Hydrocarbons in the Antarctic Marine Environment: Monitoring and Background

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HYDROCARBONS IN THE ANTARCTIC MARINE ENVIRONMENT: MONITORING AND BACKGROUND

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The Antarctic marine ecosystem is proposed as an environment in which to monitor global hydrocarbon background levels. Hydrocarbon concentrations are probably uniform throughout the Southern Ocean and it is difficult to resolve low levels of contamination against this background. Indices for identifying anthropogenic hydrocarbons have been found to be ambiguous, but principal component analysis has successfully identified potentially polluted inshore waters. Hydrocarbon contamination in the Antarctic occurs only at a small number of coastal locations and is limited in extent. This paper is a review of the work on hydrocarbons in the Southern Ocean by the British Antarctic Survey in the Bransfield Strait and Scotia Sea regions. Analytical methods are discussed and a monitoring programme is developed.

KEY WORDS: Antarctic environment, hydrocarbons, marine monitoring.

INTRODUCTION

The Antarctic marine ecosystem although essentially in pristine condition, contains a range of hydrocarbons which are largely biogenic, but only occur in low concentrations. There may be low level anthropogenic input from the rest of the world due to oceanic mixing, atmospheric transport and locally from research stations. The low natural levels and the small amount of human activity make the Antarctic suitable as a yardstick against which future global pollution by hydrocarbons can be assessed [1]. Prior to 1985 there had been no systematic studies of hydrocarbons in the Antarctic. Previous work by the British Antarctic Survey (BAS) was a survey of an inshore site at King Edward Cove, South Georgia [2-6] and Signy Island, South Orkney Islands [7,8]. This paper reviews work on hydrocarbons in the Antarctic by BAS, discussing analytical techniques, methods of interpreting data and anthropogenic input to the Antarctic. Studies carried out in the Atlantic sector of the Southern Ocean (see Figure 1) were used to estimate the variation in the natural background and the limits of local contamination. A circumpolar Antarctic programme to define the natural background and monitor changes in the future is proposed.
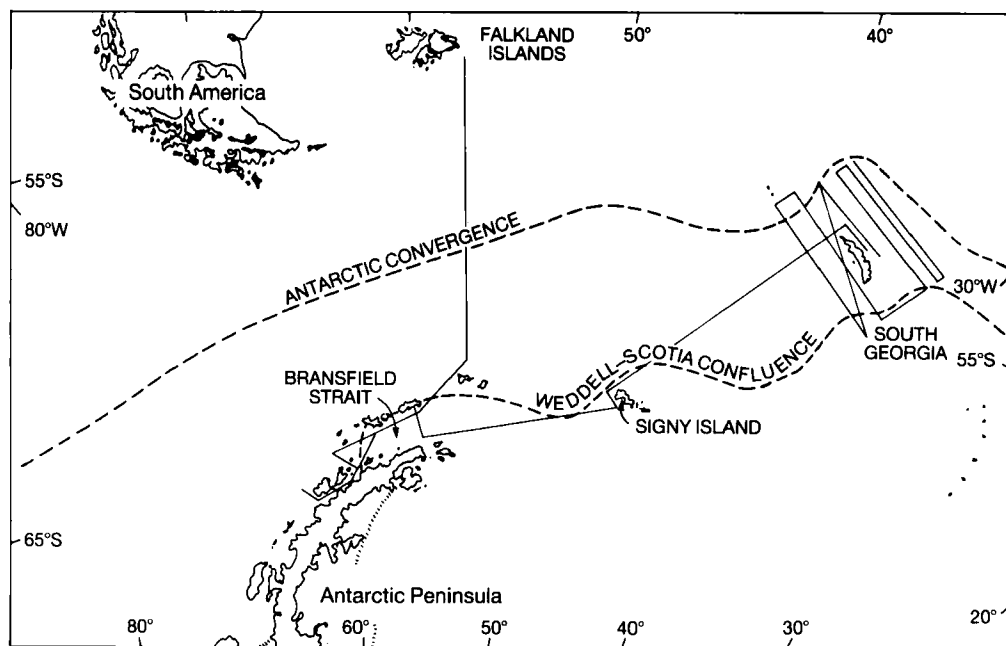
Figure 1. The Atlantic sector of the Southern Ocean showing the major oceanographic features and the cruise track of the 1988 study [15].

ANALYTICAL METHODS

A circumpolar monitoring programme would by necessity involve several groups of workers. In such collaborative studies the analytical technique of each group of workers needs to be comparable and should be tested by the analysis of standard samples from the study area. There are many methods available, in particular for the analysis of seawater [9]. Some of these are appropriate for an Antarctic monitoring programme and are discussed below.

Monitoring hydrocarbons in a pristine region, such as the Antarctic, emphasises the need to avoid contamination during sample collection and processing. The platform from which marine samples are taken is often an ocean going vessel, which is itself a source of a number of hydrocarbon materials and combustion products. It is best to take samples whilst the vessel is under way or immediately it arrives on station. The processing of samples whilst at sea is desirable, but limited space and facilities can be restrictive. Laboratory methods which are used on land might not be appropriate for working on board ship and modification of these procedures may compromise accuracy and precision.

One technique, solid phase extraction (SPE), is an efficient method of isolating hydrocarbons from seawater, convenient for use at sea and preferable to storing large volumes of frozen seawater for later analysis on land. SPE with a reverse phase support such as C_{18} modified silica is less specific than solvents (e.g. hexane) and will extract the total dissolved organic fraction. The highly ionic nature of seawater enhances the extraction efficiency of

Table 1 Comparison of methods and results for n-alkanes and polycyclic aromatic hydrocarbons in surface seawater from the Antarctic, Canada and the Mediterranean.

	Extraction method	Instrumentation	n-alkanes ng l^{-1}	PAH ng l^{-1}
Bransfield Strait Antarctica [14]	SPE—C_{18} silica	GC-FID, HPLC	1100–21800	0–1700
Terra Nova Bay Antarctica [16]	Solvent	GC-MS	18–488	37–580
Ebro Delta, West Mediterranean Coast [21]	XAD-2 resin	GC-MS	1–530	2–180
Western Mediterranean [22]	Solvent	GC-FID	100–5660	–
Saanich Inlet BC, Canada [10]	Chromosorb T resin	GC-MS	6–14	4–10
Baffin Sea NWT, Canada [23]	Solvent	GC-FID	1400–2000	1100–2100

non-polar compounds by reverse phase SPE. This method only requires small volumes of solvent and reduces the loss of more volatile compounds. Typically, the organic fraction of seawater (500 ml) is concentrated on a SPE cartridge and eluted with hexane (1 ml). Larger sample volumes are preferred when analysing for trace constituents. Up to 1200 l h^{-1} of seawater can be sampled using in-situ pumps. Lower sampling rates ($\approx$ 10 l $hour^{-1}$) are more appropriate for the extraction of hydrocarbons with adsorption resins such as XAD-2 (a polystyrene-divinylbenzene copolymer) and Chromosorb T (porous PTFE). N-alkane levels in seawater extracted with in-situ pumps and resin columns are reportedly lower than those using solvent extraction or SPE on C_{18} modified silica (Table 1). The efficiency of XAD-2 resin has been questioned in the past and was evaluated by Yunker, Gomez-Belinchon and coworkers [10–12]. A decrease in n-alkane concentration with increasing sample volume was observed, whereas PAH levels were constant.

A proportion of the hydrocarbons in the seawater will be associated with suspended and sinking particulate matter. In the Antarctic the suspended particulate fraction will be mainly phytoplankton, in particular diatoms. These are usually collected in fine mesh nets or filtered from seawater on 0.7 μm glass fibre filter pads. The hydrocarbons are then extracted using a chloroform and methanol mixture. Sinking material is collected in conical sediment traps suspended at various depths. In situations where the density of particulate matter is low (e.g. at depth) in-situ pump samplers can be used to filter large volumes of seawater to collect sufficient material for analysis.

Some analytical procedures are complicated and not suitable for use at sea, such as those for animal tissue or sediment cores. Animal tissue such as that from Krill have a high lipid content and only a small percentage of the compounds of may be of interest. This requires a complicated extraction procedure involving a time consuming alkaline digest followed by solvent partition and extraction [13]. Hydrocarbons are normally extracted from sediment samples using Soxhlet extractors with solvents such as chloroform and methanol. Tissue and sediment samples can be stored for several months at −60°C without deterioration.

Aliphatic and aromatic hydrocarbon fractions are separated from the final extract by liquid chromatography on silica, before analysis by capillary GC (alkanes and PAH) and HPLC (PAH only). N-alkanes have been analysed routinely by capillary GC with flame ionisation detection (GC-FID) for a number of years. The use of GC-Mass Spectrometry (GC-MS) has increased recently with increasing availability of compact bench-top instruments. A monitoring programme requires standardisation of techniques as problems can arise when comparing

data from workers whom have used different methods. For example, Cripps [14,15] used GC-FID to measure n-alkane concentrations in Antarctic seawater in the $\mu g\ l^{-1}$ range, whereas Desideri [16,17] made the same type of measurement using GC-MS in the $ng\ l^{-1}$ range. Variation in hydrocarbon levels reported from other parts of the world (Table 1), suggests it may be related to analytical technique. However, there is no evidence to suggest that one method is better than the other. As n-alkanes are naturally present in the lipid fraction of all marine biota the variations in the concentrations in seawater could be due to biological processes and may be a reflection of variation in productivity. It is clear that the analytical method requires careful consideration before a monitoring programme is embarked upon.

RESULTS AND DISCUSSION

Data analysis

After the establishment of a database of hydrocarbons levels in the Antarctic, future monitoring may have difficulty in resolving low level contamination as many compounds
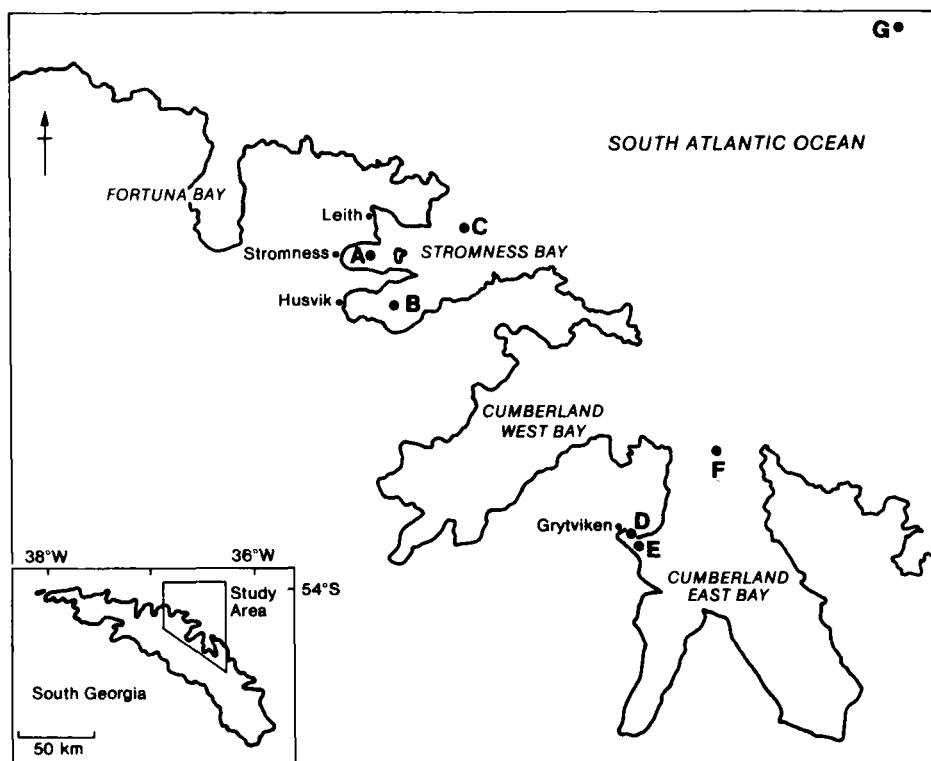

Figure 2. South Georgia showing the location of derelict whaling stations and sample sites, see Table II, (n.b. site G is in open ocean) [18].

Table 2 Total *n*-alkanes and polycyclic aromatic hydrocarbons (PAH), and alkane indices for seawater and tar on the shore at South Georgia March 1988 [18](see Figure 2)

Sample	Odd-even ratio	Pristane-phytane ratio	n-alkanes ($\mu g \ l^{-1}$)	PAH ($\mu g \ l^{-1}$)
A. Stromness	0.8	0.9	7.5	1.2
B. Husvik	0.9	1.3	2.4	0.4
C. Stromness Bay	0.8	0.6	3.2	0.4
D. Grytviken	0.9	1.1	3.9	0.1
E. King Edward Point	1.0	1.4	10.1	0.4
F. Cumberland Bay	1.0	1.4	10.0	0.7
G. Open ocean	1.0	0.5	2.1	0.2
Stromness tar	0.8	0.7	5.7×10^7	4.0×10^5
Weathered tar	1.0	0.9	2.4×10^6	1.8×10^4

also have biogenic origins. Some methods of distinguishing biogenic from anthropogenic hydrocarbons can be misleading. This problem was addressed in a short study on hydrocarbons in the seawater at South Georgia in the vicinity of derelict whaling stations [18] (Figure 2). Two established indices were tested—the pristane-to-phytane ratio and the odd-to-even carbon number ratio for *n*-alkanes—and were found to contradict each other at several sites (Table 2). A value of less than one for both ratios has been taken to indicate anthropogenic origin. The odd-to-even ratio showed little variation (0.8–1.0) and the pristane-phytane ratio ranged from 0.4 to 1.4, with the lowest value for the open ocean sample. Subsequent work showed that these ratios were typical of Antarctic open ocean water. The high value found at one inshore site may have been due to input of pristane from the extensive kelp beds in the cove. The concentration gradient for PAH (which are assumed to be wholly anthropogenic) did not correspond with that of the n-alkanes.

Biogenic compounds were probably contributing to the total *n*-alkane levels. It was suggested that recognition of anthropogenic input was based on quantification of all compounds against a database of background levels. There was evidence that the pattern of compounds in a sample was a more reliable indicator (Figure 3). The pattern of *n*-alkanes in the seawater for Cumberland Bay, South Georgia, was similar to that found throughout the Southern Ocean. Near derelict whaling stations the pattern appeared to indicate residual petroleum products. The *n*-alkane pattern of likely pollution in the area was given by a sample of tar found on a beach. Underlying patterns may be difficult to detect but with the aid of methods such as principal component analysis (PCA) low level contamination may be detected.

Representative case studies

A range of studies have been carried out by the British Antarctic Survey which provide case studies illustrating the various requirements and problems associated with a monitoring programme. Two major surveys have been carried out, one centred on the Bransfield Strait in 1985 and the other covering the whole of the Atlantic sector of the Southern Ocean in
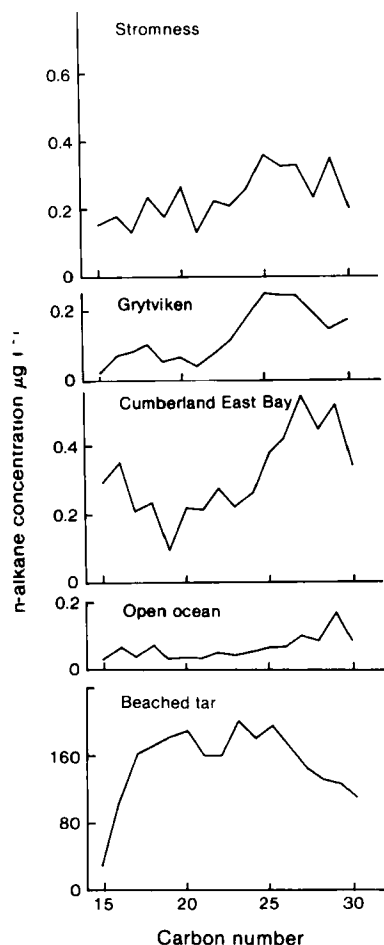
Figure 3. *N*-alkane patterns in seawater from sites at South Georgia [18].

1988 (Figure 1) [14,15]. The aim of this work was to survey the hydrocarbons in the Antarctic marine environment and assess the variation in levels within the region. At a smaller scale, the impact of a research station at Signy Island and derelict whaling stations at South Georgia on the local marine environment was estimated by comparing inshore and oceanic data.

Bransfield Strait   The Bransfield Strait is an area of complex oceanography where water from the Weddell Sea mixes with water from the Bellingshausen Sea and the South East Pacific Basin. It is essentially in pristine condition but there are a number of research stations, in particular on King George Island, which contribute low levels of hydrocarbons to the marine environment. The hydrocarbons in the seawater and marine pelagic organisms from the Bransfield Strait area were generally biogenic in origin and there was no evidence of

Table 3 Hydrocarbons in the Antarctic marine ecosystem compared to typical global values [1]

Sample	Antarctic alkanes	Global alkanes	Antarctic PAH	Global PAH
Seawater (μg l^{-1})	1–22.1 [14]	1–6 [22]	0–1.7 [14]	0–6.2 [24]
Phytoplankton (μg l^{-1})	0.02–0.09 [14]	0.3–0.4 [22]	0.03 [14]	10 [25]
Mixed zooplankton (μg kg^{-1})	370–3800 [14]	100–4400 [26]	70–640 [14]	–
Fish (μg kg^{-1})	1900 [14]	10–12000 [26]	3.2 [14]	4–43 [27]

anthropogenic input to the pelagic environment. Hydrocarbon constituents of man made materials were present throughout the region but not in the patterns characteristic of anthropogenic origin. This work did not corroborate previous reports of an even carbon number predominance for n-alkanes in Antarctic marine organisms, no particular predominance was observed. N-alkanes levels in seawater were highest in a zone to the west of the Bransfield Strait which coincided with high phytoplankton density. PAH were present in all organisms analysed but were only detectable in 44% of the seawater samples. The highest PAH levels in seawater did not coincide with those for n-alkanes. The origin of the PAH in Antarctic organisms was not clear, the levels were higher than predicted if the main mechanism of accumulation was feeding. The concentrations of n-alkanes and PAH were lower than for the rest of the world and indicate that there was no pollution in the area (Table 3). This prompts the question, were the levels observed those of the natural background? The following work over a wider area of the Southern Ocean estimates the limit of variation in the background.

Southern Ocean The seawater from ten water masses (identified from temperature and salinity data) in the Southern Ocean was analysed for n-alkane and PAH content in the austral summer 1988. There was no systematic variation in the levels of hydrocarbons between the water masses and concentrations were similar to those for the Bransfield Strait (see above). The highest levels of n-alkanes were in water originating from the Bellingshausen Sea which corresponded with earlier work. The frequency distributions of n-alkanes and PAH concentrations for the complete study area were markedly skewed. The range of concentrations were 0.2–33.1 μg l^{-1} (median 5.3 μg l^{-1}) for n-alkanes, and 0–884 ng l^{-1} (median 21 ng l^{-1}) for PAH. The highly skewed data set for PAH levels had a standard deviation which was greater than the median and mean values. Hence the median and upper quartile values were used in preference to the mean and standard deviation. The upper quartiles of the n-alkane and PAH data sets were proposed as the practical limits of the natural variation of hydrocarbons in Southern Ocean seawater at 8.2 μg l^{-1} for total n-alkanes and 76 ng l^{-1} for total PAH. The n-alkane pattern for seawater from the Gerlache Strait was different from the rest of the Southern Ocean and was not included in the dataset. The Gerlache Strait, an inshore area influenced by glacier melt, also had the lowest levels of hydrocarbons in the region. Principal component analysis (PCA) when applied to the complete PAH dataset, identified potentially contaminated inshore sites at South Georgia and Signy Island, a pristine inshore site at King George Island and seawater from a field of icebergs in the Scotia Sea. PCA on the n-alkane data did not separate particular sites, only sorting the samples by concentration.
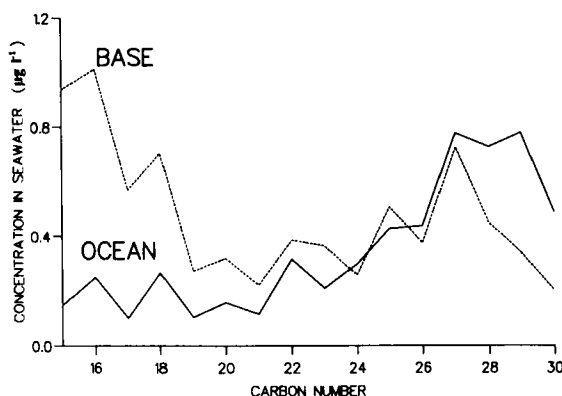
Figure 4. Patterns of n-alkanes in seawater nearest to the research station at Signy Island and the open ocean [19].

Signy Island   The limits of variation proposed above were used for comparison when investigating the impact of an Antarctic research station on the local marine environment. The levels and patterns of hydrocarbons at Signy Island indicate that contamination was confined to the immediate vicinity of the station [19]. In the seawater, total n-alkane concentrations decreased from 7.6 to 2.6 µg l^{-1} within 500 m of the station, all the samples were below the limit of variation for the open ocean (see above). The n-alkanes in the seawater nearest the station suggested some input from < 20 carbon n-alkanes overlying the pattern for oceanic waters (Figure 4). PAH concentrations showed no trend, varying between 110 and 216 ng l^{-1} in the cove close to the research station, but the level in adjacent oceanic water was lower (50 ng l^{-1}). Analysis of different depths of the sediment core revealed a continuous input of hydrocarbons close to the station in recent years and a record of a pollution incident approximately 30 years ago. Alkane and PAH levels in the surface sediment decreased with distance to what were probably background concentrations within 250 m of the station (Figure 5).

South Georgia   The inshore sites of South Georgia provide a comparison to that at Signy Island. Several of the coves and bays at South Georgia have a history of pollution from the whaling industry and associated activities. Eight years after whaling had ceased the hydrocarbons in the biota of King Edward Cove were reported to have recovered from contamination [4]. However there remained elevated concentrations of hydrocarbons in the sediment close to the Grytviken whaling station situated in the cove. Later work in 1980 found hydrocarbon concentrations in benthic invertebrates continued to be higher at King Edward Cove than at a pristine site near Signy Island [7].

Hydrocarbons in the seawater and sediment from South Georgia have been studied since 1973 (Table 4), and the levels of n-alkanes and PAH in seawater have been similar to those at Signy Island. Concentrations in the sediment of King Edward Cove reduced sharply within a few hundred metres of the derelict whaling station, but were higher overall than at Signy
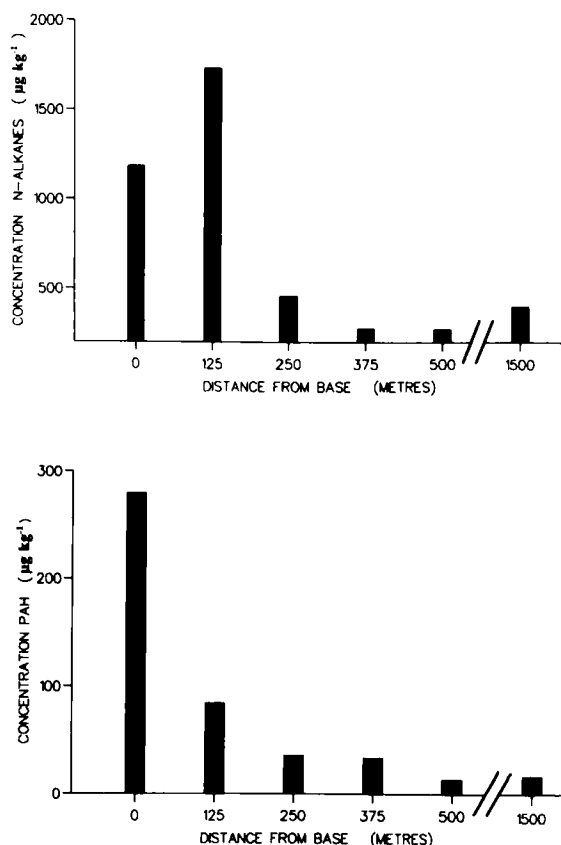
Figure 5. Levels of n-alkanes (6A) and PAH (6B) in the surface sediment plotted against distance from the research station at Signy Island [19].

Island [2]. N-alkane concentration in the top sediment was 1000 μg kg^{-1} at a site 1200 m from the station compared to 400 μg kg^{-1} at 1500m from the Signy Island research station. The data show that concentrations at South Georgia inshore sites have not changed significantly over the last 20 years, but remain slightly elevated compared to pristine Antarctic sites. This is probably due to gradual leakage of oil from the derelict whaling stations, shipping and activities associated with a garrison at King Edward Point [20]. Shoreline contamination can be locally severe and result in the oiling of King Penguins and Elephant Seals. There have been no reports of oiled birds or seals from Signy Island.

MONITORING PROGRAMME

In summary, hydrocarbon pollution in the Antarctic is localised and restricted to a small number of sites. The concentrations in seawater are probably uniform throughout the

Table 4　Total n-alkanes and total polycyclic aromatic hydrocarbons (PAH) in the seawater and sediment from South Georgia and Signy Island, South Orkney Islands.

	1973[5]	South Georgia 1988[18]	1990[20]	1991[20]	Signy Island 1988[19]
Seawater					
Total alkanes (μg l^{-1})	5.8	3.2–10.1	2.0–12.9	7.7–9.0	2.6–7.6
Total PAH (μg l^{-1})	–	0.1–1.2	0–0.1	0–0.1	0.1–0.2
Sediment					
Total alkanes (mg kg^{-1})*	2.3–17.8	5.2–85.1	–	0.3–0.4	0.4–2.1
Total PAH (μg kg^{-1})*	97	10–126	–	8–42	14–280

*—Dry mass

Southern Ocean. This suggests the Antarctic may be used as an indicator of changes to global marine hydrocarbon background levels. A circumpolar monitoring programme is proposed.

From the evidence of the BAS work a small number of sample stations will be sufficient. It is proposed that seawater, suspended and sinking particulates and zooplankton should be sampled annually from six sites distributed in the Southern Ocean. These would be located for convenience close to routes which are traversed regularly by Antarctic research and supply vessels. One site should be remote from any regular shipping and located for example in the Bellingshausen Sea. This will give increased confidence to the resulting data set. This brief sampling regime will account for all the hydrocarbons in the marine ecosystem and form a database of Antarctic background concentrations. It will be highly important that each contributor to the programme uses the same extraction procedures and comparable instrumentation. Intercomparisons should be carried out with a set of standard samples from the Antarctic.

Global input will be dominant in the open ocean, but research stations and other sites will have the major local impact on inshore marine environments. Marine environments in the vicinity of research stations should also be monitored deviations from background levels. Sampling from inshore sites should be more frequent than for the open ocean, as local conditions may show more variation, for example the extent of ice cover. The evaluation of background concentrations inshore will entail sampling at a site distant from the station. It is important to establish these levels in order to estimate the effect of any spills that may occur. However, priority should be given to the analysis at offshore sites so that a data base can be accumulated which is effective as a global indicator.

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