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Aliphatic and polycyclic aromatic hydrocarbons in surface sediments in Admiralty Bay, King George Island, Antarctica

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Abstract: Aliphatic (AHs) and polycyclic aromatic hydrocarbons (PAHs) concentrations were measured in marine surface sediments around the Brazilian station in Admiralty Bay, during the summers of 1997/98 and 1999/2000 using GC-FID and GC-MS. Total aliphatic hydrocarbons ranged from 0.15 to 13.28 $\mu g.g^{-1}$ (dry weight) while *n*-alkanes varied between 0.10 and 9.63 $\mu g.g^{-1}$. The highest concentrations were obtained at the sewage outfall, with decreasing levels away from the outfall. The distribution of *n*-alkanes showed significant quantities of long chain *n*-alkanes (n-C_{22} to n-C_{34}) at sites near the Brazilian station that may be attributed to the station activities. A short chain *n*-alkanes sequence (n-C_{12} to n-C_{21}) associated with diesel fuel arctic (DFA) was present in all the samples. Total PAHs varied from 9.45 to 270.5 $ng.g^{-1}$. The higher PAHs level and the presence of an unresolved complex mixture only in sediment from the sewage outfall is an indication of oil contamination at this location. A slight increase in PAHs near the Brazilian station since 1993 may be attributed to an increase in the number of staff over recent years. In general, the concentration of AHs and PAHs was similar to that found in other Antarctic areas.

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Key words: AH, oil, PAH, pollution, South Shetland Islands

Introduction

Scientific, logistic and tourist activities in Antarctica have introduced anthropogenic compounds in otherwise pristine locations. The long-term contributions from transport and oil storage, fossil fuel combustion and human waste are the main sources of hydrocarbons to the Antarctic environment. Around 90 million litres of fuel a year, of which 75% is diesel fuel, is used by research stations (Cripps & Shears 1997). The use of fuels and oils has a risk for direct releases of hydrocarbons to the environment (Cripps 1992a).

N-alkanes are an important constituent of the aliphatic hydrocarbons that are present in petroleum and fossil fuels. *N*-alkanes are also the predominant constituent of biogenic hydrocarbons, and have been identified in many species of marine organisms (Reinhardt & Van Vleet 1986, Cripps 1990, Cripps & Priddle 1991). *N*-alkanes from oil show no predominance of odd or even carbon chain lengths (NRC 1985, UNEP 1991) while *n*-alkanes from biogenic sources are variable depending on the organisms present in a given study area.

Polycyclic aromatic hydrocarbons (PAHs) are present in petroleum and its products. They are also formed during the process of incomplete combustion of fossil fuels. They are rarely found as products of biosynthesis and have environmental significance because of their toxic properties (NRC 1985, UNEP 1991). These compounds reach the marine environment by atmospheric transportation or by the direct input from oil spills and sewage discharge.

Some incidents in Antarctica have caused severe localized short-term effects on the biota but the recovery has been shown to be rapid (Cripps & Shears 1997). Many studies of hydrocarbon contaminants associated with research stations in Antarctica have been conducted over the last 15 years (e.g. Cripps 1989, 1992a, Kennicutt *et al.* 1992a, 1992b, 1992c, Green *et al.* 1992, Bícego *et al.* 1996, 1998). Cripps (1992b) has summarized a review of major marine hydrocarbon incidents release in Antarctica. In most cases, away from spills, hydrocarbon concentrations are low, indicative of natural background levels.

The aim of this report was the evaluation of the input of anthropogenic hydrocarbons from the Brazilian Antarctic station in Admiralty Bay, King George Island. The data obtained are also compared with those of a previous study undertaken in the same area (Bícego *et al.* 1998) to test for changes over time.

Sampling and methods

Study locations and sediment collection

Marine sediment samples were collected in the summers of 1997–98 and 1999–2000 at several points near the scientific stations in Admiralty Bay, especially the Brazilian station (Fig. 1). Samples were collected at different distances from the coast on horizontal transects at sites A, B and C (Table I).

Admiralty Bay is situated in King George Island, in the South Shetland Islands. There are three research stations in this bay: the Comandante Ferraz Brazilian research station (EACF), the Henryk Arctowski Polish research station, on

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Table I. Sediment sampling stations and grain size in Admiralty Bay.

Site	Sampling locations and distance (m) from the coast	Approximate distance (km) and direction from Brazilian station	Percentage of (silt+clay) and visual description of grain size of sediment
A_1	Ferraz 0 m (sewage outfall)	0.00	0.02 (gravel)
A_2	Ferraz 10 m	0.01	0.20 (gravel)
A_3	Ferraz 20 m	0.02	12.2 (medium sand)
A_4	Ferraz 50 m	0.05	84.0 (mud)
A_5	Ferraz 100 m	0.10	81.2 (mud)
A_6	Ferraz 200 m	0.20	86.5 (mud)
A_7	Ferraz 400 m	0.40	85.9 (mud)
B_1	Whale 100 m	0.5 (N)	13.6 (gravel → mud)
B_2	Whale 200 m	0.6 (N)	78.4 (mud)
C_1	Refugee 1100 m	0.6 (S)	23.7 (gravel → mud)
C_2	Refugee 1200 m	0.7 (S)	38.4 (mud)
D	Stenhouse Point	0.7 (N)	80.7 (mud)
E	Plaza Point	1.0 (S)	16.9 (fine sand → mud)
F	Mackelar Glacier	5.5	51.0 (gravel → mud)
G	Crepin Point (near Peruvian station)	3.5	31.5 (mud)
H	Arctowski (near Polish station)	10.0	0.03 (coarse sand)
I	Barrel Point	15.0	65.1 (mud)

the western side of the bay, near Thomas Point and the Macchu Picchu Peruvian research station located near Crepin Point (Fig. 1). The majority of sampling sites were located close to the Brazilian station. This station was established in the summer of 1984, and nowadays is a medium sized research station with a summer population of 50 people. Diesel generators supply power to the station which has a 380 t Antarctic grade diesel oil tank that is replenished by ship every year. Average monthly fuel consumption of the diesel generators is about 23 t. Ships, motorboats and other vehicles also use fuel in the area (Bícego *et al.* 1996).

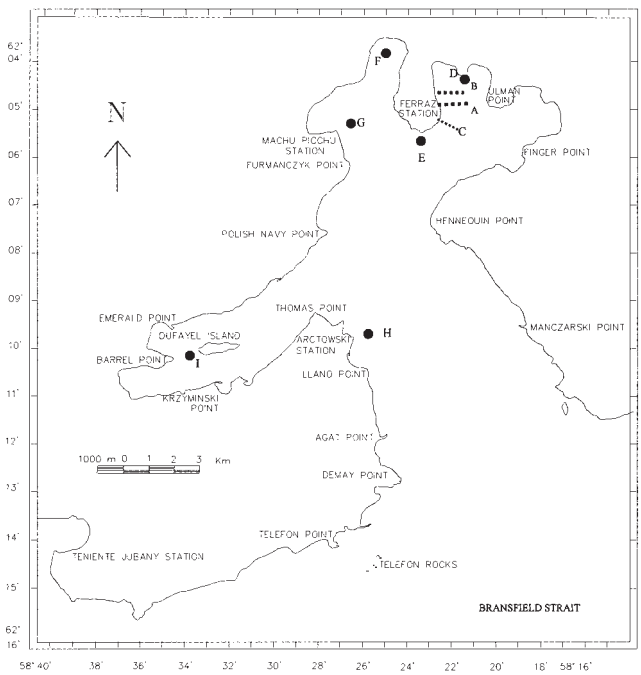

Fig. 1. Sampling stations at Admiralty Bay, King George Island, Antarctica. See Table I (A–I).

Marine sediments were collected with a modified stainless steel Van Veen sampler. Approximately 200 g of surface sediment (first 3–5 cm) was wrapped in aluminium foil, oven dried at 50°C for two days, homogenized with a mortar and pestle and stored in glass bottles.

Analytical procedures

The analytical procedure used is described in Martins (2001). Briefly, 25 g of sediment were extracted for eight hours with 80 mL of a mixture dichloromethane (DCM) and n-hexane (1:1, 8 h) in a Soxhlet apparatus. Before extraction, hexadecene and eicosene (for aliphatic

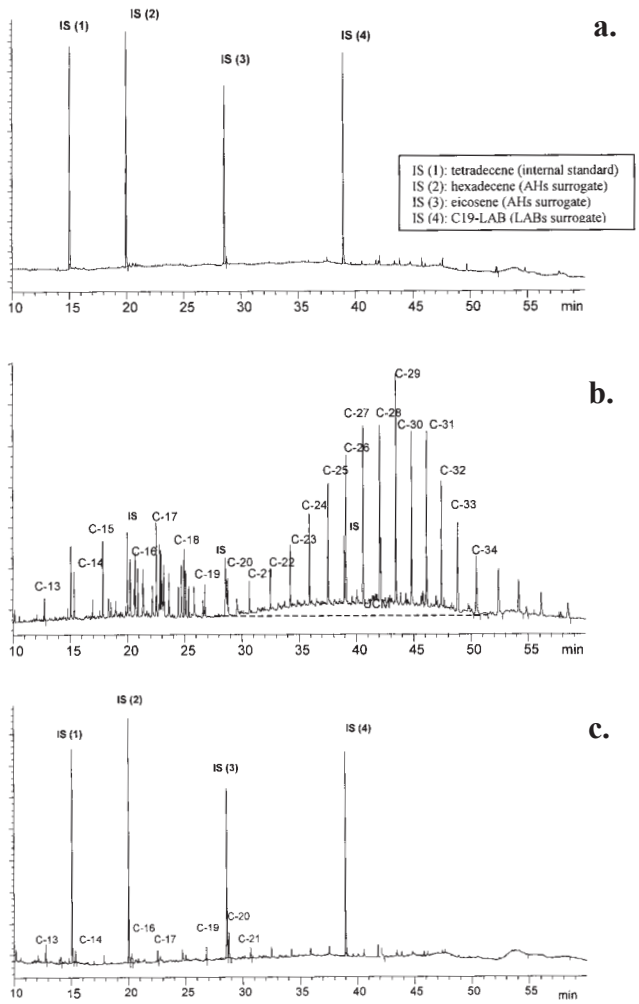

Fig. 2. Chromatograms of aliphatic hydrocarbons. **a.** Blank of the method, **b.** sediment from A_1, sewage outfall, and **c.** sediment from H, low contamination site.

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Table II. Total aliphatic hydrocarbons (Σ-AHs), total *n*-alkanes (Σ-*n*-alkanes), Unknown Complex Mixture (UCM) ($\mu g.g^{-1}$ dry weight) and odd/even ratio, in sediment samples from Admiralty Bay.

Sample Sites	Σ-AHs ($\mu g.g^{-1}$)	Σ-*n*-alkanes ($\mu g.g^{-1}$)	UCM ($\mu g.g^{-1}$)	odd/even ratio
A_1	13.28	9.63	1.24	1.18
A_2	0.48	0.28	n.d	0.93
A_3	0.92	0.31	n.d	1.46
A_4	0.27	0.16	n.d	1.24
A_5	0.18	0.12	n.d	1.21
A_6	0.48	0.22	n.d	1.07
A_7	0.22	0.14	n.d	1.00
B_1	0.15	0.10	n.d	0.47
B_2	0.53	0.32	n.d	0.96
C_1	0.76	0.28	n.d	1.26
C_2	0.59	0.31	n.d	0.91
D	0.57	0.32	n.d	1.15
E	2.40	1.32	n.d	1.05
F	0.49	0.23	n.d	1.00
G	0.67	0.25	n.d	0.85
H	0.25	0.10	n.d	1.27
I	0.40	0.20	n.d	1.04

n.d. = not detected

hydrocarbons - AHs), naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12} (for PAHs) were added in all samples, blank and reference material as surrogates. The extract was purified by column chromatography using 5% deactivated alumina and silica. The components of interest were eluted in two fractions using 10 mL of n-hexane (fraction 1 - AHs) and 15 mL of 30% dichloromethane in n-hexane (fraction 2 - PAHs). Sample extracts were concentrated to 1 mL in n-hexane and the internal standards tetradecene and 9,10 dihydroanthracene were respectively added in fraction 1 and 2 before gas chromatographic analysis. The AHs were quantified using an HP 5890A Series II gas chromatograph, fitted with a 5% dimethyl diphenyl polysiloxane Ultra II (Hewlett Packard) capillary column (25 m x 0.32 mm ID and 0.25 µm film thickness) and a flame ionization detector (FID). PAHs were quantified by GC-MS using an HP 5890 series II coupled to a VG Mass Lab Fisons Model Trio 1000. Regular analyses of certified reference material and intercomparison exercises from the International Atomic Energy Agency (MEL/IAEA) have shown that the procedure is adequate and was giving satisfactory results. Surrogate recoveries ranged from 70 to 120%. Procedural blanks revealed no contamination as shown in Fig. 2a.

Results and discussion

Aliphatic hydrocarbons

Total aliphatic hydrocarbons and *n*-alkane concentrations are shown in Table II. The highest concentration (13.28 $\mu g.g^{-1}$ dry weight) of total aliphatic hydrocarbons (Σ-AHs) in sediments was found at A_1, where the sewage outfall is located. Among the points located 20 to 400 m from the outfall, the concentration varied from 0.18 to 0.92 $\mu g.g^{-1}$.

Total *n*-alkanes (Σ-*n*-alkanes) ranged from 0.10 to 9.63 $\mu g.g^{-1}$. The highest values occurred at sites A_1 (9.63 $\mu g.g^{-1}$) and E (1.32 $\mu g.g^{-1}$). The other sites had levels below 0.32 $\mu g.g^{-1}$. A decrease in concentration was observed from site A_1 to A_3 (20 m from the outfall). All other sites further away than 50 m contained low and constant concentrations, except the site E.

The evaluation of individual *n*-alkanes in sediments can provide information about the biogenic or anthropogenic source of the hydrocarbons. A predominance of odd numbered compounds is an indicative of a biogenic origin, while no predominance is an indicative of petroleum products (NRC 1985). In the Antarctic environment, however, the different pattern of distribution of those compounds in the marine biota makes the source evaluation very complex. According to Reinhardt & Van Vleet (1986), *n*-alkanes from 16–21 carbon atoms were verified in Antarctic marine organisms with no predominance of odd or even numbers of carbons. Studies in phytoplankton and zooplankton from the Antarctic environment show an irregular profile sequence for long chain *n*-alkanes (n-C_{22} to n-C_{30}). As described in Cripps (1989), the analysis of the odd/even carbon in the Antarctic environment is not conclusive indication of the real source of these compounds.

The majority of the samples presented odd/even ratio values between 0.85 and 1.27 indicating there is little predominance of odd over even *n*-alkanes. These data are similar to previous data from Admiralty Bay (Bícego *et al.* 1998) and other Antarctic areas (Cripps 1989, 1991, Green *et al.* 1992). The distribution of short and long chain *n*-alkanes may also be a useful tool for the elucidation of the origin of hydrocarbons and has been used to distinguish between hydrocarbons from oil and biogenic sources. Only site A_1 presented high concentrations of long chain *n*-alkanes (n-C_{27}–n-C_{30}), typical of oil contamination (Fig. 2b). A complete sequence of short and long chain *n*-alkanes was present at sites $A_1 \rightarrow A_7$ and D, indicating some oil contamination. Other samples (B, C, E, F, G, H and I) presented all sequence of short chain *n*-alkanes, with similar chromatographic profile found by Kennicutt *et al.* (1992b) for samples of marine sediment collected near Palmer station, which sources was attributed to the diesel fuel arctic (DFA) input.

Another useful parameter to predict the source of hydrocarbons is the unresolved complex mixture (UCM). UCM is due to a structurally complex mixture of hydrocarbons and is normally associated with petroleum residues (Readman *et al.* 2002). Only sample A_1 had an UCM corresponding to 9.3% of total aliphatic hydrocarbons indicating degraded oil.

Table III presents data from other studies on aliphatic hydrocarbons in the Antarctic environment. The highest

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Table III. Concentrations of total aliphatic and *n*-alkanes (µg.g^{-1} dry weight), total PAHs (ng.g^{-1} dry weight) and odd/even ratios to sediments from different Antarctic study areas.

Study areas analysed	Authors	Σ-AHs (µg.g^{-1})	Σ–*n*-alkanes (µg.g^{-1})	odd/even	Σ-PAHs (ng.g^{-1})
Antarctic pristine areas	Cripps & Priddle (1991)	n.p	0.10–9.30	n.p	50–200 70–4500
Palmer station (USA)	Kennicutt II *et al.* (1992a)	n.p	1.44–121 0.26–1.183	n.p	200–14500[1] 5640–59500 [1]
Areas near oil spill from ship *Bahia Paraíso* (5 km distant)	Kennicutt II *et al.* (1991)	n.p	n.p	n.p	200–1650 [1]
Davis station (AUS)	Green *et al.* (1992)	n.p	0.70	0.89	7.00
Davis Station (AUS)	Green & Nichols (1995)	0.26–10.1 5.46 *	0.79–2.24 1.65 *	n.p	n.p
Admiralty Bay (1993)	Bícego (1996)	0.44–7.05 5.62	0.27–2.89	0.75–1.14	0.47–37.8
Admiralty Bay (1990, 1992)	Bícego *et al.* (1998)	n.p	0.14–5.48	0.61–1.18 0.85–1.27	1.00–32.0 *
Admiralty Bay (1998–2000)	this paper	0.15–13.3*	0.10–9.63*	0.47 (B_1) 1.46 (A_3)	271 (A_1)

n.p. = not presented * = sewage outfall (A_1) [1] = contaminated sediments

concentrations of Σ-AHs and Σ-*n*-alkanes (sites A_1 and E) are similar for Admiralty Bay (Bícego 1996, Bícego *et al.* 1998), near Davis station (Australia) (Green *et al.* 1992, Green & Nichols 1995) and other pristine areas of the Antarctic continent (Cripps & Priddle 1991). The levels were lower than those found at Palmer station, where there is consumption of 4.0 x 10^5 l yr^{-1} of diesel fuel for power generation as well as gasoline for outboard motors (Kennicutt *et al.* 1992b).

The analysis of aliphatic hydrocarbons showed only A_1 as a critical area contaminated by fossil fuel. This site had the highest concentrations of Σ-*n*-alkanes and Σ-AHs and the UCM. The other sites showed little oil contamination

Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs concentrations are shown in Table IV. The values of total PAHs (Σ-PAHs) ranged from 9.45 to 270.5 ng.g^{-1} and are comparable to those low-level pollution locations and the open sea worldwide (Venkatesan & Kaplan 1982, Gogou *et al.* 2000, Readman *et al.* 2002). The highest concentration of Σ-PAHs in sediments was found at site A_1

Table IV. Total PAHs content (ng.g^{-1} dry weight) in sediment samples from Admiralty Bay.

PAHs analysed	Sampling Sites A_1	A_2	A_3	A_4	A_5	A_6	A_7	B_1	B_2	C_1	C_2	D	E	F	G	H	I
naphtalene	9.55	5.88	26.95	6.84	12.2	42.8	25.8	13.7	40.1	8.78	1.80	n.d	n.d	n.d	n.d	n.d	n.d
Σ-alkyl-naphtalenes	7.93	3.48	7.53	8.53	7.78	28.7	4.71	9.08	16.8	13.6	11.9	11.9	15.5	6.18	16.2	1.62	4.70
biphenyl	7.51	1.02	2.52	3.56	4.01	9.51	2.85	9.47	19.5	7.00	5.78	6.71	6.06	3.27	23.1	25.2	2.25
acenaphtylene	n.d	n.d	3.96	n.d	1.12	2.48	1.71	6.83	9.81	1.31	n.d	n.d	n.d	n.d	n.d	n.d	n.d
acenaphthene	0.79	n.d	1.50	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
fluorene	1.61	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
phenanthrene	73.2	4.17	12.7	21.0	2.96	n.d	n.d	3.26	4.71	n.d	n.d	1.53	2.73	n.d	n.d	n.d	3.28
anthracene	20.5	7.61	n.d	8.13	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	1.58	n.d	1.01	n.d	2.31
Σ-methyl-phenanthrenes	n.d	2.73	3.46	9.43	2.27	2.71	2.93	0.53	1.58	n.d	1.78	2.45	n.d	n.d	n.d	n.d	3.02
fluoranthene	42.3	2.12	5.40	10.3	n.d	n.d	n.d	n.d	n.d	1.00	n.d	n.d	n.d	n.d	2.39	0.82	n.d
pyrene	34.8	n.d	3.96	7.65	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	1.09	n.d	n.d
benzo(*a*)anthracene	6.50	0.65	1.57	6.76	0.27	n.d	n.d	n.d	n.d	n.d	0.83	0.32	n.d	n.d	0.50	0.25	n.d
chrysene	27.1	n.d	4.85	17.1	1.45	1.87	n.d	n.d	n.d	n.d	3.05	n.d	n.d	n.d	n.d	n.d	n.d
benzo(*b*)fluoranthene	10.6	n.d	5.00	21.4	n.d	n.d	n.d	1.10	n.d	n.d	1.34	n.d	n.d	n.d	n.d	n.d	n.d
benzo(*k*)fluoranthene	1.01	n.d	2.76	3.38	n.d	n.d	n.d	0.52	n.d	n.d	1.06	n.d	n.d	n.d	n.d	n.d	n.d
benzo(*e*)pyrene	2.37	n.d	2.26	9.57	0.77	1.02	n.d	n.d	0.67	n.d	0.58	n.d	n.d	n.d	n.d	n.d	n.d
benzo(*a*)pyrene	n.d	n.d	1.52	5.75	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
perylene	n.d	n.d	n.d	3.49	n.d	1.60	1.51	n.d	n.d	n.d	1.90	n.d	n.d	n.d	n.d	n.d	n.d
indeno(123-*cd*)pyrene	15.1	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	2.56	n.d	n.d	n.d	n.d
dibenzo(*ah*)anthracene	n.d	n.d	n.d	n.d	3.51	2.49	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
benzo(*ghi*)perylene	9.70	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	3.91	n.d	n.d	n.d	2.80	1.91	5.52
Σ-PAHs	270.5	27.66	85.90	142.9	36.34	93.19	39.50	44.44	93.18	31.72	33.89	22.93	28.41	9.45	47.02	29.82	21.08

n.d = not detected

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at the sewage outfall (270.5 ng.g^{-1}), followed by sites A_4 (142.9 ng.g^{-1}), A_6 (93.19 ng.g^{-1}), B_2 (93.18 ng.g^{-1}) and A_3 (85.90 ng.g^{-1}). At other stations, Σ-PAHs were less than 50 ng.g^{-1}. PAHs may be introduced into environment by various processes, and originate mainly from anthropogenic sources such as the combustion of fossil fuel and the direct release of oil and its products (Law & Biscaya 1994).

In the study area, the main source of PAHs is the EACF, due to transport and fuel usage. The most widely used fuel in the Antarctic operations of the EACF is DFA. The predominant PAHs in DFA are naphthalene, alkylated naphthalenes and other semi volatile aromatics with 3 or 4 rings (Kennicutt *et al.* 1991). Weathering effects, such as biodegradation and photo oxidation, cause preferential depletion of alkyl substituted (Davies & Tibets 1987, Ehrhardt *et al.* 1992, Yu *et al.* 1995), causing preferential accumulation of the parent PAH. The alkyl naphthalenes/naphthalene ratio of DFA, calculated in accordance with Yu *et al.* (1995), is 7.3. For the sediment samples collected on Admiralty Bay on transects A, B and C, the ratio ranged from 0.18 to 1.55 (Table IV) indicating a predominance of degradation processes of alkyl naphtalenes.

Relatively high concentrations of phenanthrene, anthracene, fluoranthene, pyrene and chrysene (unsubstituted PAHs with three or four aromatic rings) found at sites A_1, A_2 and A_4, are indicative of oil input from Ferraz station.

Table III presents several studies related to PAHs in the Antarctic environment. In general, the levels of this study are similar to those places of low contamination. The effect of increased human activity in Admiralty Bay over the last decade may be observed by comparing the data with those of Bícego *et al.* (1998). Concentrations of sediments from the same area in 1990–93 are shown in Table III. Between 1993 and 1998, the number of people on the station increased, causing a corresponding increase in both the discharge of sewage and utilization of fossil fuels.

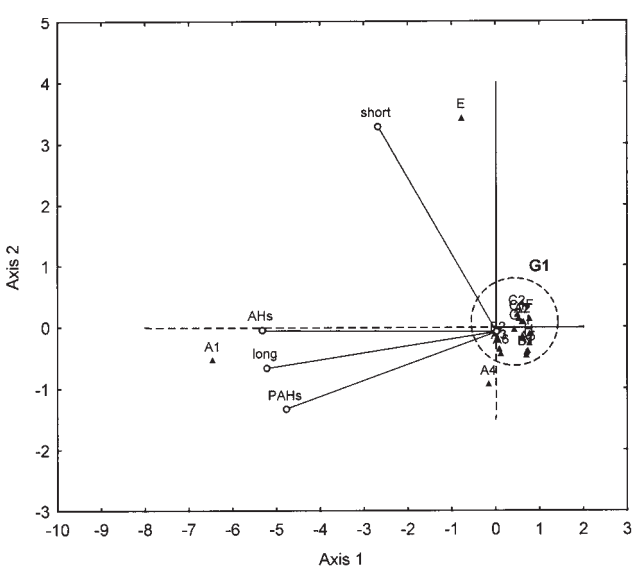

Fig. 3. Principal Component Analysis of *n*-alkanes (short and long chain), Σ-AHs (aliphatics), Σ-PAHs and study sites.

Multivariate statistics

Principal component analysis (PCA) was applied to *n*-alkanes (short and long chains), Σ-PAHs and Σ-AHs (aliphatic) parameters. This analysis was done based on the calculation of the coefficient of variation for each variable.

Figure 3 presents the loadings and scores where axis 1 shows the variation of the Σ-AHs, Σ-PAHs and long chain *n*-alkanes while axis 2 shows the variation of level of the short chain *n*-alkanes. The highest values (loadings) are associated to the higher levels of PAHs and *n*-alkanes. This plot presented the distinction between the samples A_1, A_4, E and a group (G1) formed by the other points.

The site A_1, located at the sewage outfall, is characterized by the highest values of Σ-*n*-alkanes and Σ-PAHs. The site A_4, 50 m away from the outfall, is characterized by relatively high value of PAHs and low concentrations of short chain *n*-alkanes. Although the samples A_2 and A_3 are closer to the sewer source than A_4, the grain size (Table I) of these sediments could explain the accumulation of organic compounds and consequently the difference in concentrations.

Site E was characterized by relatively high value of *n*-alkanes and low level of PAHs. The presence of PAHs indicates a small contribution of oil. The relatively high value of *n*-alkanes is not associated with sewage outfall. Previous studies on the dispersion of faecal sterols showed that this site does not receive sewage contribution from Ferraz station (Martins *et al.* 2002). The source of the hydrocarbons can be attributed to ship traffic of Admiralty Bay. All sites in Group G1 presented low concentrations of *n*-alkanes and PAHs.

Conclusion

In general, the concentrations and composition of aliphatic hydrocarbons were similar to those observed at other pristine Antarctic areas. Only the sediment from A_1 was considered to be significantly contaminated by hydrocarbons. A predominance of long chain *n*-alkanes (more than *n*-C_{22}), associated with a small UCM and a relatively high concentration of PAHs indicate fuel oil contamination. The concentrations of hydrocarbons decreased with increasing distance from the sewage outfall. The distribution pattern for the individual compounds suggests a low oil discharge to Admiralty Bay. A slight increase of Σ-PAHs in sediments near the Brazilian station since 1993 may be attributed to an increase in the number of staff over recent years and the consequent growth in activities that use fossil fuels and an increased sewage

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discharge.

Understanding the distribution of natural and anthropogenic hydrocarbons in Antarctic surface sediments is important for assigning origins. Monitoring is useful to verify the contribution of anthropogenic compounds to pristine environments.

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