrier in sediments and choosing the best geochemical normalizer has also been done by other authors (Liu et al., 2003).

Enrichment factor calculations using average earth crust as reference and iron as a geochemical normalizer showed elevated values for Ferraz sediments (Fig. 5). When *t*-test was applied for comparing EF of the studied elements between control and Ferraz sediments, the

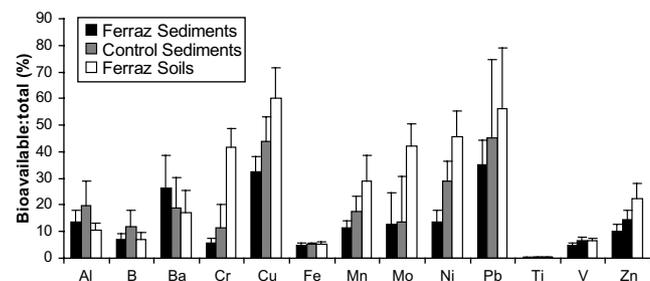


Fig. 4. Average percentage and standard deviation of total metal content extracted with 1M HCl for three groups of samples.

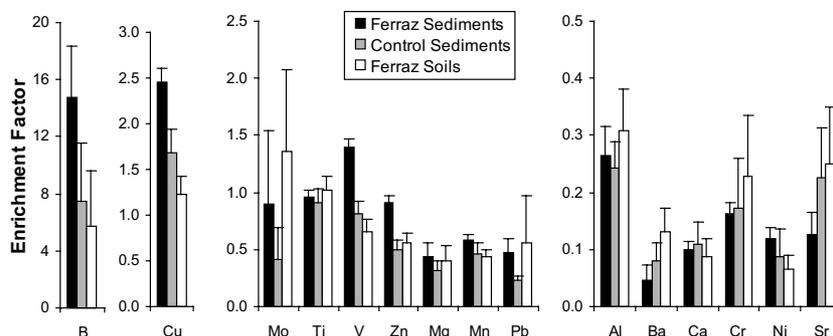


Fig. 5. Average and standard deviation of enrichment factor of metals for three groups of samples. Values normalized by iron and using earth crust average as reference (Wedepohl, 1995).

results were similar to those of the raw data. The EF of B, Cu, Mg, Mn, Pb, V and Zn were higher in Ferraz sediments, while Ba and Sr were higher in control sediments.

Control sediments have no important local anthropogenic contamination sources, have similar geochemical properties (i.e. major element content) compared with Ferraz sediments, and other works (e.g. Pride et al., 1990; Groeneweg and Beunk, 1992) did not show any special kind of mineralization near Ferraz Station. Taking into account these characteristics and in the absence of other reference values, such as sediment core data, the average elemental concentrations of control sediments may represent background levels of Admiralty Bay, and could be used for estimating the role played by Ferraz Station activities in changing metal levels of its adjacent sediments.

Fig. 6 shows average enrichment factors for metals in Ferraz sediments using average metallic values of control sediments as reference. It demonstrates an enrichment of several metals, which could not be attributed to natural characteristics. Based on this figure, it is possible to estimate that after 19 years of activities, Ferraz Station has increased natural metal concentration in adjacent surface sediments as follows: B, Mo, and Pb (>90%); V and Zn (70–80%); Ni, Cu, Mg, and Mn (30–40%). For other metals there were no indications of anthropogenic input. Despite evidence of contamination in these sediments, low

bioavailability indicates minimum environmental risks. Molybdenum is closely related with redox conditions in marine sediments. While it is conservative in the oxygenated ocean, it accumulates in anoxic sediments (Bertine, 1972; François, 1988). Thus, enrichment of Mo may be due to human input associated with redox conditions of sedimentary environment.

Relationships between Zn and Pb with fine-grained particles in Ferraz soils associated with its high bioavailability (mainly for Pb) suggest local contamination. However, the absence of control soil samples make the assessment of Ferraz soils contamination difficult.

The possible anthropogenic sources of metals for Ferraz sediments are petroleum contamination, sewage disposal and paints. Studies concerning hydrocarbon (Bicego et al., 1998) and wastewater (Martins et al., 2002) contamination in sediments near Ferraz Station have shown low and localized levels of pollution, similar to our results. Several metals (V, Ni, Zn, Cu, Cr, Pb, Ba, among others) have been associated with petroleum contamination (Alam and Sadiq, 1993; Caccia et al., 2003). Paints are also another possible source of metals, such as Pb and Cu (Webster et al., 2003), and it is very likely that the structure of the helicopter landing area contributes to the increase of these elements in Ferraz sediments. In McMurdo Sound region, crushed batteries, scattered rubbish and buildings are point sources

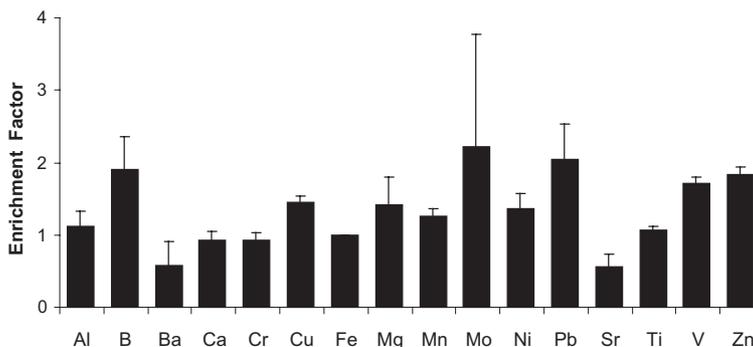


Fig. 6. Average and standard deviation enrichment factor of metals in Ferraz sediments. Values were normalized by concentrations of Control sediments.

of metals (Pb, Zn and Cu) in soils, while burning fuel results in widespread contamination of lead (Claridge et al., 1995). Sewage has also been considered an important source of metals both for lower latitude and Antarctic regions. Near the McMurdo Station, for example, higher concentrations of metals were observed in sediments around the sewage outfall (Kennicutt et al., 1995; Lenihan, 1992).

#### 4. Conclusions

In this paper, soil and coastal sediments of Admiralty Bay were characterized in reference to heavy metal concentrations, serving as basis for environmental monitoring programmes in the region. In general, our results agree with other Antarctic sediments and rocks from King George Island. Factor analysis allowed us to distinguish three groups of samples: (1) Ferraz Station sediments, with higher total metals and organic matter content; (2) control sediments, with intermediate characteristics; and (3) Ferraz soils, with higher bioavailability of most metals due to its oxidizing condition, low organic matter content and coarser grains.

Statistical procedures indicated iron as the main geochemical carrier in the studied sediments therefore iron is preferred as a geochemical normalizer for enrichment factor calculations. Sewage disposal, paint residues from buildings and/or petroleum are probably the sources of trace metals enrichment in sediments collected near Ferraz Station. On the other hand, anthropogenic input of organic matter to sediments favors sulfide formation and reduction of metal bioavailability, consequently decreasing adverse effects on local biota. The relatively low availability of metals in Ferraz sediments appears to counteract the local enrichment of most metals.

The small area of contaminated sediments and low bioavailability of heavy metals suggest that this would not adversely affect Antarctic benthic marine organisms. Furthermore, contamination levels are lower than other Antarctic Research Stations and industrialized regions. Continuous environmental monitoring, determination of local background through sediment cores, transference rates to biota, and further ecotoxicological studies are essential for identifying and preventing pollution in Admiralty Bay.

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