

Problems in the identification of anthropogenic hydrocarbons against natural background levels in the Antarctic

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Abstract: Hydrocarbons in the environment occur as complex mixtures. The detection of low-level anthropogenic contamination can be difficult as many of the compounds can also be found in biogenic materials. Results obtained in the Antarctic show that accepted methods of distinguishing biogenic from contaminating hydrocarbons are inconsistent. The samples taken from South Georgia in the vicinity of derelict whaling stations had odd-to-even carbon number ratios in the range 0.8–1.0. An offshore site had the highest levels for phytane and the lowest for pristane. The pristane-to-phytane ratio varied between 0.4 and 1.4 and contradicted the interpretation of the odd-to-even ratio at several sites. A value of less than 1.0 for these ratios has been taken to indicate anthropogenic origin. A number of polycyclic aromatic hydrocarbons were detected at all the sites, but the concentration gradient did not correspond with that of the n-alkanes. It is therefore recommended that recognition of anthropogenic input is based on quantification of all compounds against a well-defined baseline. The source of the pollution can then be estimated from the distribution patterns of the hydrocarbons.

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Introduction

The Antarctic as a whole is considered to be uncontaminated by hydrocarbons (and by most other pollutants), although increasing activity by man is likely to alter this situation. For example, the recent oil spill following the *Bahia Paraiso* shipwreck off Anvers Island. It is important to identify any introduction of pollutants swiftly so that remedial action may be implemented. Polluting materials such as diesel and lubricating oils have characteristic n-alkane distributions which are distinct from those of biogenic origin. However the detection of low-level hydrocarbon pollution can be difficult as many compounds are also present as part of the natural background. The early establishment of a reliable baseline is therefore essential. This can be achieved by examining a small number of essentially pristine sites for which the hydrocarbon baseline is the same as the natural background. In a global context, the Antarctic is the last region in the world where this is possible and therefore has the potential to provide a baseline for global pollution monitoring. This paper discusses established methods of identifying hydrocarbon pollution, applies the methods to a test case and proposes that a regular monitoring programme should be undertaken. The study has been restricted to the marine environment for brevity, although it is obvious that pollution monitoring must also encompass terrestrial environments.

Existing techniques for assessing hydrocarbon pollution

In order to assess possible anthropogenic input of hydrocarbons, various techniques have been devised to identify pollution against the background of biogenic compounds. The techniques focus on individual compounds, or indices calculated for homologous series of compounds, which supposedly distinguish between the composition of the hydrocarbon fractions of anthropogenic and biogenic materials. Three approaches are discussed below.

Odd-to-even carbon number ratio for n-alkanes

Marine and terrestrial organisms synthesize a range of n-alkanes which are reported to be dominated by compounds with odd numbers of carbon atoms (Schenck & de Leeuw 1982). A predominance of odd numbered compounds has thus been taken as an indication of biogenic origin, whereas petroleum products show no bias towards either odd or even numbered compounds. In evaluating this approach it has not always been possible to make valid comparisons between studies as the ranges of n-alkanes are not standardized and frequently not even quoted. This is critical because the odd-to-even ratio has been found to vary depending on the range of alkanes investigated (Table I).

A number of studies on Antarctic marine biota have shown

Table I. Odd-to-even carbon number ratios and CPI for n-alkanes in Antarctic sea-water and biological material (Bransfield Strait 1985), expressed for different ranges of carbon numbers and for two methods of calculating CPI.

Sample	Range of n-alkanes (carbon number)			CPI ¹	CPI ²
	16-25	16-35	26-35		
Sea-water (10 m)	0.65	0.78	0.93	1.0	1.0
Phytoplankton (mostly diatoms)	1.25	1.09	1.02	1.0	1.1
Crustacea, <i>Euphausia superba</i>	1.06	0.94	0.97	1.0	1.1
<i>Notocrangon antarctica</i>	0.93	0.91	0.89	0.9	1.0
Fish, <i>Electrona antarctica</i>	2.62	1.60	1.14	1.5	0.9

¹ Cooper & Bray (1963)

² Farrington & Tripp (1977)

equivocal values for these indices. Reinhardt & Van Vleet (1986) and Nachman (1985) found that even numbered n-alkanes predominated in Antarctic marine organisms from the Croker Passage and the Ross Sea respectively, whilst Platt & Mackie (1980) reported a predominance of odd numbered n-alkanes in the equivalent species from South Georgia. Investigations carried out on a number of pelagic species from the Bransfield Strait showed no particular trend in the odd to even ratio, with values in the range 0.7-1.4 (Table I). Thus in work already carried out in the Antarctic the odd-to-even ratio has been demonstrated as unreliable as an indicator of hydrocarbon origin.

The carbon preference index (CPI) is a more complex method of calculating the predominating n-alkanes in a sample. However the method of evaluation of the CPI also varies. Two examples of the equations used are given below.

$$CPI = \frac{1}{2} \left[\frac{\sum_{n=21}^{n=31} HC_{\text{odd}}}{\sum_{n=22}^{n=32} HC_{\text{even}}} + \frac{\sum_{n=21}^{n=31} HC_{\text{odd}}}{\sum_{n=20}^{n=30} HC_{\text{even}}} \right] : (1) \text{ Cooper \& Bray (1963)}$$

$$CPI = \frac{2(nC_{27} + nC_{29})}{nC_{26} + 2nC_{28} + nC_{30}} : (2) \text{ Farrington \& Tripp (1977)}$$

Values for the CPI were calculated with the formulae above on data from the Antarctic. The variability in the results is illustrated in Table I. A reason put forward for using a CPI is to eliminate bias caused by high concentrations of very short or very long chain compounds (Reinhardt & Van Vleet 1986). However this ignores a number of major components of the aliphatic hydrocarbon fraction, in particular those alkanes with carbon numbers less than 20.

Pristane and phytane

Pristane and phytane are branch chain alkanes (isoprenoids) which are present in the marine environment as the result of natural processes. Diagenic pathways for the transformation of the phytol moiety of chlorophyll *a* to pristane and phytane have been proposed by Didyk *et al.* (1978). The formation of pristane is favoured under oxidative conditions while phytane is produced by reductive paths. Thus pristane is normally found at higher concentrations than phytane in the marine environment (Table II). Values greater than unity for the pristane-to-phytane ratio are a reliable indicator of the absence of petroleum. However, the converse does not apply and values of less than one are not reliable as an indicator of the presence of petroleum (Humphrey *et al.* 1987). The relationships between pristane and n-C₁₇, and phytane and n-C₁₈ have also been used as indicators. Pristane dominates over n-C₁₇ in marine organisms and phytane will predominate over n-C₁₈ in degraded fuel oils. In Antarctic sea-water from the Bransfield Strait pristane and phytane occur at approximately equal concentrations (0.2 µg l⁻¹), consistently less than the n-C₁₇ and n-C₁₈ alkanes. Thus the indices using pristane and phytane also appear to be unreliable indicators of pollution.

Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAH) are a complex mixture of compounds many of which are proven carcinogens (Neff 1979). Generally the presence of PAH is considered to be an indication of anthropogenic input, since these compounds are formed during the pyrolysis of organic materials, for example the combustion of fuel oil. However not all pollutants manifest themselves by a PAH 'signal'.

Table II. Pristane and phytane in Antarctic sea-water and biota (Bransfield Strait 1985).

Sample	Pristane (µg kg ⁻¹)	Phytane (µg kg ⁻¹)	Pristane-to-phytane ratio
Sea-water (µg l ⁻¹)	0.18	0.17	1.1
Phytoplankton (mostly diatoms, µg l ⁻¹ sea-water)	0.03	0.02	1.7
Crustacea, <i>Euphausia superba</i> (µg kg ⁻¹)*	390	23	17
<i>Notocrangon antarctica</i> (µg kg ⁻¹)*	106	18	6
Fish, <i>Electrona antarctica</i> (µg kg ⁻¹)*	187600	60	3127

* wet weight

The aromatic fraction of crude and fuel oils is predominately naphthyl (2-ring) compounds and generally deficient in 3-, 4- or 5-ring compounds. These larger molecules are more likely to occur as combustion products, hence pollution by petroleum may have high levels of alkanes but only low levels of those PAH with three or more ring structures. The PAH in the Antarctic are probably biogenic, originating from micro-organisms. The highest concentrations have been found in fish and zooplankton (Cripps, in press *a*). The range of PAH found in sea-water, phytoplankton, Antarctic krill (*Euphausia superba*) and a bituminous tar are compared in the discussion.

Case study

A case study was undertaken to test the validity of the methods discussed above as indicators of anthropogenic hydrocarbons. The samples were taken from a small area (Fig. 1) over a period of four days to compare sites under threat from pollution and those not immediately at risk.

Materials and methods

Samples of sea-water from seven sites at or near South Georgia (Fig. 1) were analysed for alkanes and polycyclic aromatic hydrocarbons (PAH). Sites A, B, D and G were located in the coves adjacent to derelict whaling stations (Stromness, Grytviken and Husvik). All the stations had ceased working by 1965, but they still retain quantities of fuel oil, lubricants and whale oil which are leaking into the environment as the oil tanks decay. Site B was also close to

an operational military base where petroleum products have been stored. The whaling station at Stromness (A) was found to be leaking heavy tar directly into the cove. The tar sample (K) was taken from a stretch of contaminated shoreline nearby. Sites E and C were at the entrances to Cumberland East Bay and Stromness Bay, where mixing with oceanic water might be expected to reduce hydrocarbon levels. Site H, located in the open ocean, was included as an uncontaminated comparison. The sample of the particulate fraction (F) was taken at site B. The sample of *Euphausia superba* (J) was taken by trawl net to the north of South Georgia (54°20'S 35°45'W).

The analytical procedure has been described in detail by Cripps (in press *b*). All samples except that for site D were taken from a clean water inlet located on the hull of the research vessel, approximately amidships and three metres below the surface, whilst underway. The water from site D was sampled by hand from the shore. All sea-water samples (500 ml) were filtered under vacuum through 0.45 µm cellulose nitrate membranes and extracted immediately with C₁₈-modified silica cartridges. The resulting concentrate was eluted from the cartridge with hexane and separated into alkyl and aromatic hydrocarbon fractions by liquid chromatography. The n-alkanes were quantified by capillary gas chromatography and the PAH by high performance liquid chromatography. The particulate fraction (F) was collected on an ashed glass fibre filter pad (nominal retention 0.7 µm) and extracted with acetone. The *Euphausia superba* (J) were digested in methanolic potassium hydroxide; the resulting liquor being extracted with hexane. The tar sample (K) was dissolved in hexane. Any insoluble material was allowed to settle out before further analysis. The alkyl and aromatic hydrocarbon fractions of *Euphausia superba*, the particulate fraction and the tar were then isolated and analysed as for the water samples.

Results and discussion

The n-alkanes were quantified over the range C₁₅ to C₃₀ (Fig. 2 and Table III). The values for n-alkanes found at sites A, B and E were higher than normal for the Antarctic. The remaining samples had levels which were comparable to previous Antarctic studies (Cripps, in press *a* and literature cited above). The lowest values were at Husvik (G) and the open ocean sample (H). Fig. 2 illustrates the variation in the distribution patterns of n-alkanes found in the study area. The prevalent compounds were in the range C₂₅–C₃₀ for all the samples except for C which was dominated by the C₁₈, C₁₉ and C₂₀ compounds (possibly of biogenic origin). Sample A had a comparatively even distribution with a maximum at C₂₅, sample D also had maximum at C₂₅ but with a skewed distribution towards the alkanes above C₂₂. Sample B had a distribution pattern strongly dominated by the C₂₃–C₃₀ alkanes, as did sample B and the particulate sample taken off King

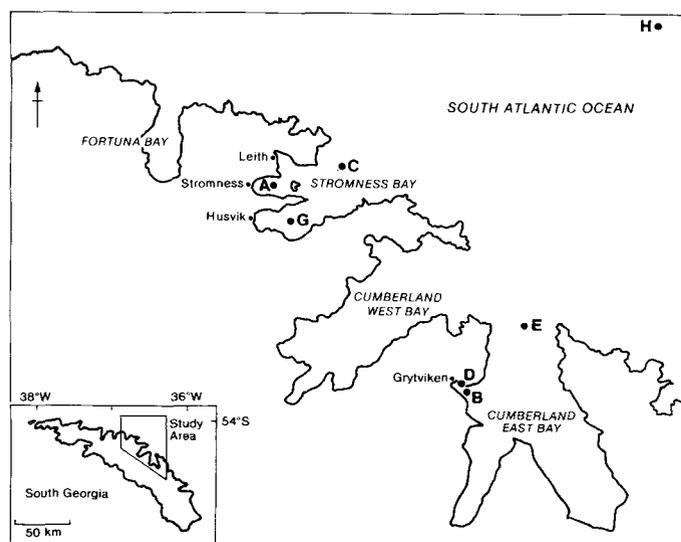


Fig. 1. Sample sites in the vicinity of the derelict whaling stations at Grytviken and Stromness Bay. (Sample F was taken from site B.)

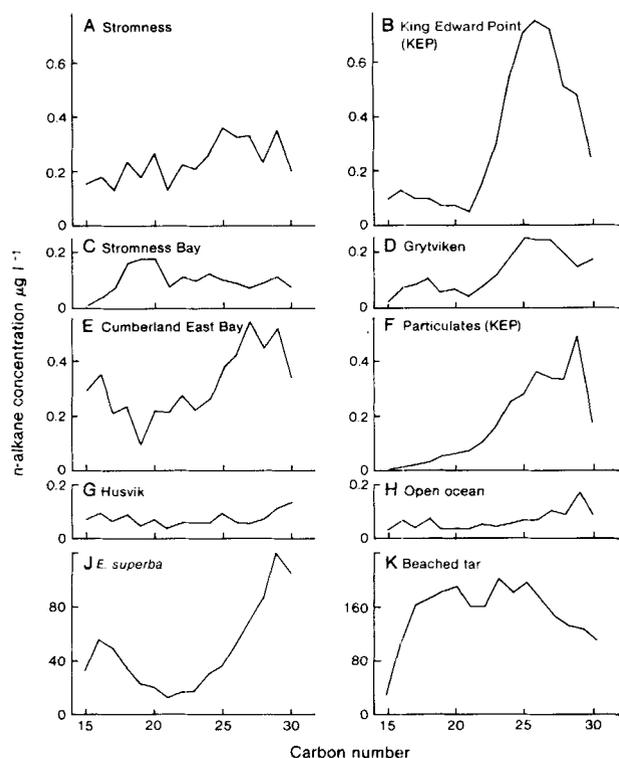


Fig. 2. Distribution of n-alkanes in sea-water and particulates ($\mu\text{g l}^{-1}$), *Euphausia superba* ($\mu\text{g kg}^{-1}$) and tar washed ashore (mg kg^{-1}), South Georgia, March 1988. (The area under the traces is not significant, the points are connected so as to highlight the distribution patterns.)

Edward Point, KEP (F). This is typical of contamination by weathered or degraded fuel oil (Boehm *et al.* 1987). Two sources of contamination were observed in this study — tar at Stromness and fuel oil at Grytviken. This is why the n-alkane distribution patterns were different. Sample E had a bimodal distribution with maxima at C_{16} and C_{27} . This pattern has been found previously in Antarctic sea-water (Cripps, in press *a*). Such a pattern may have a biological origin, for example compare the distribution with that for krill, *Euphausia superba* (Fig. 2J). The considerable freshwater

input from rivers at Stromness (A) and Husvik (G) may influence the sea-water composition in the coves. Sample H, with a maximum value at C_{29} , was comparable to that found by previous workers (Platt & Mackie 1980) at South Georgia. Only samples, B, D and F taken in the same cove, had distribution patterns which were similar. The sample from the open ocean (H) can be considered to be close to the baseline level. Sample G, taken close to a whaling station where a small quantity of tar was present but not in contact with the sea, had a low n-alkane concentration, comparable to the open ocean sample H but was not suitable for establishing a baseline due to the proximity of a derelict whaling station. A similar pristine site in the area, for example Fortuna Bay 15 km to the west of Stromness Bay would be more appropriate (Fig. 1).

The variation in the odd-to-even carbon number ratio between sites was small. Values ranged from 0.8 to 1.0 suggesting a tendency to anthropogenic input. For all the samples the odd-to-even ratio was less than 1.0 for the range C_{15} – C_{22} and greater than one for the range C_{23} – C_{30} . From a study in the Bransfield Strait area it was found that Antarctic sea-water had a mean value of 0.8 for the odd-to-even ratio. The pristane and phytane levels were approximately the same for all the samples (Table III). The pristane-to-phytane ratio was less than 1.0 for samples A, C and H, indicating anthropogenic input. Contamination by petroleum products was observed at Stromness (A) but samples C and H were not expected to have higher phytane values.

The analysis of PAH revealed the presence of phenanthrene, anthracene, fluoranthene and pyrene in all the samples. Phenanthrene is generally the predominant PAH in both Antarctic and global sea-water samples. In some samples naphthalene, benz(a)anthracene, chrysene, benz(b)fluoranthene and benz(a)pyrene were also detected (Table IV). There was no discernible pattern in the distribution of PAH. The highest values were from the polluted Stromness Cove (A), but sample B which had high alkane levels, had similar concentrations of PAH to samples D and G. Sample E from Cumberland East Bay had the second highest values for PAH and also had high alkane levels, the open ocean sample (H) had the lowest values. The PAH fraction of the beached

Table III. Alkanes in sea-water and biota, South Georgia, March 1988.

	Samples ¹									
	A	B	C	D	E	G	H	F	J	K
Total alkalines ($\mu\text{g l}^{-1}$)	7.46	10.11	3.16	3.91	9.98	2.36	2.06	1.04	980	2409
Odd/even for n-alkanes*	0.9	1.0	0.8	0.9	1.0	0.90	1.0	1.1	0.9	0.9
Pristane ($\mu\text{g l}^{-1}$)	0.40	0.27	0.21	0.20	0.72	0.24	0.05	0.01	390	139
Phytane ($\mu\text{g l}^{-1}$)	0.46	0.20	0.37	0.19	0.50	0.18	0.11	0.01	23	147
Pristane/phytane	0.87	1.35	0.57	1.05	1.44	1.33	0.45	0.40	16.6	0.9

* Evaluated for C_{15} to C_{30} n-alkanes.

¹ A–E, G & H, sea-water samples; F, Particulate sample from the same site as B, levels expressed as $\mu\text{g l}^{-1}$ sea-water; J, *Euphausia superba* ($\mu\text{g kg}^{-1}$); K, Tar washed ashore at Stromness (mg kg^{-1})

Table IV. Polycyclic aromatic hydrocarbons (PAH) in sea-water and biota, South Georgia, March 1988.

Compound ($\mu\text{g kg}^{-1}$)	Samples ¹									
	A	B	C	D	E	G	H	F	J	K
Napthalene	—	0.03	—	—	—	—	0.01	0.02	—	—
Phenanthrene	0.13	0.06	0.19	0.03	0.18	0.07	0.04	0.02	—	14.3
Anthracene	0.06	0.11	0.19	0.03	0.16	0.10	Tr	Tr	—	Tr
Fluoranthene	0.22	0.05	Tr	0.01	0.14	0.04	Tr	Tr	3.57	3.6
Pyrene	0.69	0.08	Tr	0.02	0.15	0.16	—	Tr	1.45	—
Benz(a)anthracene	—	Tr	Tr	0.01	—	Tr	0.09	0.01	0.09	—
Chrysene	0.09	0.02	Tr	Tr	0.03	Tr	0.01	—	0.22	—
Benz(b)fluoranthene	—	Tr	Tr	0.02	Tr	—	Tr	—	0.20	—
Benz(a)pyrene	—	—	—	—	Tr	—	Tr	—	0.22	Tr
Total PAH (sum of the above)	1.19	0.35	0.38	0.12	0.66	0.37	0.15	0.05	5.75	17.9

— not detected

Tr Trace amount detected, less than $0.01 \mu\text{g l}^{-1}$ ¹ As for Table III

tar (K) was predominantly phenanthrene — other components may have been lost by microbial degradation or atmospheric oxidation. In comparison *Euphausia superba* (J) had only 4- and 5-ring PAH.

Assessment of methods of identifying anthropogenic hydrocarbons

The ambiguity of the methods of identifying anthropogenic hydrocarbons was exemplified by these results. The odd-to-even ratio indicated polluting hydrocarbons for all the samples. At four sites (B, D, E, and G), in *Euphausia superba* (J) and the tar sample (K) the pristane-to-phytane ratio contradicted the odd-to-even ratio (Table III). The concentration gradient of PAH values did not correspond with that for the n-alkanes. Table V summarizes the indications afforded by each of the methods for all the samples analysed.

Table V. Summary of the indication of anthropogenic and biogenic hydrocarbons by the methods discussed in the text.

— biogenic, + anthropogenic, o no indication

Method	Samples ¹									
	A	B	C	D	E	G	H	F	J	K
Pristane-to-phytane ratio	+	—	+	—	—	+	+	—	—	—
Odd-to-even ratio for n-alkanes	+	o	+	+	o	+	o	—	+	+
CPI (1)	—	o	+	o	—	o	—	—	—	o
CPI (2)	+	—	o	—	+	—	—	—	o	—
Total PAH*	+	—	o	—	+	—	—	—	N/A	N/A

* For PAH, levels are defined as follows:

— less than the mean level in sea-water, South Georgia zone

January to March 1988 ($0.52 \mu\text{g l}^{-1}$)

o equal to the mean value

+ greater than the mean value

N/A not applicable

¹ As for Table III

If long term monitoring of hydrocarbons in the Antarctic is undertaken, it is suggested that a database of the distribution patterns of the natural background is constructed for each monitoring site. Subsequent analyses can be compared to the stored values. Any change in the patterns and levels of hydrocarbons can be matched with a database of the distributions of potential contaminants and likely biogenic sources. The origin of any increase in hydrocarbon levels can then be suggested.

Conclusions

The results in this study demonstrate that the ratios of odd-to-even carbon numbers and pristane-to-phytane are unreliable as indicators of contamination by alkyl hydrocarbons. The analysis of polycyclic aromatic hydrocarbons (PAH) is not a straightforward method of detecting contamination, as the compounds found in sea-water and sediment may have been derived from marine biota. Hydrocarbon pollution may only have a small proportion of PAH as these are more often associated with the combustion products of petroleum and other organic material, rather than the raw material itself. Although there is greater concern over PAH the analysis for alkanes should not become redundant. The interpretation of the distribution patterns of n-alkanes is the most accurate method for indentifying the origins of hydrocarbons.

The variation in n-alkane distribution patterns observed underlined the fact that baselines are not universally valid. Global monitoring of hydrocarbons will therefore require the establishment of a number of baselines corresponding to different environments. For example, the properties which can influence the chemistry of hydrocarbons will not be the same in a fjord and the open ocean (e.g. particulate load, salinity and temperature). The variation in the patterns and indices illustrated in this work highlight the need for a strict sampling regime in any monitoring programme. Working

from a database of baselines and distribution patterns, both local and global variations can be kept under scrutiny.

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