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Sediment geochemistry in Admiralty Bay (Antarctica): trace, rare earth elements and radionuclides

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ABSTRACT

The main goal of the present study was to assess some trace and major elements, total mercury, natural and artificial radionuclides, organic carbon, sulfur, organic matter in Admiralty Bay sediments. The samples were collected in January/February 2003 (XXI OPERANTAR) summer southern season. Trace elements (As, Ba, Br, Co, Cr, Cs, Hf, Rb, Sb, Sc, Ta, Tb, Th, U, Zn), rare earth elements (Ce, Eu, La, Lu, Nd, Sm, Tb and Yb) and major elements (Fe, K and Na) were determined by instrumental neutron activation analysis. Total mercury was determined by cold vapor atomic absorption technique (CV AAS) technique. ^{226}Ra, ^{228}Ra and ^{210}Pb were measured by gamma spectrometry. The strontium (Sr) and plutonium ($_{94}$Pu) determinations were based on the selective separation by chromatography and measurement by beta scintillation counting and alpha spectrometry, respectively. C, N and S were analyzed by LECO-CNS2000 Analyzer and organic matter (OM) by combustion. The P sedimentary fractions were determined by extraction and colorimetric determination. The results obtained for the elemental concentrations were quite uniform and corresponded to the natural levels of the region considering the natural level, in the soil composition found. Cluster analysis showed two distinct groups: i) one group included mainly Fe group elements (Sc, Cr, Co and Zn) and ii) a second group included mainly heavy mineral constituents (rare earth elements, Th and Hf). Only one point presented Hg and As concentrations above natural levels.

Key words: bottom sediments, chemical composition, natural and artificial radionuclides, Antarctica.

INTRODUCTION

The Antarctic region is a remote area known to present referential data that show natural concentrations of elements and compounds, frequently without anthropogenic influence. Therefore, it is important to assess the natural levels of environmental components as well as the anthropogenic contributions due to human installations for development of scientific research activities and in function of the touristic activities in the region (PROANTAR 2009).

The terrestrial Antarctic ecosystems are characterized by discontinuity, by inhospitable environmental conditions, by low species diversity, and very slow growth rates (PROANTAR 2009).

The Brazilian Antarctic Program (PROANTAR) was implemented in January 1982. Brazilian activities in Antarctic are based at "Comandante Ferraz" Antarctic Station (EACF), on King George Island

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(62°05′S and 58°25′W), in Bransfield strait. Admiralty Bay is located at King George Island and has three inlets: i) Martel, ii) Mackellar and iii) Ezcurra. The EACF is located at the left entrance of Martel Inlet (PROANTAR 2009).

Since 1982, several Brazilian scientific projects have been developed by the Oceanographic Institute of São Paulo University, and more recently, the project "Hydrogeochemistry of Admiralty Bay" (CNPq Process 550439/2002-2) was developed by Nutrient, Micronutrient and Traces in the Oceans Laboratory (LABNUT-IOUSP), with collaboration of the Neutronic Activation Laboratory (LAN/CRPq-IPEN) and LRA/CMR and COLAB/CNEN and also from Institute of Energetic and Nuclear Researches (IPEN). The objective of this collaboration was to integrate some sedimentary and chemical parameters with special focus on the traces, earth elements and radionuclides distribution in this remote bay observing its role on biogeochemical processes.

The richness of elements in the cryogenic soil and the guano influence on the phosphorus contents were demonstrated for soils of King George Island lowlands, and in some marine coastal sediments in Admiralty Bay (Schaefer et al. 2004, Santos et al. 2004).

Santos et al. (2007) demonstrated the geochemistry variation in three core samples collected in the soil and coastal region of the Admiralty Bay, observing the local element sources, the weathering transportation, deposition and diagenesis. The trace metal contamination signals in the soil around the Brazilian Antarctic Station (EACF – King George Island) were identified by Santos et al. (2005).

Santos et al. (2004) observed that there are important differences between the Fe, Mn, and OM contents in the soil located in front of the "Comandante Ferraz" Brazilian Research Station and in sediments from Admiralty Bay. In general, Fe and Mn are abundant in the soils. The Hg content did not present a strong correlation with Fe, Mn and organic matter (OM) evidencing a probable association with residual origin (Santos et al. 2004). The small variation of the Pb, Cd, Ni, Zn, Li, Sn, U, Al and Fe contents in 12 sampling stations at Admiralty Bay was first shown by Gomes (1999), and confirmed by Santos (2004). An evaluation of granulometric characteristics, oxy-redox horizons and organic matter contents constitute a complementation of information on the environment in Admiralty Bay.

The quality of analytical results was maintained since published analytical neutron activation analysis (NAA) has been widely applied to soil and sediment analysis (Crespi et al. 1993, Bulnayev 1995, Dinescu et al. 1998, Larizzatti et al. 2001) and allows the simultaneous determination of several elements such as Mn, Zn, As, Ba, Br, Ca, Co, Cr, Cs, Fe, Hf, Sb, Se, Ta, Th, U, W, Zr and rare earth elements. For total Hg determination, the cold vapor atomic absorption technique (CV AAS) is largely used for biological, geological and environmental samples (Horvat 1996).

The purpose of this study also assessed total mercury, phosphorus (organic and total), total nitrogen, organic carbon, sulphur, natural and artificial radionuclides, and some trace and major elements concentrations in sediments from Admiralty Bay.

MATERIAL AND METHODS

SAMPLING AND SAMPLE PREPARATION

Bottom sediments were collected during the sampling trip (XXI OPERANTAR), in January/February Southern summer 2003, at Admiralty Bay (George King Island) by using a steel Van Veen-type dredge. Considering the sampling region (Fig. 1), 15 sediment samples were effectively collected at stations: 1, 5, 6, 8, 9, 11, 12, 13, 15, 18, 21, 22, 23, 24 and 26 that integrated total stations included in XXI OPERANTAR. After collection the samples were frozen at −20°C and kept in this condition until analyses. In the laboratory all unfrozen samples were first dried at 60°C in a ventilated oven and then passed through a 0.063 mm sieve. The smaller than 0.063 mm fraction was homogenized before analysis.

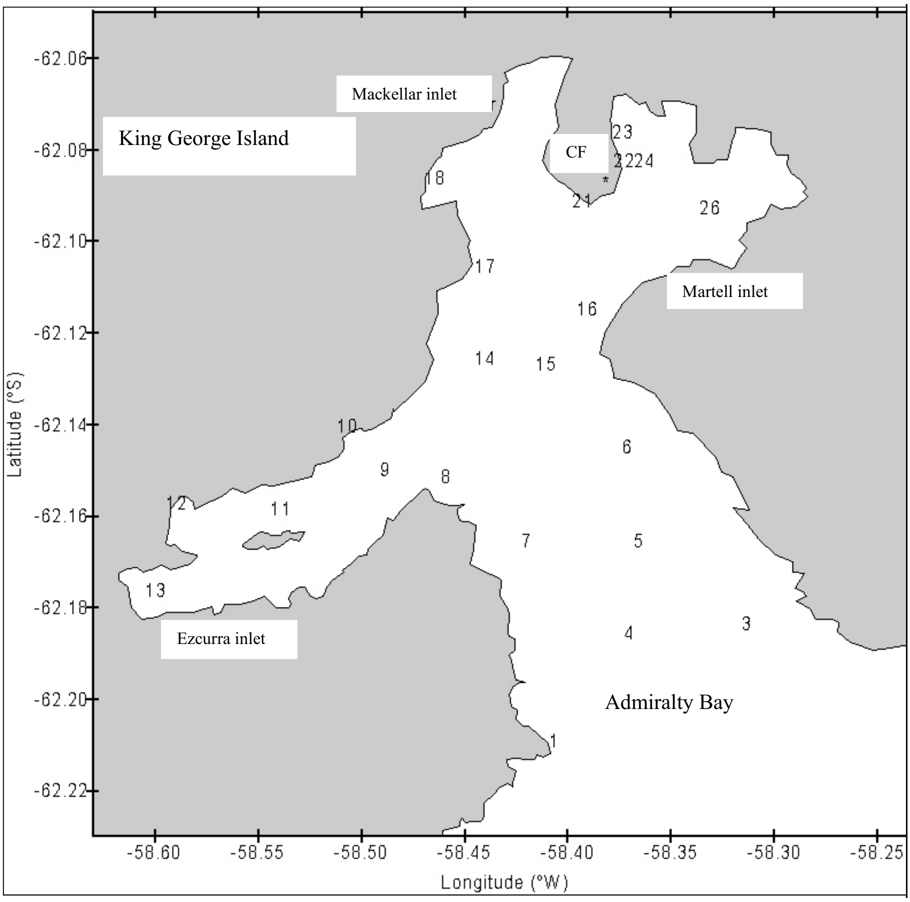

Fig. 1 – Localization of sediment sampling points in Admiralty Bay. CF – Brazilian Research Base.

GRANULOMETRIC DATA

From total sediment samples reserved, the granulometric analyses were obtained using grain size analysis as described by Suguio (1973) using sieve assembly from 2 mm to 0.063 mm.

INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA)

This method was used for determinations of As, Ba, Br, Ca, Co, Cr, Cs, Fe, Hf, Sb, Se, Ta, Th, U, An and rare earth elements in sediments. For the multielemental analyses approximately 150 mg of duplicate samples of the sediments (<0.063 mm fraction) and reference material were accurately weighed and sealed in pre-cleaned double polyethylene bags. Single and multielement synthetic standards were prepared by pipetting convenient aliquots of standard solutions (SPEX CERTIPREP) onto small sheets of Whatman no. 41 filter paper. Sediment samples, reference materials and synthetic standards were irradiated for 16 hours, under a thermal neutron flux of 10^{12} n cm^{-1} s^{-1} in the IEA-R1m nuclear reactor at IPEN – Instituto de Pesquisas Energéticas e Nucleares, São Paulo, Brazil. Two counting series were performed: the first after a seven days decay period and the second after a 15-20 days decay period. The counting time was 2 hours for each sample and reference materials, and half an hour for each synthetic standard.

Gamma spectrometry was performed by a Canberra gamma X hyperpure Ge detector and associated electronics, with a resolution of 0.88 keV and 1.90 keV for ^{57}Co and ^{60}Co, respectively. Data analysis was made by VISPECT program to identify gamma-ray peaks and by ESPECTRO program to calculate concentrations. Both programs were developed at the LAN/CRPQ, IPEN. The analytical quality was checked by measuring Buffalo River Sediment (NIST SRM 2704), Soil 7 (IAEA) and BEN (Basalt-IWG-GIT) reference materials.

COLD VAPOR ATOMIC ABSORPTION TECHNIQUE (CV AAS)

The total mercury in sediment samples were determined by cold vapor atomic absorption technique (CV AAS) in a Perkin Elmer Flow Injection Mercury System (FIMS). Samples were digested by a mixture of concentrated HNO_3 and H_2SO_4 and 30% H_2O_2 in Teflon vials. The vials were closed and left at room temperature overnight. On the following day, the vials were put into an aluminum block at 90°C for 3 hours. The analytical quality was checked using certified reference materials: Buffalo River Sediment (NIST SRM 2704), Estuarine Sediment (NIST SRM 1646^a) and Lake Sediment (BCR CRM 280). These reference materials have different total Hg concentrations.

GAMMA SPECTROMETRY

This technique was used for natural radionuclides determinations. Activity concentrations of ^{226}Ra, ^{228}Ra and ^{210}Pb were measured in sediment samples by gamma spectrometry with a hyper-pure germanium detector, GEM-15200, from EG&G Ortec (Silva et al. 2005). The detector was calibrated using natural soil, rock and water spiked with radionuclides certified by Amersham. Samples were packed in 100 cm^3 cans and sealed for about four weeks prior to the measurement in order to ensure that equilibrium has been reached between Ra-226 and its decay products of short half-life. The Ra-226 activities were determined by taking the mean activity of three separate photopeaks of its daughter nuclides: Pb-214 at 295 keV and 352 keV, and Bi-214 at 609 keV. The Ra-228 content of the samples was determined by measuring the intensities of the 911 keV and 968 keV gamma-ray peaks from Ac-228. The concentration of Pb-210 was determined by measuring the activity of its low energy peak (47 keV). Self-absorption correction was applied since the attenuation for low energy gamma rays is highly dependent upon sample composition. The approach used was modified from that suggested by Cutshall et al (Cutshall et al. 1983).

ALPHA SPECTROMETRY AND LIQUID SCINTILLATION

These techniques were used for Plutonium (Pu) and Strontium (Sr) determinations (Ligero et al. 2001). Approximately 3.0 g of sediment was weighed and digested with conventional acids. Strontium carrier and spikes of $_{94}$Pu-242 tracer were added to the final solution. Sample solution was loaded into the column; $_{94}$Pu is retained, and the effluent is used for the analysis of Sr. $_{94}$Pu was stripped with 0.1 M NH_4I in 9 M HCl and the solution was evaporated to dryness. $_{94}$Pu(III) was oxidized to $_{94}$Pu(IV) by adding NaNO2 and then electrodeposited onto small silver plates. $_{94}$Pu was analyzed by alpha spectrometry. The combined effluent from the anion exchange column was evaporated and diluted to 150 ml with distilled water. Sr was co-precipitated by the addition of oxalic acid. The oxalate precipitate was destroyed by evaporation with 65% HNO_3.

The strontium present in the combined effluents from the anion exchange column was separated and purified by extraction chromatography using Sr-Spec resin. The Sr was stripped, precipitated with oxalic acid and analyzed by liquid scintillation counting.

ELEMENTAL ANALYSES

Carbon, nitrogen and sulfur determinations used 0.2000g of sediment samples previously treated with HCl (10%) to eliminate $CaCO_3$, and then washed. The treated sediment was introduced into an Elemental Analyzer 2400 – CHN, Perkin-Elmer. Calibration process used a solution of sulphametazine as recommended by Mahíques et al. (2002).

COLORIMETRIC METHOD

Total particulate and organic phosphorus were analyzed following the method proposed by Aspila et al. (1976). The phosphate obtained was determined according to the method of Grasshoff et al. (1983). Organic P was determined by subtracting inorganic phosphorus from total phosphorus.

GRAVIMETRIC METHOD

Organic matter and $CaCO_3$ was determined from aliquots of 30g of dry sediment treated with HCl and H_2O_2 (10% each) to eliminate $CaCO_3$ and organic matter, respectively, and then weighed after drying.

RESULTS AND DISCUSSION

In function of trace and rare earth microelements determined in this study, the reference materials Soil 7 (IAEA), Buffalo River Sediment (NIST SRM 8704) and BEN (Basalt – IWG-GIT) were adopted for checking the precision and accuracy of the method. The calculation of the standardized difference or z-value of the result by

$$Z_i = C_i - C_{ref,i} \big/ \left(\phi_i^2 + \phi_{ref,i}^2\right)^{1/2} \qquad (1)$$

is an accepted approach to establish if the result meets the control limits as defined by the laboratory. In this,

C_i = concentration of element i in the reference material analysis;
$C_{ref,i}$ = concentration of the certified or consensus value for element i;
ϕ_i = uncertainty of the concentration of element i in the reference material analysis;
$\phi_{ref,i}$ = uncertainty of the certified respectively consensus value for element i.

If $|Z| < 3$, the individual result of the control sample (reference material) lies on the 99% confidence interval of the target value. All Z-score values were in this interval ($|Z| < 3$), indicating a good precision and accuracy of the INAA technique. Figure 2 presents the results obtained for the reference materials analyses.

The results obtained for Buffalo River Sediment (NIST SRM 2704), Estuarine Sediment (NIST SRM 1646[a]) and Lake Sediment (BCR CRM 280) reference materials, as well as for certified and recommended values are presented in Table I. Relative standard deviations ranging from 1.3 to 2.9% and relative errors from 1.4 to 3.7% were found for the analyses of the reference materials for total Hg determinations, showing that the precision and accuracy of the analytical technique are acceptable.

The granulometric characteristics (Table II) of Admiralty Bay demonstrated the presence of coarse sediments (gravel and sand) mainly in the external and central part of the Admiralty Bay (stations 1, 3, 6, 8, 9 and 15). The points located at Martell Inlet, in the inner part of the Bay, demonstrated an important silt fraction (>50%). The lowest C organic concentration was associated with the highest S concentration (station 26). Ezcurra Inlet (stations 11, 12, 13) presented a silt fraction over 30%, and the organic C concentrations were lower at the inner most stations (12 and 13) near the terrestrial margin, while in the Mackellar Inlet, represented station 18, the sediments had an important S content (> 1%), low organic matter and consequently, low organic C concentration.

The multielemental results obtained by INAA for sediment samples, Hg concentrations obtained by CVAAS were compared with Upper Continental Crust Tconcentrations (UCC) (Wedepohl 1995) and presented in Table III. Comparing the mean values obtained in the present study with the UCC values, in general, for these marine sediments, it was observed that:

- Highly enriched elements (EF>2): As, Br, Hg, Sb and Zn;
- Slightly enriched elements (1.1<EF<2): Co, Cr, Eu, Fe, Lu, Na, Nd, Sm, Tb and Yb;
- Depleted elements (EF<0.9): Ba, Ce, Cs, Hf, K, La, Rb, Th and U.

Table IV presents the results for total, inorganic and organic P, organic C, organic N, organic S, organic matter that demonstrate the low values for its organic components, with exception for the P content in function of the organic P input and the in-

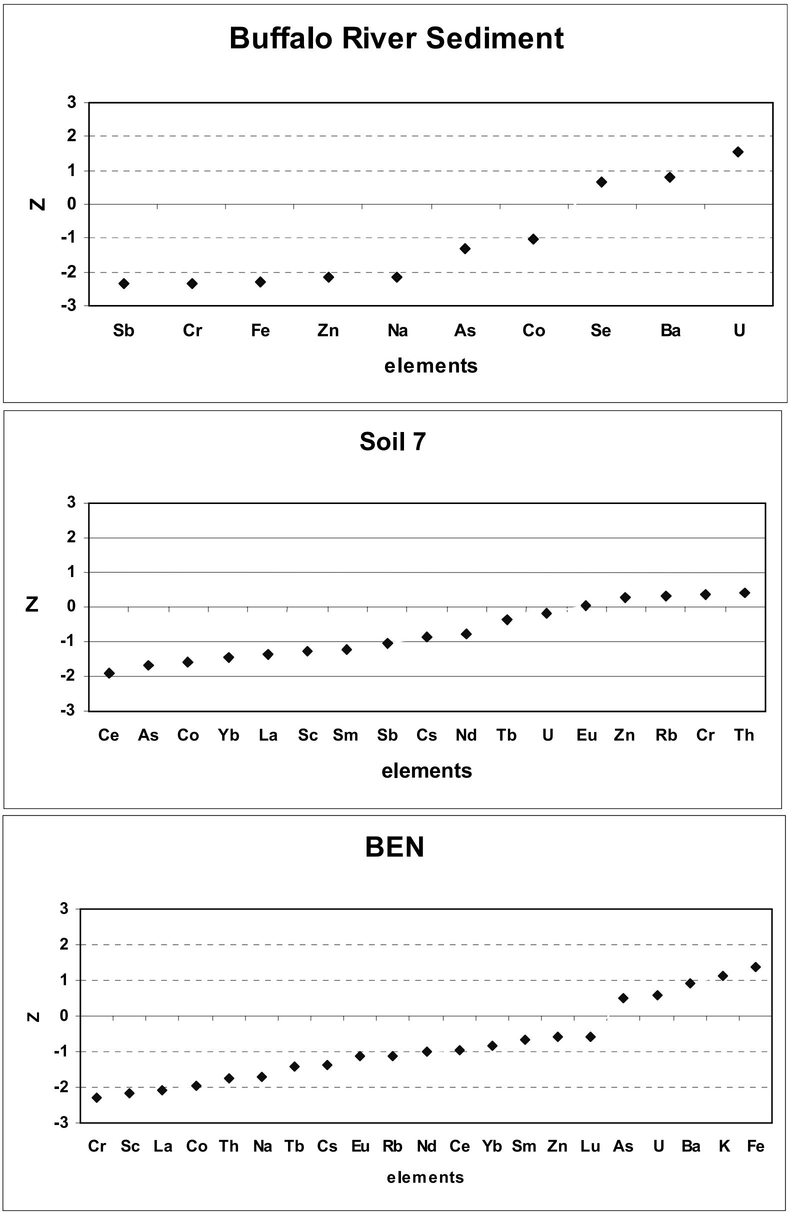

Fig. 2 – Control chart (z-values) for inspection of the normalized concentrations of some elements in the NIST SRM 2704, SOIL-7 and BEN reference material samples.

organic P richness of the soil and consequent sea input. The radionuclides Pb-210, Ra-226, Ra-228, K-40, Pu-238, Pu-239 and Sr-90 for all sediment samples are also presented in Table IV. The concentration of total mercury in the sediment samples varied from 53 to 210 μg kg^{-1} in all but one (sample 18, located at Mackellar Inlet). This sample presented a 1789 μg kg^{-1} concentration value, which was considered high for this region. Sample 18 also presented 75% of inorganic P, indicating terrestrial input of inorganic matter in this location with low contribution of organic matter. Most of the phosphorus in the sediment was represented by the inorganic fraction (65-93%).

TABLE I
Results obtained for total mercury concentration (μg kg^{-1}) in Reference Material Analysis by CV AAS.

Reference material	Certified value	Found value	RSD (%)	Relative error (%)
Estuarine Sediment	40	40.2 ± 0.8	2.0	–
Lake Sediment	670 ± 19	695 ± 20	2.9	3.7
Buffalo River Sediment	1470 ± 70	1490 ± 19	1.3	1.4

TABLE II
Granulometric characteristics (%) and $CaCO_3$, Corg, S and OM in the Admiralty Bay.

	Gravel	Sand	Clay	Silt	$CaCO_3$	Corg	S	OM
1	38.97	46.79	2.48	11.77	18.00	0.08	0.12	3.57
5	–	–	–	–	–	–	–	–
8	7.70	57.85	4.41	30.03	36.99	0.30	0.22	5.16
9	–	–	–	–	–	–	–	–
11	16.16	45.27	5.78	33.79	20.64	0.21	0.15	5.54
12	6.53	15.71	16.56	61.19	17.35	0.03	0.50	4.72
13	42.62	5.92	10.46	41.01	15.55	0.06	0.38	5.32
15	4.61	69.11	3.35	22.92	16.46	0.15	0.19	3.42
18	2.77	50.77	10.15	36.29	13.00	0.15	1.14	2.75
21	24.33	16.19	15.80	43.69	16.75	0.15	0.52	6.16
22	16.52	12.76	17.71	53.02	18.15	0.20	0.48	5.38
23	2.98	33.53	7.01	56.49	18.15	0.25	0.39	5.14
24	4.51	35.49	11.41	48.60	21.27	0.17	0.21	5.89
26	1.48	4.48	31.98	62.06	16.98	0,15	1.18	5.95
Max.	50.18	69.11	31.98	62.06	36.99	0.30	1.18	6.16
Min.	1.48	4.48	5.78	22.92	13.00	0.03	0.15	2.75

A *cluster* analyses was applied for these samples considering the sampling locations and results are shown in Figure 3. As can be seen the set of samples was divided in two main groups. Group 1 contains mainly samples located in the inner parts of the Bay (stations 1, 5, 6, 8, 9, 11), whereas group 2 (stations 12, 13, 15, 18, 21, 22, 23, 24, 26) comprises samples located in the entrance of the Bay under influence of the water of the Bransfield Strait and located in deeper waters.

Figure 4 presents the *cluster* analysis of chemical data, two main groups were identified. The first one (group a) is comprised of iron group elements: Sc, Cr, Co and Zn. These elements present relatively higher concentrations (Table III) in the samples located at the entrance of the Bay (Group 2 from Fig. 3). The second group is comprised of rare earth elements, Th, Hf, Rb, Ba, Sb, Hg, As, K and Cs. These last two elements are related to grain size variations (Wedepohl 1995). All elements of this group are more concentrated in the samples that belong to the inner part of the Bay. In this region, low energy prevails and enables the deposition of fine grains of sediments, as previously verified by the silt and clay fractions in these samples.

Statistical data analysis applied to the results of the samples chemical composition showed good correlation between RRE, Th, Rb, Hf, Ba, K, Cs, Sb, As, Hg, Sr-90, K-40 and silt content. These elements are more concentrated in the samples that belong to the inner part of the Bay. Silt content is also well correlated with organic matter and nutrients

TABLE III

Results of the multielemental analysis (mg kg^{-1}) in sediment samples obtained by INAA and CV AAS (Hg).

station no.	As	Ba	Br	Ce	Co	Cr	Cs	Eu	Fe (%)	Hf	Hg (μg kg^{-1})	K (%)	La
01	7.8	304	88	41.7	22.2	105	3.1	1.5	5.9	4.1	60	1.2	16.9
05	5.9	537	115	35.4	20.2	37	2.6	1.4	5.4	3.3	185	1.0	14.3
06	5.7	289	68	40.3	21.5	145	2.2	1.5	5.6	3.6	210	1.4	16.0
08	7.7	277	131	36.2	18.5	40	2.3	1.2	5.6	3.6	164	1.6	14.5
09	7.4	269	145	38.5	18.0	31	2.0	1.2	5.3	3.7	55	1.7	15.5
11	8.1	432	125	42.9	20.3	93	2.8	1.4	5.2	4.0	55	1.0	16.1
12	11.0	349	44	56.9	15.8	19	3.9	1.5	4.4	5.7	151	1.7	22.6
13	8.6	386	90	45.5	17.9	23	4.7	1.3	4.9	4.5	126	2.0	17.6
15	10.9	312	93	43.3	17.9	27	3.3	1.5	5.0	4.4	107	1.4	17.6
18	17.7	312	71	45.2	19.6	26	2.8	1.5	5.3	4.1	1789	1.7	18.4
21	10.1	373	76	46.8	18.7	33	3.3	1.4	4.9	4.2	72	1.6	17.9
22	9.4	344	60	46.1	17.8	30	2.7	1.4	4.9	4.3	102	1.8	19.6
23	10.0	463	84	47.6	17.3	29	5.5	1.4	4.5	4.5	52	2.5	19.1
24	10.7	438	82	47.1	19.2	33	3.9	1.4	5.1	4.6	92	2.9	18.4
26	8.0	364	77	47.7	21.1	39	2.8	1.4	5.2	4.3	53	1.7	18.7
Mean	9.3	363	90	44.1	19.1	47	3.2	1.4	5.2	4.2	218	1.7	17.5
SD	1.1	28	20	3.1	3.1	53	0.2	0.1	0.7	0.2	29	0.5	1.9
Min	5.7	269	44	35.4	15.8	19	2.0	1.2	4.4	3.3	52	1.0	14.3
Max	17.7	537	145	56.9	22.2	145	5.5	1.5	5.9	5.7	1789	2.9	22.6
UCC[9]	2	668	1.6	65.7	11.6	35	5.8	0.95	3.09	5.8	56	2.87	32.3

station no.	Lu	Na (%)	Nd	Rb	Sb	Sc	Sm	Tb	Th	U	Yb	Zn
01	0.38	3.44	39	56	0.5	26.6	5.2	0.74	4.5	0.8	2.5	121
05	0.38	3.70	43	39	0.7	24.0	4.5	0.70	3.5	1.3	2.2	137
06	0.29	3.13	36	39	0.4	24.0	5.2	0.47	3.7	1.3	2.1	131
08	0.33	3.78	40	44	0.4	23.5	5.2	0.42	3.5	1.1	2.1	138
09	0.36	4.32	47	38	0.2	21.8	5.3	0.57	3.7	N.D.	1.9	131
11	0.31	3.86	41	51	0.4	24.1	4.9	0.54	4.2	1.2	2.1	108
12	0.45	2.39	33	77	1.0	21.0	6.7	0.68	6.0	2.2	2.5	86
13	0.37	3.22	38	67	0.7	22.7	5.5	0.47	5.3	2.0	1.8	201
15	0.32	3.03	26	53	0.7	23.3	5.4	0.68	4.4	2.5	1.9	101
18	0.32	2.43	29	53	0.9	23.5	5.5	0.70	4.4	2.2	1.8	71
21	0.34	2.86	25	71	0.7	23.6	5.8	0.52	4.6	1.9	1.9	148
22	0.31	2.53	34	55	0.7	24.6	6.3	0.80	4.5	2.6	2.2	99
23	0.31	2.85	37	67	0.7	25.3	5.8	0.55	4.8	2.1	2.0	94
24	0.36	2.73	34	62	0.7	25.5	5.8	0.91	5.1	2.2	2.1	100
26	0.31	3.09	34	61	0.4	23.8	5.9	0.66	5.0	1.6	2.0	100
Mean	0.34	3.2	36	56	0.6	23.8	5.5	0.63	4.5	1.8	2.1	118
SD	0.05	0.6	4	1	0.1	1.4	0.8	0.04	0.0	1.2	0.2	16
Min	0.29	2.4	25	38	0.2	21.0	4.5	0.42	3.5	0.8	1.8	71
Max	0.45	4.3	47	77	1.0	26.6	6.7	0.91	6.0	2.6	2.5	201
UCC[9]	0.27	2.57	25.9	110	0.31	7	4.7	0.5	10.3	2.5	1.5	52

*ND = not determined.

TABLE IV
Concentration (mg kg^{-1}) (range, mean values and standard deviation) of the analyzed sediment samples.

	Pb-210	Ra-226	Ra-228	K-40	Pu-238	Pu-239	Sr-90
minimum	< 15	13	< 11	356	< 0.1	< 0.1	< 2.6
maximum	176	40	27	1066	0.5	0.29	111
mean	105	21	17	612	0.3	0.19	31
SD	44	8	5	222	0.1	0.07	40

	C-org %	S-org %	OM %	P-total μmol g^{-1}	P-inorg μmol g^{-1}	P-org μmol g^{-1}	N-org μmol g^{-1}
minimum	0.18	0.64	1.12	639	495	44	0.02
maximum	0.61	1.13	3.81	839	631	265	0.34
mean	0.34	0.84	2.56	754	546	209	0.13
SD	0.13	0.16	1.02	53	43	64	0.12

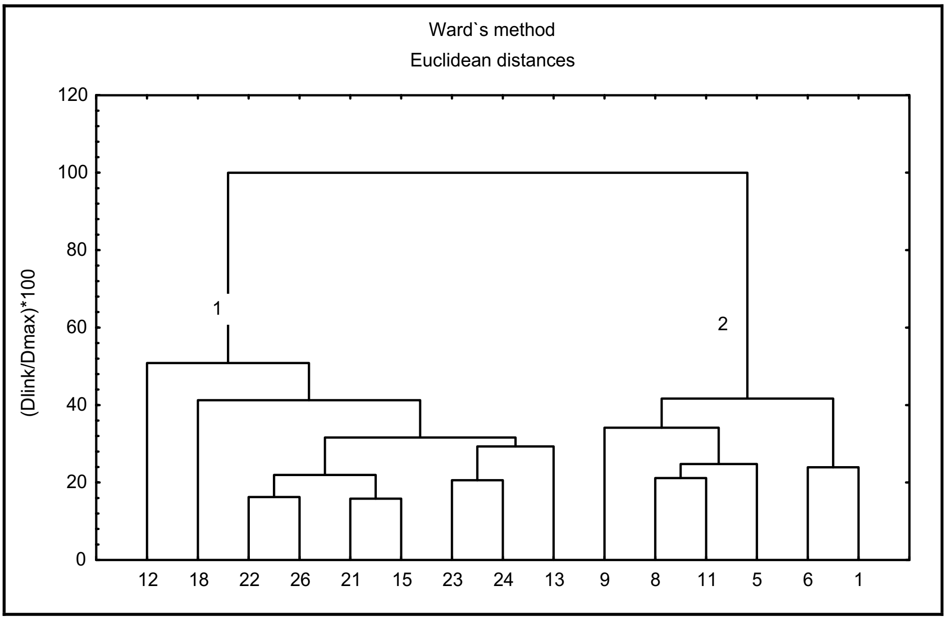

Fig. 3 – Cluster analysis results for the sampling locations.

(organic S, N, C, P and inorganic P). The elements Fe, Zn, Cr, Co, Sc, U and Nd presented relatively higher concentration in the samples located at the entrance of the Bay. They also showed good correlation with sand, clay content and nutrients. The same pattern was also found for radionuclides Pu-238, Pu-239, Ra-226, Ra-228 and Pb-210 that present an inverse correlation with nutrient concentrations. However, for the artificial elements these results must be used carefully since in many samples the concentrations are below the detection limits. Ra-226, Ra-228 and K-40 concentrations were of the same order of magnitude as the results obtained by Godoy (Godoy et al. 1998) for sediment samples collected in the same region.

Figure 5 presents the box plot for all elements analyzed in the present study the groups 1 (G1: 1, 5, 6, 8, 9, 11 stations) and 2 (G2: 12, 13, 15, 18, 21, 22, 23, 24, 26 stations). We could observe that group 1 presents higher concentrations for the elements As,

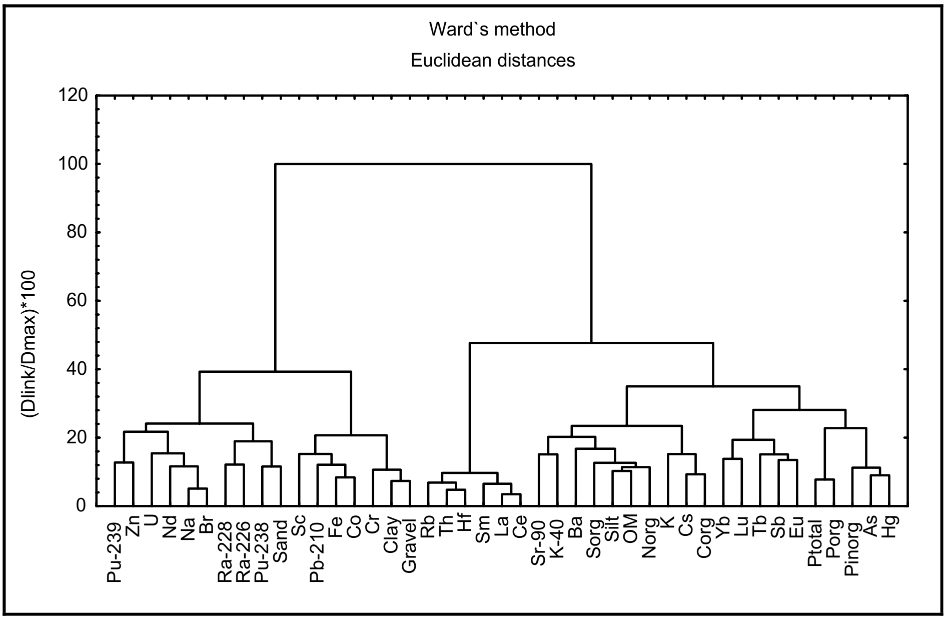

Fig. 4 – Cluster analysis results for chemical data.

Ce, Cs, Eu, Hf, Hg, K, La, Rb, Sb, Sm, Tb and Th while group 2 presents higher concentrations for the other elements investigated: Br, Co, Cr, Fe, Na, Nd, Sc, Yb and Zn.

In order to investigate element association in sediments, R-mode factor analysis was performed through the Varimax method. Six factors were extracted considering factor loadings higher than |0.7|. The results can be interpreted as follows:

- Factor 1 (F1, which corresponds to 42.5% of the total variance) is formed mainly by the elements Ce, Hf, La, Rb, Sm and Th. These elements are positively correlated but negatively correlated with Fe, Na and Br;
- Factor 2 (F2, which corresponds to 14.5% of the total variance) is formed mainly by Cr, although loading factors close to |0.7| can be observed also for Co, Eu, Sc and Yb;
- Factor 3 (F3, which corresponds to 10.8% of the total variance) includes As and Hg;
- Factor 4 includes Ba (7.9%); Factor 5 includes Tb (6.3%) and Factor 6 includes Lu (5.6%).

Altogether, the six factors account for 87.6% of the total variance. It is interesting to note the strong correlation between As and Hg in F3. These elements present unexpected elevated concentrations at point 18 and this fact should be further investigated.

The results obtained for the elemental concentration in the sediment samples are quite uniform and correspond to the natural levels of the region (Table II). One exception is the sample collected at point 18, which presented Hg and As concentrations above the natural levels, and deserves further investigation. Two main groups were observed, one formed by samples collected inside the Bay (Group 1) and the second one (Group 2) formed by samples collected around the entrance. The processes of intense terrestrial input prevail in the first group, whereas in the second group the differences can be explained by sediment accumulation.

CONCLUSION

The analytical techniques used in the determination of the trace elements presented sensitivity appropriate for the monitoring of this remote environment, providing data for global climate definition.

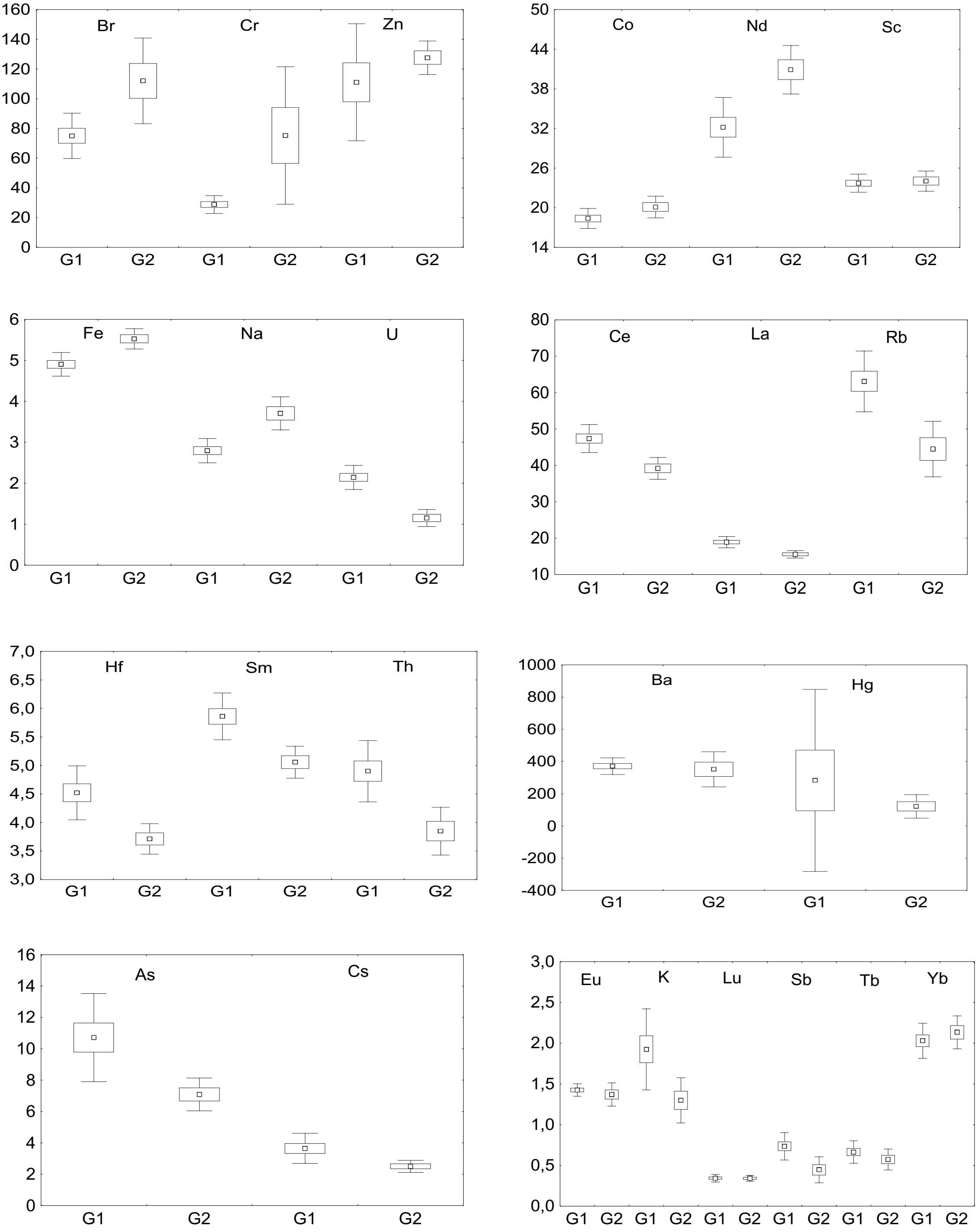

Fig. 5 – Box plot for all elements analyzed: G1 (group 1) and G2 (group 2).

The results obtained for the elemental composition of sediments were associated to granulometric characteristics that reflect its lithologic origin associated to the hydrodynamic processes at the Bay that present, low circulation process in the inlets with important terrestrial inputs in the coastal region and more intensive and energetic processes at the entrance of the Bay, with low terrestrial input. The ice movements contributed with terrestrial input and with remobilization of the bottom sediments at the Bay.

Natural level of elements at this region is relatively high due to the richness of the terrestrial soil originated mainly from the volcanic rocks. The assemblage of chemical parameters as trace and rare earth elements and radionuclides, rarely determined at this region, allowed a configuration of two distinct sediment groups at Admiralty Bay, mainly in relation to the chemical composition. One formed by samples collected in the inlets, under restricted water circulation processes and influenced by terrestrial inputs and the more significant presence of fine sediments. The second one formed by samples collected around the Bay entrance, submitted to an intense water circulation process, more distant from terrestrial inputs and from fine sediment and organic matter retention.

In general, the results obtained for the elemental composition related to the sediments characteristics revealed that the region is well preserved due to the similarity of values obtained in each distinct group. One exception was observed at station 18, which presented Hg and As concentrations above the natural levels, and deserves further investigation.

The slightly high content of structural trace metal elements in this region and the high contribution in P from guano to sediments constitute an important input to the Admiralty Bay. The oxy-redox conditions in the inlets associated to the restricted water circulation contribute to the differences in the quality of the organic matter available observed in the different inlets. Chemical speciation of the compounds is another point to study in this environment.

Thinking about a monitoring program, two points should be further investigated: the natural element richness of island soil and the input to the marine sediments both associated to ice movement and by influence of human occupation, the last one can contribute to a strong increase of the reference levels.

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RESUMO

O principal objetivo deste estudo foi avaliar alguns elementos maiores e traços, mercúrio total, radionuclídeos naturais e artificiais, carbono orgânico, enxofre e matéria orgânica em sedimentos da Baía do Almirantado. As amostras foram coletadas em Janeiro/Fevereiro de 2003 (XXI OPERANTAR), verão no hemisfério sul. Elementos traço (As, Ba, Br, Co, Cr, Cs, Hf, Rb, Sb, Sc, Ta, Tb, Th, U, Zn), elementos terra raras (Ce, Eu, La, Lu, Nd, Sm, Tb and Yb) e elementos maiores (Fe, K e Na) foram determinados por análise por ativação neutrônica. O mercúrio total foi determinado pela técnica de absorção atômica com vapor frio (CV AAS). ^{226}Ra, ^{228}Ra e ^{210}Pb foram medidos por espectrometria gama. As determinações do estrôncio (Sr) e do plutônio ($_{94}$Pu) foram baseadas na separação seletiva por cromatografia e medidas por contagem de cintilação beta e espectrometria alfa, respectivamente. C and S foram analisados pelo LECO-CNS 2000 e a matéria orgânica, por combustão. As frações de P nos sedimentos foram determinadas por extração e determinação colorimétrica. Os resultados obtidos para as concentrações elementares foram bastante uniformes e corresponderam aos níveis naturais da região considerando a composição do solo. A análise de *cluster* mostrou dois grupos distintos: i) um grupo que inclui principalmente elementos do grupo do Fe (Sc, Cr, Co e Zn) e ii) um segundo grupo que inclui principalmente constituintes minerais pesados (elementos terra raras, Th e Hf). Somente um ponto amostrado apresentou concentrações de Hg e As acima dos níveis considerados naturais.

Palavras-chave: sedimentos, composição química, radionuclídeos naturais e artificiais, Antártica.

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