Results from a 15-year study on hydrocarbon concentrations in water and sediment from Admiralty Bay, King George Island, Antarctica

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Abstract: Admiralty Bay on the King George Island hosts the Brazilian, Polish and Peruvian research stations as well as the American and Ecuadorian field stations. Human activities in this region require the use of fossil fuels as an energy source, thereby placing the region at risk of hydrocarbon contamination. Hydrocarbon monitoring was conducted on water and sediment samples from the bay over 15 years. Fluorescence spectroscopy was used for the analysis of total polycyclic aromatic hydrocarbons (PAHs) in seawater samples and gas chromatography with flame ionization and/or mass spectrometric detection was used to analyse individual n-alkanes and PAHs in sediment samples. The results revealed that most sites contaminated by these compounds are around the Brazilian and Polish research stations due to the intense human activities, mainly during the summer. Moreover, the sediments revealed the presence of hydrocarbons from different sources, suggesting a mixture of the direct input of oil or derivatives and derived from hydrocarbon combustion. A decrease in PAH concentrations occurred following improvement of the sewage treatment facilities at the Brazilian research station, indicating that the contribution from human waste may be significant.

Introduction

The Antarctic region is located far from inhabited continents and is relatively free from human influence. However, transportation and energy needs for research stations need fossil fuel, which makes the region susceptible to localized oil contamination in areas of human activity (Priddle 2002). According to COMNAP (2008), there are about 4000 people working at research stations in the summer and around 86.5×10^6 l of oil are used every year to support their activities (SCAR 1997 - http://www.scar.org/publications/reports/14/). Accidents have occurred in the area, such as the MV *Explorer* incident in 2007 (SCAR 2007 www.scar.org/media/pressreleases/fuel_spill_pr_2007.pdf), the fuel spill at the Faraday Research Station in 1992 (Cripps & Shears 1997), the *Bahia Paraiso* shipwreck in 1989 (Cripps 1992) and the oil pipeline rupture at the Brazilian Station in 1987.

Petroleum is composed of thousands of different compounds and hydrocarbons, such as n-alkanes, isoprenoid hydrocarbons and polycyclic aromatic hydrocarbons (PAHs). Studies carried out in the Antarctic region have revealed high concentrations of hydrocarbons in the vicinity of some research stations (Kennicutt *et al.* 1991, 1992, 1995, Cripps 1992, Kim *et al.* 2006, Cincinelli *et al.* 2008). A study conducted near the McMurdo Station, which is the largest Antarctic research facility, reported hydrocarbon concentrations in sediments comparable to the most polluted harbours in temperate regions (Lenihan 1992). The study also found drastic changes in the local biota due to contamination.

Increasing research and tourism activities in the Antarctic and the resulting increased exposure of the region to hydrocarbons requires continual attention to conserve the local biota. Between 1989 and 2004, a monitoring programme was conducted by the Brazilian Antarctic Programme in Admiralty Bay, although the monitoring was not carried out every year. The objectives were to investigate the presence of hydrocarbons in particular marine ecosystem elements and establish a baseline for the local area (Bícego *et al.* 1996, 1998, 2002, 2003, Martins *et al.* 2004).

The present study combines previously published data with new data on hydrocarbons in seawater and sediments
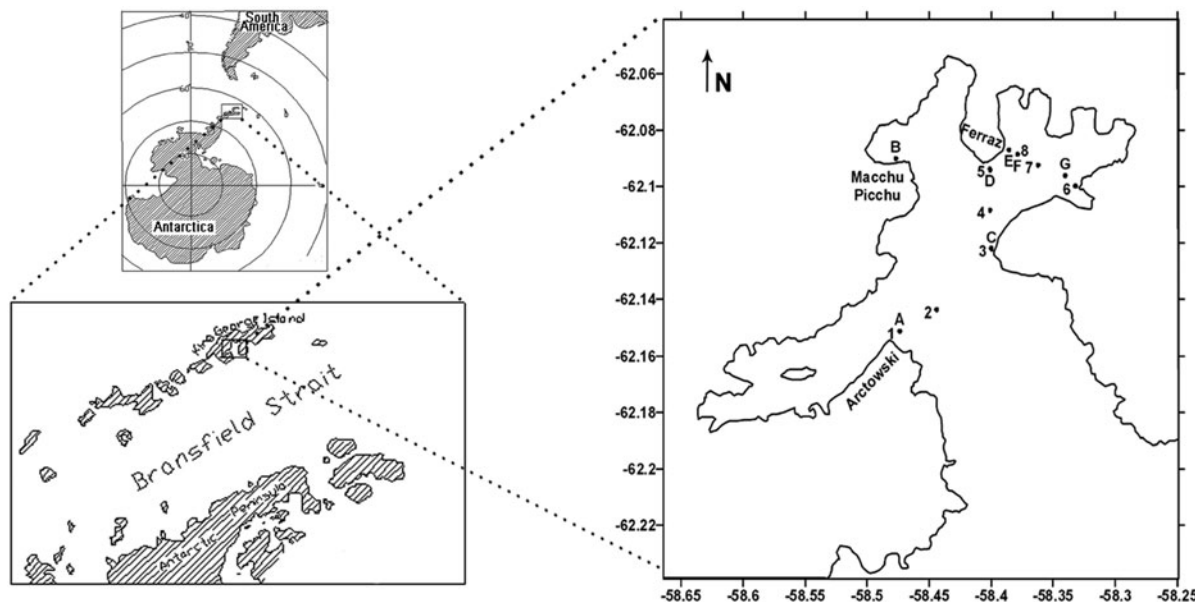
Fig. 1. Seawater (1 to 8) and sediment (A to G) sampling locations in Admiralty Bay, King George Island.

over this 15-year period, thereby revealing the temporal and spatial trends.

Study area

Admiralty Bay is 131 km wide and one of the largest bays in the South Shetland Islands. It hosts a number of research stations operated by Brazil, Poland, Peru, the United States of America and Ecuador. The Brazilian Comandante Ferraz Station was established in the summer of 1984 on the eastern coast of the Keller Peninsula and is currently a medium-sized research station with power supplied by six generators. The summer population ranges from 40 to 60 people, with only 10–15 people in winter. Annually, the station uses 320 000 l of Arctic-grade diesel oil stored in 17 double-walled steel tanks, which are refilled every summer by ship. The mean monthly consumption of 23 tons of fuel in the diesel generators poses a potential risk of the direct release of hydrocarbons into the environment and exhaust emissions are a source of combustion-derived PAHs released into the local atmosphere. The Polish Henryk Arctowski Research Station, was established in 1977 in western Admiralty Bay at Thomas Point. This station has a total storage capacity of 1 000 000 l of fuel. The Peruvian Machu Picchu Station was built in 1988 at Crépin Point in Mackellar Cove on King George Island and is currently used only for summer operations (COMNAP 2008). The Copacabana Field Station, formerly known as Pieter J. Lenie (USA) and the Refugio Ecuador (an Ecuadorian field hut) are also located in Admiralty Bay (COMNAP 2008) and only used in summer.

In addition to the land-based activities of these stations, the researchers use small boats as a means of transportation as well as for collecting samples throughout the area, which results in further potential marine contamination from oil residues during boating operations. The area also receives several tourist and research vessels every year, which may contribute further to this type of contamination.

Materials and methods

Two different methods were employed to analyse hydrocarbons. UV-fluorescence spectroscopy was used to analyse total polycyclic aromatic hydrocarbons (PAHs) in seawater samples. Gas chromatography with flame ionization (GC/FID) and gas chromatography with mass spectrometric detection (GC/MS) were used to analyse individual n-alkanes and PAHs in sediment samples.

Seawater samples

Sub-surface seawater samples were taken in summer in 1989 and 1990 as well as from 1992 to 1997. Samples were collected in January and/or February of each year (see Fig. 1 for locations). Over the first four years, each location was sampled only once, except Station 8 in front of the Brazilian research station, for which samples were taken twice (once in January and once in February) in 1989 and 1990. In 1992 and 1993, samples from Station 8 were collected five times at one-week intervals. From 1994–97, five water samples were taken at one-week intervals during the summer at each station.

Seawater was sampled at a depth of 1 m, using 4 l amber glass bottles attached to a weighed metal frame. Sampling was performed immediately prior to stopping the boat at the location in order to avoid contamination. All glassware used

Table I. Mean concentration and standard deviation of total PAHs ($\mu g\ l^{-1}$) in seawater samples from eight locations in Admiralty Bay, King George Island 1989–97.

Station	Year							
	1989	1990	1992	1993	1994	1995	1996	1997
#1	0.42	1.1	2.5	1.2	1.6 ± 0.8	0.18 ± 0.10	0.39 ± 0.50	1.2 ± 0.6
#2	< DL*	0.65	0.96	0.68	0.91 ± 0.40	0.09 ± 0.03	0.14 ± 0.08	0.81 ± 0.48
#3	2.7	< DL*	0.52	0.91	0.81 ± 0.43	0.18 ± 0.16	0.26 ± 0.34	0.51 ± 0.45
#4	1.0	0.14	0.96	< DL*	0.95 ± 0.49	0.11 ± 0.08	0.50 ± 0.50	0.55 ± 0.60
#5	2.1	2.5	0.92	0.68	1.1 ± 0.5	0.08 ± 0.02	0.19 ± 0.17	0.51 ± 0.53
#6	2.0	0.99	0.80	-	0.31 ± 0.16	0.08 ± 0.02	0.20 ± 0.16	0.64 ± 0.40
#7	0.78	0.90	0.75	1.5	0.63 ± 0.20	0.08 ± 0.02	0.24 ± 0.16	0.67 ± 0.81
#8	3.6 ± 2.4	2.1 ± 0.2	1.1 ± 0.4	2.7 ± 3.5	1.4 ± 0.7	0.08 ± 0.02	0.36 ± 0.36	0.90 ± 0.89

*DL = detection limit = $0.07\ \mu g\ l^{-1}$.

during the analysis was meticulously cleaned using Extran 20%, then rinsed with distilled water, followed by ethanol and dried in an oven at 100°C. Immediately prior to use, all glassware was rinsed with n-hexane. All solvents were pesticide grade and the entire procedure was continually checked by running procedural blanks. Extraction of the seawater was performed with n-hexane and the extracts were concentrated to 5 ml. Fluorescence of the samples was measured in a Perkin-Elmer Spectrofluorimeter (Model LC 240), with an excitation wavelength of 310 nm and an emission wavelength of 360 nm, according to IOC/UNEP (1984) procedures, with the extraction modifications proposed by Ehrhardt (1983). The calibration curve was constructed with an artificially weathered crude oil standard, obtained by distilling Carmópolis crude oil (Brazil) at 110°C. Samples outside the calibration curve range were diluted with n-hexane in order to fall within the appropriate range. The mean blank value was $0.02\ \mu g\ l^{-1}$, which was subtracted from all samples. The detection limit (DL) was calculated as the blank signal plus three standard deviations of the blank, corresponding to $0.07\ \mu g\ l^{-1}$. In order to calculate the mean concentration at each station, results below the DL (Table I) were substituted for a value of $0.07\ \mu g\ l^{-1}$.

There are methodological limitations to the use of UV-fluorescence spectrometry, such as the undistinguishable fluorescence characteristics of biosynthesized compounds from oil residues (Ehrhardt & Knap 1989) and the fact that fluorescence due to PAHs may be quenched in the presence of humic material in the aqueous solution (Gauthier *et al.* 1986), thereby leading to a possible underestimation of concentrations. Moreover, unlike GC-MS methods, fluorescence data does not provide any insight into molecular composition. Despite these limitations, this method is very fast and is a useful screening tool in monitoring studies prior to the use of more sophisticated techniques.

Sediments

Sediment samples were collected using a stainless steel van Veen grab sampler in January/February 1990, 1992, 1993,

1999, 2003 and 2004, during the summer. The area sampled was that surrounding the Brazilian, Polish and Peruvian research stations (see Fig. 1 for locations). Data from 1990 to 1999 have been published elsewhere (Bícego *et al.* 1996, 1998, 2003, Martins *et al.* 2004), whereas the more recent data (2003 and 2004) are published for the first time here.

Samples were kept at -15°C until laboratory analysis. After drying in an oven at 50°C, 30 g of the sample was Soxhlet extracted with a 50% mixture of n-hexane and dichloromethane for eight hours. The organic extracts were concentrated on a rotary evaporator, purified and fractionated by silica/alumina gel chromatography. The n-alkanes were determined on a Hewlett Packard 5890 II high-resolution gas chromatograph with flame ionization detection, equipped with a 25 m SE-54 capillary column. Aromatic hydrocarbons were measured on a Fisons Trio 1000 GC/MS system, with mass detection in the selected
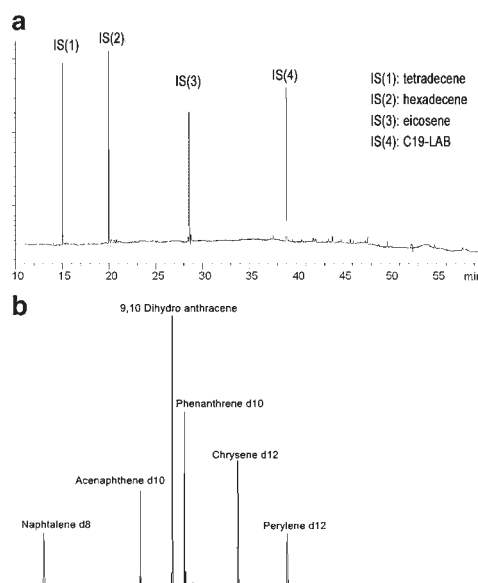

Fig. 2. Chromatograms of blanks with the internal standards used. **a.** N-alkane hydrocarbons fraction, **b.** PAH hydrocarbons fraction.

ion-monitoring mode. All instruments were calibrated by the injection of certified standards at five different concentrations. Calibration curve checks were performed once a week. Individual PAH and n-alkane identification was based on GC retention times. For PAHs mass spectra were also used. The method detection limit (DL) was $0.001-0.5$ µg g^{-1} for n-alkanes, and $0.39-0.72$ ng g^{-1} for PAHs, and was determined at least once a year. DL was based on the standard deviation (3x) of seven replicates of a sediment sample containing hydrocarbons at a level of one to five times the expected DL. All solvents were pesticide grade and the blanks were checked under the same conditions as those of the analyses. Quantification was performed using internal standards, which were added to all samples, blank and reference material prior to the extraction process. Quality control was based on the analysis of procedural blanks, blank spikes, matrix spikes and duplicates of the sediment sample. Procedural blanks revealed no contamination (Fig. 2). Figure 3a & b illustrate two chromatograms of sediment samples from the GC/FID and GC/MS for n-alkanes and PAHs, respectively. Standard reference material (SRM 1941b or SRM 1944) from the National Institute of Standards and Technology (NIST) was analysed for each sample batch of approximately 30 samples. The results fell within the standard deviation for all compounds analysed. The laboratory participates annually in "inter-laboratory comparison exercises" promoted by the Marine Environment Laboratory of the International Atomic Energy Agency (MEL-IAEA) and has obtained satisfactory results regarding hydrocarbon analyses in sediment. The complete analytical protocol was described in detail by
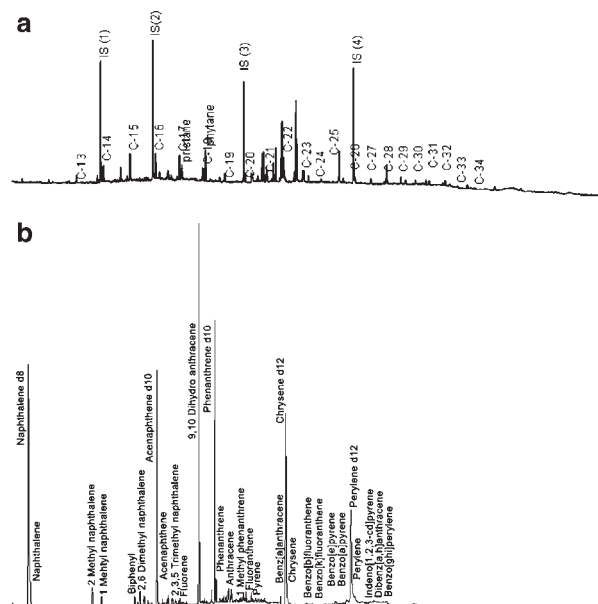
UNEP (1992) and elsewhere (Bícego et al. 1996, 1998, 2003, Martins et al. 2004).

Results and discussion

Hydrocarbons in seawater

Petroleum and derivatives released into seawater undergo physical, chemical and biological transformations, such as evaporation, dissolution, adsorption, microbial degradation and photochemical oxidation. Dissolution accounts for only a small portion, but is considered an important behaviour due to the soluble components, particularly smaller aromatic compounds, which are more toxic to aquatic species than aliphatic components. Solubility decreases with an increase in molecular weight (May et al. 1978). The solubility of aliphatic oil components is very low in comparison to that of aromatic hydrocarbons and is considered negligible (NRC 2003), whereas low molecular weight polycyclic aromatic hydrocarbons (PAHs) are partially soluble in water.

Table I displays the mean concentration and the standard deviation of total PAHs in the seawater sampled throughout eight non-consecutive years (1989–97). From 1989–93, only Station #8 was sampled more than once: twice in 1989 and 1990 and five times in 1992 and 1993. In the following years, five seawater samples were taken during the summer at each station. Law (1981), and Cripps (1992), considered that concentrations above 1.0 µg l^{-1} of dissolved/dispersed petroleum hydrocarbons denoted polluted waters. Such concentrations are considered to be of an anthropogenic source, whereas lower values could be attributed to natural sources. Recently, Bícego et al. (2002) proposed a baseline concentration of 0.31 µg l^{-1} for non-polluted open waters in the south-west Atlantic based on

Fig. 3. Chromatograms of sediment samples. a. Fraction of n-alkane hydrocarbons at #F collected in 1999, b. fraction of PAHs at #F in 2003.
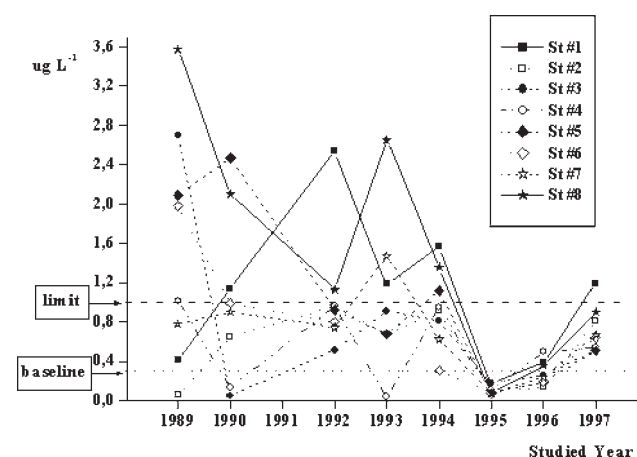

Fig. 4. Mean concentration of total PAHs in seawater samples from 8 locations in Admiralty Bay, King George Island 1989–97. The legend "limit" refers to 1.0 µg l^{-1}, based on Law (1981), and the legend "baseline" refers to 0.31 µg l^{-1}, based on Bícego et al. (2002).
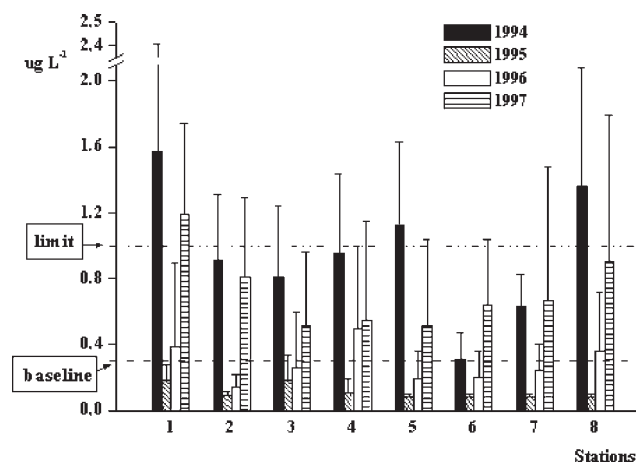
Fig. 5. Total concentration and standard deviation ($\mu g\ L^{-1}$) of PAHs in seawater samples from Admiralty Bay, King George Island 1994–97. The standard deviation was calculated based on the mean of five sample replicates. The legend "limit" refers to 1.0 $\mu g\ l^{-1}$, based on Law (1981), and the legend "baseline" refers to 0.31 $\mu g\ l^{-1}$, based on Bícego et al. (2002).

the mean concentration measured during an exhaustive sampling programme in the area. Although the study was conducted in open waters, a concentration of 0.31 $\mu g\ l^{-1}$ could be considered the natural baseline in Admiralty Bay off King George Island due to its proximity to open waters. However, this should be considered with caution, as coastal areas are richer in organisms that may contribute toward natural fluorescence.

In the present study, most of the samples (71%) had concentrations of PAHs above this baseline (Fig. 4). Seventeen (27%) out of the 63 samples were above 1 $\mu g\ l^{-1}$, but not more than 3.6 $\mu g\ l^{-1}$ (Fig. 4), which suggests a low contribution of petroleum hydrocarbons. The majority of samples from 1989 had high concentrations and no clear pattern was observed between 1989–94 for the sampling locations. Little can be said about these data, as there were no replicated samples and no standard deviation could be calculated. A decrease in PAH concentrations was observed at all locations from 1994–95, which is probably related to an improvement that summer in the sewage treatment facilities at the Brazilian research station. On this occasion, the septic tank was replaced with a better system with filters to decrease the introduction of organic matter and associated PAHs. The new system also controls the internal heating, thereby avoiding ruptures in the pipes and consequent sewage spillage due to freezing. Although the data are not statistically different, an increasing trend was observed for the following years (1995–97) (Figs 4 & 5). Interestingly, 1995 was the "cleanest" year, with none of the samples above 0.31 $\mu g\ l^{-1}$, in contrast with the sampling carried out in 1997, in which all samples were above this limit (Table I; Fig. 5). This may have been due to the increase in the number of researchers and staff since

1995, as well as a lack of maintenance and cleaning procedures on the sewage treatment facilities.

In general, the highest concentrations were observed at the Brazilian (Station 8) and Polish (Station 1) research stations, which have the highest staff number during the summer, with intense boat activities and a subsequent increase in the use of diesel fuel. Station 5 had concentrations similar those of Station 8, suggesting that this location receives oil contamination mainly from the Brazilian station, probably carried by local currents (Rakusa-Suszczewski 1980, Pruszak 1980, Bícego et al. 1996). A similar situation was found at Station 2 near the Polish research station (Station #1) (Fig. 1; Table I). Stations 2 & 5 are located along the route of the small vessels normally used to travel between the Brazilian and Polish research stations, which could explain the relatively higher concentrations.

It should be stressed that the data reported here refer to mean concentrations and, in some cases, the standard deviation was very broad. For example, a concentration of 8.9 $\mu g\ l^{-1}$ was measured for one sample taken near the Brazilian Station (#8) in 1993 (data not shown here, but published by Bícego et al. 1996). This is evidence that, even though Admiralty Bay as a whole is not highly contaminated, the area may receive some occasional high inputs.

Hydrocarbons in the sediments

N-alkanes and isoprenoids

Table II displays the concentration of total n-alkane, pristane/phytane and odd/even ratios. The concentration of total n-alkane ranged from 0.10 to 5.5 $\mu g\ g^{-1}$. These values are considered low when compared to samples from polluted urbanized areas and are similar to those found in unpolluted sediments (Volkman et al. 1992, UNEP 1992). Moreover, these results are on the same order of magnitude as those found by other authors in Antarctic marine sediments (Cripps 1992, Green et al. 1992, Green & Nichols 1995). However, Cripps (1992) reported that the n-alkane concentration in sediments underwent a sharp decrease within a few hundred metres from Signy Station, suggesting that levels close to this station arose from human activities. Martins et al. (2004) also found a decrease in n-alkane concentration with an increase in distance (400 m) from the sewage outfall. Total n-alkane concentrations of <1.0 $\mu g\ g^{-1}$ were reported in sediments near Palmer Station, but sediments contaminated after the Bahia Paraiso wreck had values ranging from 1.0–1.7 $\mu g\ g^{-1}$ (Kennicutt et al. 1991).

The highest concentrations of n-alkanes were always in the vicinity of the Brazilian research station #F, where the local sewage is discharged. In a few cases, the sediments sampled at #D and #E, which are relatively close to the Brazilian research station, also had relatively high n-alkane concentrations. According to circulation studies, wind is a decisive factor in the oceanographic mixing process of the region (Rakusa-Suszczewski 1980, Pruszak 1980) and the

Table II. Total concentration of n-alkanes (µg g^{-1}) and pristane/phytane (pri/phy) and odd/even ratios in sediments from Admiralty Bay, King George Island 1990–2004.

Year/station	1990			1992			1993		
	n-alk	pri/phy	odd/even	n-alk	pri/phy	odd/even	n-alk	pri/phy	odd/even
#A	3.3	1.8	1.2	2.1	0.70	0.85	0.44	0.70	0.99
#B	1.4	2.8	0.89	0.32	2.0	0.81	0.27	2.0	0.87
#C	0.35	2.8	0.61	0.71	6.0	0.87	1.4	6.0	0.77
#D	4.2	0.34	1.1	1.3	1.4	1.1	1.5	1.1	1.0
#E	2.4	0.88	1.1	0.80	1.6	1.2	2.5	1.6	1.1
#F	5.5	2.1	1.2	3.3	1.0	1.0	2.9	1.0	1.1
#G	0.30	3.7	0.77	0.24	1.6	0.87	0.28	3.2	0.85

Year/station	1999			2003			2004		
	n-alk.	pri/phy	odd/even	n-alk.	pri/phy	odd/even	n-alk.	pri/phy	odd/even
#A	0.10	1.0	1.3	0.28	n.c.	0.78	0.37	2.2	1.0
#B	0.25	1.0	0.85	0.25	n.c.	1.1	0.24	nc	0.93
#C	n.s.	n.s.	n.s.	0.46	0.97	0.79	0.20	nc	1.1
#D	1.3	1.7	1.1	n.s.	n.s.	n.s.	n.s.	ns	n.s.
#E	0.28	1.0	1.3	0.30	0.57	0.74	0.21	2.6	0.82
#F	0.31	1.0	1.5	0.26	0.70	0.70	0.52	nc	0.91
#G	Ns	ns	ns	0.19	0.24	0.43	0.43	nc	0.78

ns = not sampled.
nc = not calculated.

wind blows from south-west to north-west, with west-south-west dominating. Therefore, these sites may be under the influence of oil from the research station carried by the dominant currents. Higher n-alkane concentrations were also observed in some years at #A. This is probably due to the proximity of this site to the Polish research station. Fortunately, a general trend of decreasing n-alkane concentrations was observed at this location (Fig. 6) and the n-alkane concentrations generally decreased from 1989 to 1999 and then remained nearly constant at all stations (Fig. 6).

An indicator for categorizing petroleum hydrocarbons in sediments is the relative distribution of individual n-alkanes. In general, n-alkanes from petroleum show no predominance

Fig. 6. Total concentration of n-alkanes (µg g^{-1}) in sediments from Admiralty Bay, King George Island 1990–2004.

of odd or even carbon numbers, whereas the odd carbon numbered chain dominates in n-alkanes synthesized by marine organisms (NRC 1985). Controversially, a number of studies have found Antarctic marine organisms (Nachman 1985, Reinhardt & Van Vleet 1986a, 1986b) and samples of seawater and sea-ice algae (Green et al. 1992) to exhibit an opposite natural pattern, with even-chain predominance. In any case, an odd-to-even ratio should be useful in identifying the source of hydrocarbons source in the environment, since this value is approximately 1.0 for petroleum.

The odd/even ratio at #D, #E, #F (near the Brazilian station) and #A (near the Polish station) was higher than 1.0 for the first four years studied (1990 and 1999) (Table II). A decrease in this ratio occurred in the 2003 and 2004 sediment samples, suggesting a change in the n-alkane source.

The isoprenoid hydrocarbons pristane and phytane were also investigated in sediment samples. Both of these compounds are commonly found in petroleum products, but pristane also occurs naturally in oxidative environments as a degradation product of the phytol side chain of chlorophyll. Therefore, the pristane/phytane ratio is usually greater than 1.0 in biogenic samples and is often used as an indicator of petroleum contamination (Volkman et al. 1992). Values less than one are not indicative of the presence of petroleum (Humphrey et al. 1987). The pristane/phytane ratio in the present study indicated that there was a greater oil contribution in the earlier years, mainly at the sites located near the Brazilian station (#D, #E and #F) (Table II). In the later years, the ratios indicate a stronger contribution from natural hydrocarbons at these locations.

The three parameters analysed indicated that the sites located near these research stations were under the
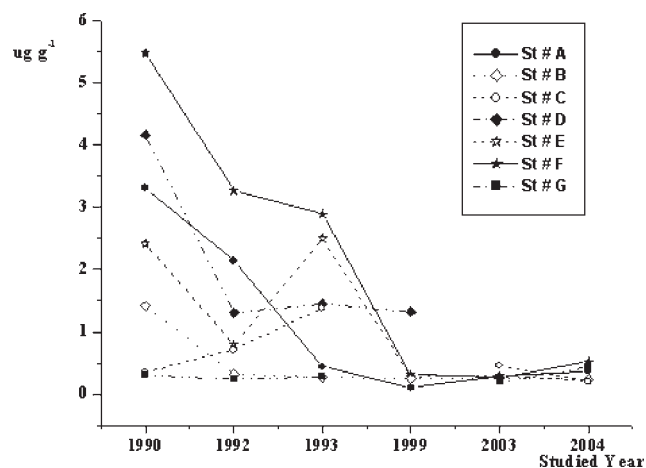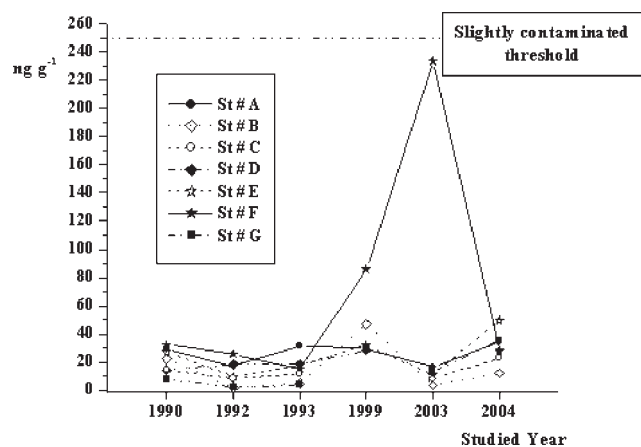
Fig. 7. Total concentration of PAHs (ng g^{-1} dry weight) in sediments from Admiralty Bay, King George Island 1990–2004.

influence of human activities. However, these indicators revealed a decrease in the human influence between 1993 and 1999 based on the data on hydrocarbons in the water, which showed an improvement in 1995. After 1999, the hydrocarbons in sediments remained nearly constant.

Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are another important class of hydrocarbons in the environment. Anthropogenic activities are believed to be the main source of such compounds in the marine environment, but they may also be synthesized by bacteria, plants and fungi or might even be released into the sea through natural fissures on the ocean bottom (McElroy *et al.* 1989). Sediments may retain toxic components such as polycyclic aromatic hydrocarbons (PAHs) on time scales of years to decades (Burns *et al.* 1994). In the 1989 *Exxon Valdez* spill, oil remained in aerated sediments for more than a decade (Short *et al.* 2007).

Tables III–VIII record the PAHs encountered. In general, the area cannot be considered particularly polluted when compared to regions with intense anthropogenic activities. However, some relatively high concentrations were observed as some of the sites, such as #A, #E and #F. The total PAH concentrations ranged from 0.71–50 ng g^{-1}, except at #F (in front of the Brazilian station), with 86 ng g^{-1} in the sample collected in 1999 and 234 ng g^{-1} in 2003 (Fig. 7). Based on international studies worldwide, Notar *et al.* (2001) have proposed three different levels of PAH contamination in sediments: slightly contaminated (total PAHs < 250 ng g^{-1}), fairly contaminated (250 ng g^{-1} < total PAHs < 500 ng g^{-1}) and relatively highly contaminated samples (total PAHs > 500 ng g^{-1}). Thus, all the sediments studied from Admiralty Bay can be classified as only slightly contaminated.

The total PAH concentration was also compared to the screening quick reference tables for pollutants (SquiRTs) from NOAA (1999), which propose values for threshold effect levels (TEL) and probable effect levels (PEL) as a guideline for marine sediments. The highest concentration in the present study was 234 ng g^{-1} (at #F in 2003), which represents less than 14% of the proposed TEL (1684 ng g^{-1}).

Table III. Concentrations (ng g^{-1} dry weight) of individual polycyclic and total aromatic hydrocarbons in sediment samples from Admiralty Bay during the summer of 1990.

	DL	#A	#B	#C	#D	#E	#F	#G
Naphthalene	< 0.45	1.6	0.94	2.8	1.8	0.52	4.7	1.7
Alkyl naphtalenes	< 0.65	5.3	5.0	6.5	6.1	2.3	14	3.4
Biphenyl	< 0.53	0.93	< DL	1.6	1.4	0.84	3.6	< DL
Acenaphthylene	< 0.50	< DL	< DL	< DL	< DL	< DL	< DL	< DL
Acenaphthene	< 0.53	< DL	< DL	0.62	< DL	< DL	0.93	< DL
Fluorene	< 0.47	0.88	0.73	< DL	< DL	< DL	0.60	< DL
Phenanthrene	< 0.65	6.7	7.5	1.2	1.7	1.4	3.7	1.0
Anthracene	< 0.48	1.4	1.7	< DL	< DL	< DL	0.94	< DL
Alkylphenanthrenes	< 0.51	2.2	2.4	< DL	< DL	< DL	0.58	< DL
Fluoranthene	< 0.55	4.5	2.0	< DL	< DL	1.4	0.58	< DL
Pyrene	< 0.57	2.0	0.89	< DL	< DL	0.67	< DL	< DL
Benz[a]anthracene	< 0.41	< DL	< DL	< DL	< DL	1.6	< DL	< DL
Chrysene	< 0.45	1.7	< DL	< DL	< DL	1.9	< DL	< DL
Benzo[b]fluoranthene	< 0.43	< DL	< DL	< DL	< DL	2.2	< DL	< DL
Benzo[k]fluoranthene	< 0.51	< DL	< DL	< DL	< DL	< DL	< DL	< DL
Benzo[e]pyrene	< 0.55	< DL	< DL	< DL	< DL	1.5	< DL	< DL
Benzo[a]pyrene	< 0.41	< DL	< DL	< DL	< DL	1.8	< DL	< DL
Perylene	< 0.72	< DL	< DL	< DL	< DL	< DL	< DL	< DL
Indeno[1,2,3-cd]pyrene	< 0.70	< DL	< DL	< DL	< DL	8.3	< DL	< DL
Dibenzo[ah]anthracene	< 0.39	0.77	< DL	< DL	< DL	< DL	< DL	< DL
Benzo[ghi]perylene	< 0.50	< DL	< DL	< DL	< DL	< DL	< DL	< DL
Total PAHs		28	21	13	11	24	30	6.1

DL = detection limit of individual compounds.

Table IV. Concentrations (ng g^{-1} dry weight) of individual polycyclic and total aromatic hydrocarbons in sediment samples from Admiralty Bay during the summer of 1992.

	DL	#A	#B	#C	#D	#E	#F	#G
Naphthalene	< 0.45	1.2	< DL	2.5	3.7	1.5	4.6	< DL
Alkyl naphtalenes	< 0.65	2.3	0.94	1.9	7.0	2.2	10	0.71
Biphenyl	< 0.53	< DL	< DL	1.3	1.2	0.70	1.3	< DL
Acenaphthylene	< 0.50	1.1	< DL	< DL	1.0	1.2	2.7	< DL
Acenaphthene	< 0.53	< DL	< DL	< DL	1.1	< DL	1.8	< DL
Fluorene	< 0.47	< DL	< DL	< DL	0.68	< DL	0.95	< DL
Phenanthrene	< 0.65	0.71	< DL	< DL	< DL	< DL	0.82	< DL
Anthracene	< 0.48	2.3	< DL	0.53	< DL	< DL	0.67	< DL
Alkylphenanthrenes	< 0.51	< DL	< DL	< DL	< DL	1.0	< DL	< DL
Fluoranthene	< 0.55	< DL	< DL	< DL	1.1	1.6	< DL	< DL
Pyrene	< 0.57	< DL	< DL	< DL	2.1	< DL	< DL	< DL
Benz[a]anthracene	< 0.41	1.3	< DL	< DL	< DL	< DL	0.56	< DL
Chrysene	< 0.45	< DL	< DL	< DL	< DL	< DL	< DL	< DL
Benzo[b]fluoranthene	< 0.43	2.3	< DL	< DL	< DL	< DL	< DL	< DL
Benzo[k]fluoranthene	< 0.51	1.2	< DL	< DL	< DL	< DL	< DL	< DL
Benzo[e]pyrene	< 0.55	< DL	< DL	< DL	< DL	< DL	< DL	< DL
Benzo[a]pyrene	< 0.41	0.54	< DL	< DL	< DL	< DL	< DL	< DL
Perylene	< 0.72	0.87	< DL	< DL	< DL	< DL	< DL	< DL
Indeno[1,2,3-cd]pyrene	< 0.70	0.98	< DL	< DL	< DL	< DL	< DL	< DL
Dibenzo[ah]anthracene	< 0.39	1.0	< DL	< DL	< DL	< DL	< DL	< DL
Benzo[ghi]perylene	< 0.50	< DL	< DL	< DL	< DL	< DL	< DL	< DL
Total PAHs		16	0.94	6.2	18	8.2	23	0.71

DL = detection limit of individual compounds.

Individual concentrations of each PAH were also compared to the SQuiRTs and none of the compounds was higher than the proposed TEL value.

The main sources of PAHs in the Antarctic environment are the direct input of fossil fuel and inputs from incomplete combustion. Arctic Grade Diesel Fuel (DFA) is the principal energy source in Antarctic operations and contains mainly semi-volatile aromatic hydrocarbons, such as naphthalene and other non-substituted PAHs with two or three aromatic rings, with a relatively high concentration

Table V. Concentrations (ng g^{-1} dry weight) of individual polycyclic and total aromatic hydrocarbons in sediment samples from Admiralty Bay during the summer of 1993.

	DL	#A	#B	#C	#D	#E	#F	#G
Naphthalene	< 0.45	5.1	1.2	1.2	1.5	1.5	< DL	< DL
Alkyl naphtalenes	< 0.65	3.4	2.1	1.2	2.0	3.6	1.6	1.8
Biphenyl	< 0.53	< DL	< DL	< DL	< DL	< DL	< DL	< DL
Acenaphthylene	< 0.50	0.96	0.60	0.58	0.61	3.2	0.63	< DL
Acenaphthene	< 0.53	0.81	< DL	< DL	< DL	2.4	< DL	< DL
Fluorene	< 0.47	0.81	< DL	< DL	0.56	1.5	0.50	< DL
Phenanthrene	< 0.65	1.7	< DL	0.77	1.4	< DL	1.2	< DL
Anthracene	< 0.48	1.7	< DL	2.1	1.3	< DL	< DL	0.53
Alkylphenanthrenes	< 0.51	1.3	< DL	1.3	1.3	< DL	1.3	< DL
Fluoranthene	< 0.55	1.3	< DL	1.5	1.1	< DL	< DL	< DL
Pyrene	< 0.57	1.3	< DL	< DL	1.1	< DL	< DL	< DL
Benz[a]anthracene	< 0.41	1.2	< DL	0.61	1.2	< DL	1.3	< DL
Chrysene	< 0.45	1.4	< DL	< DL	1.5	< DL	0.65	< DL
Benzo[b]fluoranthene	< 0.43	1.5	< DL	< DL	< DL	0.51	1.6	< DL
Benzo[k]fluoranthene	< 0.51	1.5	< DL	< DL	< DL	< DL	1.5	< DL
Benzo[e]pyrene	< 0.55	1.4	< DL	< DL	1.4	< DL	1.4	< DL
Benzo[a]pyrene	< 0.41	1.3	< DL	< DL	1.3	< DL	1.3	< DL
Perylene	< 0.72	1.0	< DL	< DL	< DL	< DL	1.0	< DL
Indeno[1,2,3-cd]pyrene	< 0.70	1.2	< DL	< DL	< DL	1.2	< DL	< DL
Dibenzo[ah]anthracene	< 0.39	1.1	< DL	< DL	0.56	0.78	< DL	< DL
Benzo[ghi]perylene	< 0.50	1.2	< DL	< DL	< DL	< DL	< DL	< DL
Total PAHs		31	3.9	9.3	17	15	14	2.3

DL = detection limit of individual compounds.

Table VI. Concentrations (ng g^{-1} dry weight) of individual polycyclic and total aromatic hydrocarbons in sediment samples from Admiralty Bay during the summer of 1999.

	DL	#A	#B	#C	#D	#E	#F	#G
Naphthalene	< 0.45	< DL	< DL		< DL	8.8	27	
Alkyl naphtalenes	< 0.65	1.6	16		16	14	7.5	
Biphenyl	< 0.53	25	23		6.1	7.0	2.5	
Acenaphthylene	< 0.50	< DL	< DL		< DL	1.3	4.0	
Acenaphthene	< 0.53	< DL	< DL		< DL	< DL	1.5	
Fluorene	< 0.47	< DL	< DL		< DL	< DL	< DL	
Phenanthrene	< 0.65	< DL	< DL		2.7	< DL	13	
Anthracene	< 0.48	< DL	1.0		1.6	< DL	< DL	
Alkylphenanthrenes	< 0.51	< DL	< DL		< DL	< DL	3.5	
Fluoranthene	< 0.55	0.82	2.4		< DL	1.0	5.4	
Pyrene	< 0.57	< DL	1.1		< DL	< DL	4.0	
Benz[a]anthracene	< 0.41	< DL	0.50		< DL	< DL	1.6	
Chrysene	< 0.45	< DL	< DL		< DL	< DL	4.9	
Benzo[b]fluoranthene	< 0.43	< DL	< DL		< DL	< DL	5.0	
Benzo[k]fluoranthene	< 0.51	< DL	< DL		< DL	< DL	2.8	
Benzo[e]pyrene	< 0.55	< DL	< DL		< DL	< DL	2.3	
Benzo[a]pyrene	< 0.41	< DL	< DL		< DL	< DL	1.5	
Perylene	< 0.72	< DL	< DL		< DL	< DL	< DL	
Indeno[1,2,3-cd]pyrene	< 0.70	< DL	< DL		2.6	< DL	< DL	
Dibenzo[ah]anthracene	< 0.39	< DL	< DL		< DL	< DL	< DL	
Benzo[ghi]perylene	< 0.50	1.9	2.8		< DL	< DL	< DL	
Total PAHs		29	47		29	32	86	

DL = detection limit of individual compounds.

of their corresponding alkyl-substituted hydrocarbons (Kennicutt *et al.* 1991). DFA also contains more complex compounds, with four or more rings in the structure. Therefore, the Σ2-3/Σ3-4 ratio is used to identify the dominance of lighter PAHs over heavier ones. On the other hand, combustion-derived PAH residues are characterized by a low concentration of alkyl-substituted hydrocarbons relative to their parent compounds (Blumer & Youngblood 1975) and also contain fluoranthene and pyrene as major components (Venkatesan 1988).

The use of some PAH ratios have been proposed to infer the source in terms of combustion versus petroleum (Yunker *et al.*

Table VII. Concentrations (ng g^{-1} dry weight) of individual polycyclic and total aromatic hydrocarbons in sediment samples from Admiralty Bay during the summer of 2003.

	DL	#A	#B	#C	#D	#E	#F	#G
Naphthalene	< 0.45	< DL	2.0	< DL		< DL	4.5	< DL
Alkyl naphtalenes	< 0.65	8.5	1.5	2.1		5.8	18	5.7
Biphenyl	< 0.53	3.2	< DL	1.4		2.0	2.0	1.4
Acenaphthylene	< 0.50	< DL	< DL	< DL		< DL	< DL	< DL
Acenaphthene	< 0.53	< DL	< DL	< DL		< DL	1.5	< DL
Fluorene	< 0.47	< DL	< DL	< DL		< DL	4.5	< DL
Phenanthrene	< 0.65	3.0	< DL	< DL		3.2	39	4.3
Anthracene	< 0.48	< DL	< DL	4.4		< DL	4.0	< DL
Alkylphenanthrenes	< 0.51	< DL	< DL	< DL		< DL	4.0	< DL
Fluoranthene	< 0.55	< DL	< DL	< DL		< DL	38	< DL
Pyrene	< 0.57	< DL	< DL	< DL		< DL	24	< DL
Benz[a]anthracene	< 0.41	< DL	< DL	< DL		< DL	13	< DL
Chrysene	< 0.45	< DL	< DL	< DL		< DL	16	< DL
Benzo[b]fluoranthene	< 0.43	< DL	< DL	< DL		< DL	11	< DL
Benzo[k]fluoranthene	< 0.51	< DL	< DL	< DL		< DL	11	< DL
Benzo[e]pyrene	< 0.55	< DL	< DL	< DL		< DL	8.0	< DL
Benzo[a]pyrene	< 0.41	< DL	< DL	< DL		< DL	12	< DL
Perylene	< 0.72	1.5	< DL	< DL		< DL	6.0	1.2
Indeno[1,2,3-cd]pyrene	< 0.70	< DL	< DL	< DL		< DL	10	< DL
Dibenzo[ah]anthracene	< 0.39	< DL	< DL	< DL		< DL	2.0	< DL
Benzo[ghi]perylene	< 0.50	< DL	< DL	< DL		< DL	5.5	< DL
Total PAHs		16	3.5	7.9		11	234	13

DL = detection limit of individual compounds.

Table VIII. Concentrations (ng g⁻¹ dry weight) of individual polycyclic and total aromatic hydrocarbons in sediment samples from Admiralty Bay during the summer of 2004.

	DL	#A	#B	#C	#D	#E	#F	#G
Naphthalene	< 0.45	< DL	< DL	< DL		5.2	< DL	4.9
Alkyl naphtalenes	< 0.65	18	1.4	15		35	12	17
Biphenyl	< 0.53	< DL	< DL	< DL		< DL	< DL	< DL
Acenaphthylene	< 0.50	< DL	< DL	< DL		< DL	< DL	< DL
Acenaphthene	< 0.53	< DL	< DL	< DL		< DL	< DL	< DL
Fluorene	< 0.47	< DL	< DL	< DL		< DL	< DL	< DL
Phenanthrene	< 0.65	3.9	< DL	2.2		2.9	2.8	5.0
Anthracene	< 0.48	< DL	8.2	< DL		< DL	2.9	< DL
Alkylphenanthrenes	< 0.51	6.4	1.3	4.4		1.8	5.1	4.4
Fluoranthene	< 0.55	< DL	< DL	< DL		< DL	< DL	< DL
Pyrene	< 0.57	< DL	< DL	< DL		< DL	< DL	< DL
Benz[a]anthracene	< 0.41	0.62	< DL	< DL		0.73	< DL	0.51
Chrysene	< 0.45	1.5	< DL	< DL		1.4	1.6	1.8
Benzo[b]fluoranthene	< 0.43	< DL	< DL	< DL		< DL	< DL	< DL
Benzo[k]fluoranthene	< 0.51	< DL	< DL	< DL		0.94	0.54	0.60
Benzo[e]pyrene	< 0.55	0.83	< DL	< DL		0.74	0.83	0.64
Benzo[a]pyrene	< 0.41	< DL	< DL	< DL		0.51	< DL	< DL
Perylene	< 0.72	2.5	0.76	1.1		< DL	1.5	< DL
Indeno[1,2,3-cd]pyrene	< 0.70	< DL	< DL	< DL		< DL	< DL	< DL
Dibenzo[ah]anthracene	< 0.39	< DL	< DL	< DL		< DL	< DL	< DL
Benzo[ghi]perylene	< 0.50	< DL	< DL	< DL		0.69	< DL	< DL
Total PAHs		34	12	23		50	27	35

DL = detection limit of individual compounds.

2002). An anthracene to anthracene plus phenanthrene (Ant/ $\Sigma178$) ratio < 0.10 usually indicates a petroleum source, while a ratio > 0.10 suggests a dominance of combustion. Yunker et al. (2002) also presented other ratios to distinguish these sources, such as fluoranthene to fluoranthene plus pyrene and indeno[1,2,3-cd]pyrene to indeno[1,2,3-cd]pyrene plus benzo[ghi]perylene.

Based on the individual concentration of the PAHs in the sediments studied (Tables III–VIII), only the alkylnaphtalenes to naphthalene (C_1-napht/napht), $\Sigma2$-3/ $\Sigma4$-6 and Ant/$\Sigma178$ ratios were calculated, since the concentrations of the other compounds were very low, as are their concentrations in DFA. There was a predominance of alkylnaphtalenes over naphthalene for most samples and no predominance of pyrene and fluoranthene throughout the years studied, suggesting a direct input of oil or derivatives (Steinhauer & Boehm 1992), such as DFA, throughout Admiralty Bay. In samples where it was not possible to determine the alkylnaphtalenes to naphthalene ratio, there was always a detectable concentration of alkylnaphtalenes against a $<$ D.L. of naphthalene, indicating once again the predominance of alkyl-substituted hydrocarbons (Tables III–VIII).

The $\Sigma2$-3/$\Sigma4$-6 ratio demonstrates that the majority of samples contained mainly volatile PAHs (Table IX), confirming that the DFA oil dominates as the PAH source for the area. In contrast to this evidence of direct oil input in most sediments, the Ant/[$\Sigma178$] ratio was ≥ 0.1 (Table IX), suggesting the presence of combustion-derived PAHs.

In a few cases, heavy hydrocarbons predominated, as registered at #E (1990), #A (1992), and #F (1993 and

2003), as shown in Table IX ($\Sigma2$-3/$\Sigma4$-6 < 1). The heavy PAHs at these sites might be from the combustion of oil at the sewage incinerator or from some other equipment that uses diesel and other, maybe heavier, combustible fuel, as they were located in the vicinity of the Brazilian (#E and #F) and Polish research stations (#A).

The individual distribution of the PAHs in the sediments at #A revealed the presence of a range of compounds in the earlier years (1990–93), in contrast to the predominance of alkyl naphtalenes in later years (Tables III–IX). This could be indicative of change in the source of hydrocarbon (combustion to direct oil input). #E followed a similar pattern, but in 2004, a range of compounds was once again observed (Tables III–IX). In summary, the results show that there is a mixture of different sources of PAHs in the study area, including direct oil inputs and combustion residues. The area near the Brazilian research station is one of the most impacted by anthropogenic hydrocarbons, but as the currents favour the dispersion of pollutants, the concentrations are not particularly high. This observation is corroborated with results from Martins et al. (2004), who reported a decrease in PAH concentrations from the Brazilian station to 400 m offshore.

Conclusions

Hydrocarbon data from several years revealed that the sites near the Brazilian and Polish research stations were more contaminated by these compounds than other locations in Admiralty Bay. The higher concentrations of PAHs in

Table IX. Total concentration of PAHs (ng g^{-1} dry weight), fluoranthene/total PAHs (% Fluor.), pyrene/total PAHs (% pyrene) and $\Sigma2$-3/$\Sigma4$-6, C_1-napht/napht and Ant/(Σ178) ratios calculated for the sediment samples from Admiralty Bay, King George Island 1990–2004.

1990	#A #1	#B #2	#C #3	#D #4	#E #5	#F #6	#G #7
Total PAHs	28	21	13	11	24	30	6.1
% fluor.	16	9	-	-	6	2	-
% pyrene	7	4	-	-	3	-	-
$\Sigma2$-3/$\Sigma4$-6	1.9	5.6	12.5	6.0	0.3	9.8	31.4
C_1-napht/napht	3.3	5.4	2.3	3.4	4.5	3.0	2.1
Ant/(Σ178)	0.2	0.2	-	-	-	0.2	-

1992	#A #1	#B #2	#C #3	#D #4	#E #5	#F #6	#G #7
Total PAHs	16	0.94	6.2	18	8.2	23	0.71
% fluor.	-	-	-	6	19	-	-
% pyrene	-	-	-	12	-	-	-
$\Sigma2$-3/$\Sigma4$-6	0.9	8.4	9.3	4.5	3.1	9.9	8.0
C_1-napht/napht	1.9		0.8	1.9	1.5	2.2	
Ant/(Σ178)	0.8	-	-	-	-	0.4	-

1993	#A #1	#B #2	#C #3	#D #4	#E #5	#F #6	#G #7
Total PAHs	31	3.9	9.3	17	15	14	2.3
% fluor.	4	-	17	7	-	-	-
% pyrene	4	-	-	6	-	-	-
$\Sigma2$-3/$\Sigma4$-6	1.1	57.6	2.0	1.0	2.5	0.6	9.9
C_1-napht/napht	0.7	1.7	1.0	1.4	2.5	-	-
Ant/(Σ178)	0.5	-	0.7	0.5	-	-	1.0

1999	#A	#B	#C	#D	#E	#F	#G
Total PAHs	29	47		29	32	86	
% fluor.	3	5		-	3	6	
% pyrene	-	2		-	-	5	
$\Sigma2$-3/$\Sigma4$-6	9.0	5.9		10.1	30.7	2.1	
C_1-napht/napht	-	-		-	1.5	0.3	
Ant/(Σ178)	-	1.0		0.4	-	-	

2003	#A #1	#B #2	#C #3	#D #4	#E #5	#F #6	#G #7
Total PAHs	16	3.5	7.9		11	234	13
% fluor.	-	-	-		-	16	-
% pyrene	-	-	-		-	10	-
$\Sigma2$-3/$\Sigma4$-6	9.6	-	-			0.5	10.0
C_1-napht/napht	-	0.8	-		-	4.1	-
Ant/(Σ178)	-	-	1.0		-	0.1	-

2004	#A	#B	#C	#D	#E	#F	#G
Total PAHs	34	12	23		50	27	35
% fluor.	-	-	-		-	-	-
% pyrene	-	-	-		-	-	-
$\Sigma2$-3/$\Sigma4$-6	4.9	14.9	19.0		8.7	4.6	8.1
C_1-napht/napht	-	-	-		6.7	-	3.5
Ant/(Σ178)	-	1.0	-		-	0.5	-

seawater sampled in front of Brazilian and Polish research stations were associated with the increased human activities undertaken during the summer. No clear pattern was observed for the first years studied, but a decrease in PAH concentrations was observed for all stations from 1994–95, followed by an increasing trend in the following years through to 1997. The decrease may be related to an improvement in the sewage treatment facilities at the Brazilian station.

The highest concentrations of n-alkanes in sediments were always in the vicinity of the Brazilian Research Station and, in some years, at the Polish Research Station. The odd/even and pristane/phytane ratios associated with n-alkane concentration indicated that the sites located near these research stations were under the influence of human activities, with a greater oil contribution in the earlier years. These results suggest that this influence decreased over the years and then remained constant after 1999.

Total PAHs in sediments remained almost constant over the years studied, but relatively high concentrations of PAHs were observed in sediments from some locations, mainly near the Brazilian station. The results revealed a direct input of oil or derivatives in addition to combustion-derived hydrocarbons in most of the samples analysed, suggesting a mixture of different sources of PAHs.

Even though the sediments sampled nearby the Brazilian research station were the most impacted by anthropogenic hydrocarbons, oceanographic mixing in the bay helps to disperse these compounds, resulting in low concentrations ($< 1.0\ \mu g\ l^{-1}$). Unfortunately, the water-monitoring programme was interrupted in 1997 and it was therefore not possible to determine whether the hydrocarbons in seawater followed the same trend as those in sediments. These results suggest that the monitoring programme should be continued at regular intervals in order to determine the contamination trend in this area and improve hydrocarbon use and management.

Acknowledgements

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