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Review
Hydrocarbons in the Antarctic marine environment

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Abstract: The Antarctic marine ecosystem contains low concentrations of a range of hydrocarbons, overwhelmingly biogenic in origin. The low natural levels of hydrocarbons and the small amount of local human activity make the Antarctic marine ecosystem suitable as a yardstick against which future global pollution by hydrocarbons can be assessed. At present, contamination is very low and difficult to resolve against the background. Local pollution is restricted to a very few events. A systematic programme with a clear definition of the natural background is proposed to monitor both global and local pollution.

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Introduction

During the latter part of this century, concern over man-made pollution of the environment has shifted from a local to a global perspective. It has become increasingly apparent that petroleum and petroleum products are serious contaminants in most of the World Ocean and have entered the marine food chain both in coastal and in open ocean waters (Goldberg 1972, Waldichuk 1977). Increasing interest in relatively unspoilt areas of the world has arisen from concern over their possible contamination and from a perception of their importance as areas where recent global changes can be studied against a supposedly clean background. Antarctica is understandably a prime focus for such attention. Distant from most major sources of pollution, it has a very small human population and no significant industrialisation. This suggests that it would make an ideal 'barometer' for large-scale change (Weller *et al.* 1987, Gregory 1990).

The popular image of the Antarctic continent, and its surrounding seas, as being unspoilt is somewhat misleading. Initial exploration of the continent was prompted as much by commercial motives as by the quest for knowledge. The living resources of the marine ecosystem have been the target for exploitation in various episodes extending back over two centuries (Everson 1987). Present human activity appears more benign - scientific stations, which are restricted mostly to ice-free coastal areas and nearby islands, are the only permanent habitation. Ships which supply most of these stations, together with substantial fishing fleets and a few tourist vessels, are probably the major marine pollution hazard. The shipwreck of the *Bahia Paraiso* near the U.S.A. Palmer research station, Anvers Island, in January 1989 illustrated the potential risk.

There has been lively debate over both the feasibility of exploitation of potential hydrocarbon reserves and other mineral resources in Antarctica. Coring activity has suggested the presence of thermogenic hydrocarbons in sediment (McIver 1975, Whiticar *et al.* 1985, Han 1989). Seismic profiling and theoretical models of hydrocarbon formation and accumulation have been used to suggest that the likely sites are in the Ross Sea Basin and in the Larsen Basin (western Weddell Sea) (Davey 1985, MacDonald *et al.* 1988). This has the obvious potential to increase greatly the risk of hydrocarbon pollution. The potential hazards for offshore oil or gas extraction resemble those encountered in the Arctic, although the Southern Ocean presents more extreme conditions (Keys 1984).

There are a number of pathways for input of hydrocarbons (Fig. 1) and most of these may be considered to cause gradual change to the environment which is not immediately obvious. It is important to assess current knowledge of hydrocarbons in the Antarctic marine ecosystem so that remedial action can be instigated before irreversible damage occurs. We need to know present background levels for a wide range of potential pollutants and how these vary both spatially and temporally. Only then can we begin to assess the magnitude and effects of either local or global input to the system. Here, we first present a systematic description of hydrocarbons present in the Antarctic marine ecosystem. These data are then evaluated in the context of the two major monitoring problems— local and global — and with regard to likely routes whereby hydrocarbons enter the system. Recommendations for a monitoring programme are discussed.

Hydrocarbons in the Southern Ocean ecosystem

Studies of hydrocarbons in the Southern Ocean have progressed over the last fifteen years as methodology has developed. In most cases, concentrations are very low and analyses require sensitive methods (Cripps 1989a). Although several sampling campaigns have provided data on hydrocarbon concentrations and distributions, very few have

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been directed at pollution monitoring. Spatial coverage is patchy, and useful time-series data are lacking. Much of the early work was carried out at coastal localities, determined by convenience of access from research stations, and thus possibly unrepresentative of the Southern Ocean as a whole.

Hydrocarbons found in the marine environment can be classified into five main categories (Saliot 1981);

(a) Polycyclic aromatic hydrocarbons (PAH). A number of PAH have been identified in Antarctic seawater, phytoplankton and zooplankton. PAH are typically considered as wholly anthropogenic in origin, but natural biosynthesis cannot be reliably excluded. Compounds reported include phenanthrene, anthracene, fluoranthene, pyrene, chrysene and benz(a)pyrene (Cripps 1990). Desideri *et al.* (1989) have also reported alkyl substituted benzenes and napthalenes in the Southern Ocean.

(b) Saturated alkyl hydrocarbons (alkanes). Normal and isoprenoid alkanes have been recorded for all levels of the Antarctic ecosystem (e.g. Mackie *et al.* 1978, Platt & Mackie 1980).

(c) Unsaturated alkyl hydrocarbons (alkenes). Alkenes occur in various components of Antarctic marine ecosystems, but have only been reported in two studies to date. Nichols *et al.* (1988) have found two unsaturated hydrocarbons in sea-ice diatoms, an isoprenoid C_{25} diunsaturated alkene and the normal alkene $C_{25:6}$. Squalene has also been detected in the Antarctic ecosytem (Cripps 1990).

(d) Saturated alicyclic hydrocarbons. Desideri *et al.* (1989) are the only workers to have analysed cycloalkanes in Antarctic seawater, and found nine compounds.

(e) Unsaturated alicyclic hydrocarbons. No unsaturated alicyclic hydrocarbons have as yet been identified in the Antarctic.

Hydrocarbons in seawater and sedimenting material of the Southern Ocean

There are few extensive analyses of the hydrocarbon content of Antarctic seawater (Table I). Ventajas (1986a) analysed sea ice and seawater in the vicinity of the research stations Belgrano II and Marambio and revealed concentrations significantly higher in the sea-ice than the seawater, which had levels within the range found by Ventajas (1985, 1986b) for the Bellingshausen Sea, Bransfield Strait and Weddell Sea. Comes *et al.* (1987) have also studied the petroleum hydrocarbons (equivalent to total PAH) in Weddell Sea water. Sanchez-Pardo & Rovira (1987) and Cripps (1990) have made a more detailed studies of alkanes and PAH in the surface seawater of the Bransfield Strait area. Sanchez-Pardo & Rovira report much lower levels for alkanes in seawater, 4.1–10.5 ng l^{-1}, compared to 1.1–21.8 µg l^{-1} by Cripps. Desideri *et al.* (1989) also found lower levels of n-alkanes (18–488 ng l^{-1}) but similar levels of PAH (23–580 ng l^{-1}) to other workers (Table I). There is a measure of variation in the concentrations throughout the region (Table II) which is probably related to complex combinations of biological and physical properties of the ocean. Weber & Bicego (1990) published similar results for the PAH from waters around Elephant Island. The alkane levels reported by Platt &

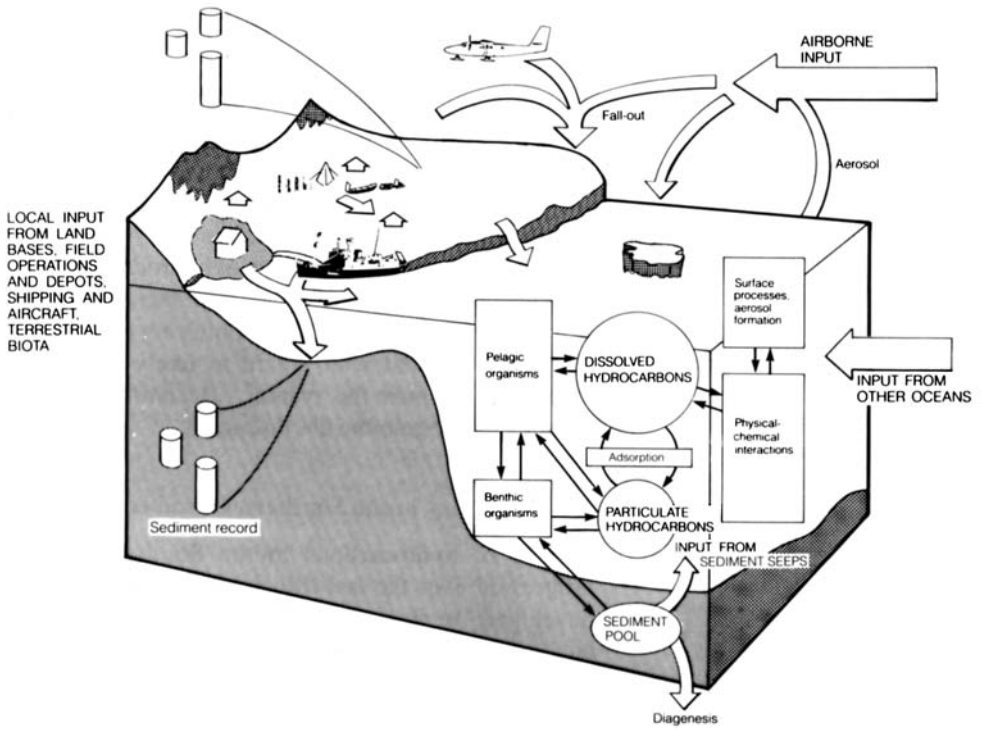


Fig. 1. Diagram summarizing the cycling of hydrocarbons in the Antarctic marine environment, and local and 'global' inputs (flow diagram after Saliot 1981).

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Mackie (1980) for the inshore site at King Edward Cove, South Georgia, were within the ranges quoted by Cripps (1990) for the Bransfield Strait.

Matsueda & Handa (1986) include a range of hydrocarbons (principally alkanes) in their analyses of the organic constituents of material from sediment traps in the Southern Ocean. Their results indicate that complex transformations can take place as particles sink down the water column. They found that the hydrocarbons in sinking particles were derived mainly from diatoms in Antarctic Ocean waters and from coccolithophores in temperate waters north of the Antarctic Polar Front. The unsaturated long chain hydrocarbons (C_{20}– C_{30}) found in sinking particles, principally zooplankton faecal pellets, were also characteristic of microalgae. The similarity of the alkane composition indicates that these compounds are transported through the food chain without biochemical alteration by the zooplankton. By contrast, the particulates suspended in King Edward Cove, South Georgia, were of terrigenous origin and had very low concentrations of both aliphatic and aromatic hydrocarbons (Cripps 1989b).

Hydrocarbons in the microplankton and sea-ice microbiota of the Antarctic

At present there are no data on the hydrocarbons of marine bacteria from the Antarctic. The microalgal community has been analysed for hydrocarbons by Nichols *et al.* (1988, 1989) (sea-ice diatoms) and Cripps (1990) (free oceanic phytoplankton) (Table III). Both studies found a similar range of n-alkanes (C_{20} – C_{36}) and the domination of the aliphatic fraction by one or two isoprenoid or alkene hydrocarbons. Nichols *et al.* (1988) identified the normal alkene $nC_{21:6}$ and an isoprenoid C_{25} diene in a number of species of diatom from the sea-ice at McMurdo Sound. The domination of one particular compound of the aliphatic hydrocarbon fraction is common in phytoplankton (Blumer *et al.* 1971). When expressed as a proportion of the dry mass the concentrations of alkyl and aromatic hydrocarbons in phytoplankton are the highest of all the pelagic organisms in the Antarctic (Cripps 1990). The particulate fraction of the upper water column of the Southern Ocean is dominated by

Table I. Current published ranges and mean values of aliphatic and polycyclic aromatic hydrocarbons (PAH) in the seawater of the Southern Ocean

	Total n-alkanes	Pristane	Phytane	Squalene	Total PAH	Ref
			($\mu g\ l^{-1}$)			
Sample						
Seawater	1.1–21.8	0–0.6	0–0.5	0–1.1	0–1.7	1
depth 10 m	5.8	0.2	0			2
					0.8–2.3	3
					0.5–7.5	4
	2.4–10	0.2–0.7	0.2–0.5	0.2–0.8	0.1–1.2	5
	2.1	0.1	0.1	0.2	0.2	6
					0.2–4.7	7
					0–9.4	8
	4.1–10.5*				18.6–86.4 *	9
	18–488*				37–580 *	10
Depth>1000 m					0.4–4.0	11
Surface film					1.1–3.2	3
					0.4–9.4	4
Sea ice					19–47	12

* - $ng\ l^{-1}$.

References

(1) Cripps (1990), Bransfield Strait.
(2) Platt & Mackie (1980), King Edward Cove, South Georgia.
(3) Ventajas (1985), Bransfield Strait and Weddell Sea.
(4) Ventajas (1986a), Weddell Sea.
(5) Cripps (1989b), Cumberland and Stromness Bays, South Georgia.
(6) Cripps (1989b), Offshore, South Georgia.
(7) Weber & Bicego (1990), Elephant Island.
(8) Comes *et al.* (1987), Weddell Sea.
(9) Sanchez-Pardo & Rovira (1987), Bransfield Strait.
(10) Desideri *et al.* (1989), Terra Nova Bay.
(11) Ventajas (1985), Weddell Sea.
(12) Ventajas (1985), research bases, Antarctic Peninsula.

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Table II. Variance in polycyclic aromatic hydrocarbon and n-alkane levels in the surface water (< 10 m depth) of the Bransfield Strait and Weddell Sea, Antarctica.

	n	x	range	σ
Total PAH (μg l^{-1})				
Cripps (1990)				
Bransfield Strait 1985	50	0.2	0–1.7	0.4
Weber & Bicego (1990)				
Elephant Island, 1987	15	0.9	0.2–4.7	1.0
Desideri *et al.* (1989)				
Terra Nova Bay.	11	0.1	0–0.6	0.2
Comes *et al.* (1987)				
Weddell Sea, 1985	137	2.6	0–9.4	1.9
Ventajas (1985)				
Bransfield Strait				
1983	8	1.9	0.4–3.2	1.2
1984	7	0.9	0.2–1.7	0.5
Weddell Sea				
1983	30	1.4	0.1–3.2	0.8
1984	33	1.5	0.1–2.8	0.7
Total n-alkanes* (μg l^{-1})				
Cripps (1990)				
Bransfield Strait	50	5.4	1.1–21.8	4.2
Desideri *et al.* (1989)				
Terra Nova Bay.	11	0.4	0.1–0.9	0.3

n - number of samples. x - mean value.
σ- standard deviation. * - sum of C_{15}- C_{30} n-alkanes.

Table III. Hydrocarbons in Antarctic marine microalgae and particulate material.

	Total n-alkanes	Pristane	Phytane	Squalene	Total PAH	Ref
Microalgae						
Oceanic μg l^{-1}*	0.02–0.09	<0.01			0.03	1
Sea ice mg m^{-2}	0.13–6.26					2
Suspended Particles ng l^{-1}	3.1–9.4				10–58	3
Sinking particles μg kg^{-1}	450–1380	1000–2900	20–60	100–1500		4

* Calculated for a phytoplankton biomass of 20 mg dispersed in 1 l of seawater.

References
(1) Cripps (1990), Bransfield Strait.
(2) Nichols *et al.* (1988), McMurdo Sound.
(3) Sanchez-Pardo & Rovira (1987), Bransfield Strait.
(4) Matsueda & Handa (1986), Australian Southern Ocean.

phytoplankton, and as PAH have a strong affinity for particulate matter they constitute a likely sink for these compounds (cf. Zsolnay 1977). The range of PAH found is more extensive than that for the seawater but similar to that found in zooplankton. The pattern of PAH in phytoplankton does not appear to be as species-specific as are aliphatic profiles. Sanchez-Pardo & Rovira (1987) identified a number of aromatic compounds in the particulate fraction including biphenyl, fluorene, anthracene, pyrene and chrysene. They report similar levels for particulates and seawater (Tables I & III) and higher values for total PAH (4.9–57.5 ng l^{-1}) than n-alkanes (3.1–9.4 ng l^{-1}).

Hydrocarbons in Antarctic zooplankton and fish

Zooplankton and fish exhibit intra- and inter-species variation in hydrocarbon content (Tables IV–VII). The alkane pattern is different for each species but the range of PAH remains similar. In addition the aliphatic fraction also includes a small number of compounds which are present in high proportion and are probably unsaturated isoprenoid hydrocarbons. Every species has its own alkyl signature.

The concentrations of total and individual alkanes, and of total PAH, varies greatly (Tables IV–VI). Gelatinous zooplankton, with their high water content and often novel biochemical composition, have hydrocarbon contents which vary widely and fall within the wide range observed for other zooplankton (Table VI). Intra-species variation in hydrocarbon levels observed by Reinhardt & Van Vleet (1986a) and Cripps (1990) for Antarctic krill, *Euphausia superba*, is a consequence of age- and sex-related differences in lipid content (see Clarke 1984). The composition of swarms of *Euphausia superba* vary spatially and temporally (Watkins 1986, Watkins *et al.* 1986), which may account for the changes in hydrocarbon level between years found by Reinhardt & Van Vleet (1986a)(Table IV).

It is customary to expect that predators will accumulate non-metabolized pollutants and thus have higher levels than their food supply. However, predators are just as likely to accumulate anthropogenic PAH directly from seawater as by food web magnification (Varansi & Malins 1977). Cripps (1990) reports weight-specific levels of the same order for PAH in the fish *Electrona antarctica* and the predatory midwater amphipod *Themisto gaudichaudii* as in other zooplankton (Tables IV, V & VII). The concentration of aliphatic hydrocarbons in *Electrona* was in excess of that for

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Table IV. Aliphatic and polycyclic aromatic hydrocarbons (PAH) in Antarctic euphausiids.

	Total n-alkanes	Pristane	Phytane	Total PAH	Ref
		(μg kg^{-1} wet mass)			
Euphausia crystallorophias	1070	142	58	2.5	1
	138000	1400			2[a]
Euphausia superba	370	390	23	5.9	1
	500	200	40		3
	18400	6400			4[a]
	110	630	2	282.0	5
Euphausia triacantha	3830	2980	12	4.2	1
Thysanoessa macrura	3134	626850			4[a]
Thysanoessa sp.	3380	8110	17	5.5	1

References
(1) Cripps (1990), Bransfield Strait.
(2) Nachman (1985), McMurdo Sound (see note *a*).
(3) Platt & Mackie (1980), King Edward Cove, South Georgia.
(4) Reinhardt & Van Vleet (1986*a*), Croker Passage, Brabant Island. (See note a).
(5) Clark & Law (1981*a*), King Edward Cove, South Georgia.

Note *a*, The results have been adjusted from the original published dry mass analysis to that representing an analysis on a wet mass basis. A water content of 75% had been assumed for euphausiids.

Table V. Aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (PAH) in Antarctic crustacea other than euphausiids.

		Total n-alkanes	Pristane	Phytane	Total PAH	Ref
			(μg kg^{-1} wet mass)			
Antarctomysis ohlinii		1242	50400			1[a]
Cyphocaris richardi		615	41000			1[a]
Eurythenes gryllus		10764	276000			1[a]
Eusirus perdentatus		13868	5375			1[a]
Notocrangon antarcticus	E	408	57	22	7.8	2
	M	392	57	20	6.0	
	V	770	169	19	2.3	
Paradania boeki		3492	24250			1[a]
Themisto gaudichaudii		3090	7740	22	6.4	2
		0	4625			1[a]
Copepoda						
Calanoides acutus		4500	3296000			1[a]
Metrida gerlachei		0	5350			1[a]
Rhincalanus gigas		0	2025			1[a]
Rhincalanus sp.		1225	59690	21	11.6	3

Key: **E**. Exoskeleton, **M**. Muscle, **V**. Viscera.

References
(1) Reinhardt & Van Vleet (1986*a*), Croker Passage, Brabant Island (see note *a*).
(2) Cripps (1990), Bransfield Strait.
(3) Cripps unpublished results, South Georgia.

Note *a*, The results have been adjusted from the original published dry mass analysis to that representing an analysis on a wet mass basis. A water content of 75% had been assumed for zooplankton.

zooplankton, but this could be ascribed to a high lipid content. Platt & Mackie (1980), Nachman (1985) and Reinhardt & Van Vleet (1986a) found levels of aliphatic hydrocarbons to be generally of the same order in Antarctic zooplankton and fish. Reinhardt & Van Vleet also found an annual variation in the hydrocarbon composition of *Electrona antarctica*. This was explained by the change in diet from the copepod, *Calanoides acutus*, to krill, *Euphausia superba*. This is evidence for transport of some aliphatic hydrocarbons, and possibly similar compounds, up the food chain. A few biogenic unsaturated aliphatic hydrocarbons were found to be unique to one or a few species by Cripps (1990) and would make excellent biomarkers. Such compounds can be used to study processes and predict pathways in the Antarctic food web. The presence of abnormal compounds in zooplankton may reveal contamination of the particulate matter in the environment.

Analytical methods and sample treatment may differ in their results. Inconsistencies can arise from chemical modification during drying or by fluid loss from fresh animals. Analysis of a dried sample can give a higher result than from fresh animal analysis, (see *Euphausia crystallorophias*, *E. superba* (Table IV), *Salpa* (Table VI) and *Electrona antarctica* (Table VII). Conversely, *Rhincalanus* and *Themisto gaudichaudii* (Table V) gave higher levels from fresh animal analysis. This highlights the requirement for the methods used in a monitoring programme to be uniform, otherwise analytical artefacts would overwhelm any changes associated with contamination.

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Table VI. N-alkanes and pristane in Antarctic gelatinous plankton.

	Total n-alkanes	Pristane	Ref
	(μg kg^{-1} wet mass)		
Atolla wyvillei	157	61	1[a]
Diphyes antarctica	445	0	1[a]
Sagitta gazellae	5115	870	1[a]
Salpa sp.	686	5	2
Salpa thompsoni	7594	1215	1[a]
Tomopteris carpenteri	2620	420	1[a]

References
(1) Reinhardt & Van Vleet (1986*a*), Croker Passage, Brabant Island (see note *a*).
(2) Cripps (1990), Bransfield Strait.

Note *a*, The results have been adjusted from the original published dry mass analysis to that representing an analysis on a wet mass basis. A water content of 95% has been assumed for the gelatinous zooplankton species.

Table VII. Aliphatic and polycyclic aromatic hydrocarbons (PAH) in Antarctic fish.

		Total n-alkanes	Pristane	Phytane	Total PAH	Ref
		(μg kg^{-1} wet mass)				
CHANNICHTHYDAE						
Champsocephalus gunnari	M	100	20	20	2.2	1
	L	2500	400	20	4.3	1
Parachaenichthys georgianus	M	100	20	tr	1.0	1
	L	1200	1300	0	0.5	1
MYCTOPHIDAE						
Electrona antarctica	M	2800	187600	60	3.2	2
	L	2000	23800	11	9.4	2
	W	1073	61300			2
	W	1315314	779275			3[a]
Electrona carlsbergi	W	374	18700			3[a]
NOTOTHENIIDAE						
Dissostichus mawsoni	W	49800	0			4[a]
Notothenia rossii	M	50	200	tr	1.3	1
	L	1200	3400	0	0.6	1
Pleurogramma antarcticum	W	144000	261000			4[a]
P. antarcticum (larvae)	W	3479000	91450			3[a]

Tissue Key: **L.** Liver, **M.** Somatic muscle, **W.** Whole animal.

References
(1) Platt & Mackie (1980), King Edward Cove, South Georgia.
(2) Cripps (1990), Bransfield Strait.
(3) Reinhardt & Van Vleet (1986*a*), Croker Passage, Brabant Island (see note *a*).
(4) Nachman (1985), McMurdo Sound (see note *a*).

Note *a*, The results have been adjusted from the original published dry mass analysis to that representing an analysis on a wet mass basis. A water content of 75% has been assumed for fish.

Hydrocarbons in mammalian and avian predators

Clarke & Prince (1976) provide the only description of hydrocarbons in higher predators of the Southern Ocean. The stomach oils of a number of seabirds from Bird Island, South Georgia, were analysed for aliphatic hydrocarbons, in particular pristane and squalene (Table VIII). The gas chromatograms of the samples analysed did not exhibit any unresolved material which could have indicated petroleum-derived aromatic hydrocarbons. The complexity of the hydrocarbons in the stomach oil samples probably reflects a wide variety of food items. The relatively high levels of pristane in three of the species analysed may be a reflection of the large proportion of crustacea, which are high in pristane (Table IV & V), in their diet. The grey-headed albatross, which feeds mainly on squid in preference to crustacea (Croxall & Prince 1980), has low levels of pristane.

Hydrocarbons in Antarctic sediment and benthos

Platt & Mackie (1979, 1980) made a detailed study of the hydrocarbons in the fauna and environment at King Edward Cove (Tables IX & X). This site had been used for shore-based whaling intermittently between 1904 and 1965, and these authors were able to identify the course of hydrocarbon pollution associated with this activity by analysing sediment core profiles (Platt & Mackie 1979). They concluded that the PAH concentrations in benthos and contemporary sediment at the site indicated input of anthropogenic compounds which were not local, and probably represented pyrolysis products derived from the burning of fossil fuels at lower latitudes (Platt & Mackie 1981). However these levels were much lower than some other sediment in the Antarctic (Table IX). Recent analysis of sediment from the Bransfield Strait by Yunqian *et al.* (1989) found levels of up to 171 μg kg^{-1} for PAH compared to 47 μg kg^{-1} from South Georgia. Clarke & Law (1981a,b) examined the hydrocarbon content and composition of benthic animals from both South Georgia and from the more southerly Signy Island (South Orkney Islands).

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Table VIII. Aliphatic hydrocarbons in the stomach oil of subantarctic seabirds, from Bird Island, South Georgia (Clarke & Prince, 1976).

	% Hydrocarbon in stomach oil	Pristane as % total hydrocarbon	Squalene as % total hydrocarbon	No. of compounds resolved
Black-browed albatross *Diomedea melanophrys*	0.15	71	<1	55
Grey-headed albatross *D.chrysostoma*	0.19	33	<1	28
Blue petrel *Halobaena caerulea*	0.46	62	<1	39
Dove prion *Pachyptila desolata*	0.74	51	<1	29

Table IX. Hydrocarbons in Antarctic marine surface sediments.

	Total n-alkanes	Pristane	Phytane	Squalene	Total PAH	Ref
			(μg kg^{-1})			
(Top 2.5 cm)	2900	200	100		47	1
	112	4	6	8		2
	421–1565	38–113	19–71			3
	100–376	10–48	4–13			4
					1–171	5
	1000–9300				84–2500	6
(Top 10 cm)	728				195	7
Contaminated samples						
	1216	208	223		68	8
					4500	9
					1000	10

References

(1) Platt & Mackie (1980), King Edward Cove, South Georgia.
(2) Matsueda & Handa (1986), Australian Southern Ocean.
(3) Mackie *et al.* (1978), King Edward Point, South Georgia.
(4) Mackie *et al.* (1978), Moraine Fjord, South Georgia.
(5) Yunqian *et al.* (1989), Bransfield Strait.
(6) Danyushevskaya *et al.* 1989, Weddell Sea.
(7) Venkatesan & Kaplan (1988), Bransfield Strait.
(8) Cripps (unpublished result) shore contaminated with diesel, Signy Island, South Orkney Islands.
(9) Lenihan *et al.* (1990), Contaminated sample from the wharf at Winter Quarters Bay, McMurdo Sound.
(10) Kennicutt (1990), Arthur Harbour and Biscoe Bay, Anvers Island, after the sinking of the *Bahia Paraiso*.

Table X. Aliphatic and polycyclic aromatic hydrocarbons in Antarctic benthos.

	Total n-alkanes	Pristane	Phytane	Total PAH	Ref
		(μg kg^{-1} wet mass)			
CRUSTACEA					
Serolis cornuta	56–97	5–25	4–14	14–23	1
Serolis	2200	100			2
pagenstecheri	36–860	2–16	2–6	40–118	3
MOLLUSCA					
Chlanidota	0–124	34–100	0–13	59–86	3
densisculpta	100	1300			2
Nacella concinna				125000	4
Neobuccinum eatoni	0–22	0–4	0–1	10	1
Philine gibba	2700	200			2
Yoldia	400	80	80		2
eightsii	3618	36	102	6	5
NEMERTEA					
Parbarlasia (Lineus) corrugatus	70–200	10–50	0–10		2
ASTEROIDEA					
Diplaster meridionalis	40–2300	0–60	0–20		2
Odontaster	526	47	23	815	4
validus	24	18	1	11	1
MACROALGAE					
Macrocystis pyrifera	6600	300	20		2
Collection of 9 species				24–106	6

References

(1) Clark & Law (1981*a*), Signy Island, South Orkney Islands.
(2) Platt & Mackie (1980), King Edward Cove, South Georgia.
(3) Clark & Law (1981*a*), King Edward Cove, South Georgia.
(4) Kennicutt (1990), Arthur Harbour and Biscoe Bay, Anvers Island
(5) Cripps unpublished result, Signy Island, South Orkney Islands.
(6) Dhargalkar & Bhosle (1987), Prydz Bay, Vestfold Hills.

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Table XI. Values for total n-alkanes and total polyaromatic hydrocarbons from the Antarctic compared to the Arctic and examples of global levels; superscripts refer to site references.

	Seawater ($\mu g\ l^{-1}$)	Phytoplankton ($\mu g\ l^{-1}$)	Mixed zooplankton ($\mu g\ kg^{-1}$) (wet mass)	Fish, somatic muscle ($\mu g\ kg^{-1}$) (wet mass)	Molluscs ($\mu g\ kg^{-1}$) (wet mass)	Sediment ($\mu g\ kg^{-1}$) (dry mass)
ANTARCTIC						
n-alkanes	1–22[1]	0.02–0.09[1]*	408–3830[1]	1940[1]	0-97[2]	366–399[3]
PAH	0–1.7[1]	0.03[1]*	72–643[1]	3.2[1]	10–23[2]	4.9–16.1[3]
ARCTIC						
n-alkanes	1.4–2.0[4]	0.6–0.7[4]	10–70000[5]	1400–6400[6]	63–2000[4]	100–700[4]
PAH	1.1–2.0[4]	0.6–0.7[4]	10–150000[5]	8.7–31.5[6]	250–32500[4]	100–1400[4]
GLOBAL						
n-alkanes	0.7–5.7[7]	0.3–0.4[7]	100–4400[10]	10–12000[10]	200–15600[10]	380–3980[14]
PAH	0–6.2[8]	10[9]	0–15[11]	4-43[12]	2500–8000[13]	4300[13]

n.b. Values are totals as quoted in the reference or a sum of the individual compounds.
*- Calculated for a phytoplankton biomass of 20 mg dispersed in 1 l of seawater.

(1) Cripps (1990), Bransfield Strait.
(2) Clarke & Law (1981*a*), King Edward Cove, South Georgia.
(3) Mackie *et al.* (1978), King Edward Cove, South Georgia
(4) Cretney *et al.* (1987*a,b*), Baffin Island, Canada.
(5) Shaw *et al.* (1978), Bering Sea.
(6) Wong *et al.* (1976), Beaufort Sea, Canada.
(7) Marty & Saliot (1976), Atlantic Ocean and Mediterranean Sea.
(8) Hardy *et al.* (1977), North Sea.
(9) Niaussat & Auger (1970), Clipperton Atoll, Eastern Pacific, (benz(a)pyrene and perylene).
(10) Whittle *et al.* (1977), North Sea.
(11) Neff (1979), Worldwide, (benz(a)pyrene only).
(12) Brown & Pancirov (1979), Baltimore Canyon, U.S.A.
(13) Follom & Moe (1988), Langesundfjord, Norway.
(14) Currie & Johns (1989), Great Barrier Reef Lagoon.

They found that the samples from Signy Island had consistently lower hydrocarbon content and argued from this that the source of aromatic hydrocarbon contamination at South Georgia was local pollution rather than long-distance atmospheric transport.

McIver (1975), Whiticar *et al.* (1985) and Han (1989) examined sediment cores from the Bransfield Strait for thermogenic hydrocarbons (C_2-C_6 n-alkanes). Thermogenic hydrocarbon seepage is a common indicator of petroleum accumulation throughout the globe. Their results suggest that this is a possible source for hydrocarbons in Antarctic near-bottom water. However the quantities of hydrocarbon reported are not of the same scale as those associated with petroleum accumulations. The surface sediments of the Bransfield Strait have a higher PAH content (195 $\mu g\ kg^{-1}$) than the polluted site at South Georgia (Ventkatesan & Kaplan 1987). It is suggested that these hydrocarbons are derived from submarine outcrops of coaliferous shales. Danyushevskaya *et al.* (1989) found even higher concentrations in sediment from the Weddell Sea (84–2500 $\mu g\ kg^{-1}$) but suggested a biological origin.

Matsueda & Handa (1986) report that the aliphatic hydrocarbon fraction from bottom sediment from an open ocean site from the Australasian sector of the Southern Ocean was devoid of unsaturated compounds and was predominantly n-alkanes. Platt & Mackie (1980) found levels of alkanes from inshore sediments at South Georgia to be of one or two orders of magnitude higher than those from a deep-water sediment sample (Matsueda & Handa 1986).

Information on macroalgae is very limited. Dhargalkar & Bhosle (1987) measured total 'petroleum' hydrocarbons (PAH) in a number of species from Prydz Bay, and Platt & Mackie (1980) analysed the n-alkanes in kelp, *Macrocystis pyrifera*, from South Georgia. A number of benthic animal species have been investigated and the results are reviewed in Table X. Molluscs, in particular bivalves, are known to accumulate hydrocarbons. They have been employed in temperate waters as pollution indicators. At pristine sites the hydrocarbon concentrations in Antarctic molluscs were lower than for other parts of the world (Table XI). However, at

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contaminated locations in the Antarctic, Clarke & Law (1981a) have shown that some benthic invertebrates had higher levels of PAH.

Sources for hydrocarbons in the Southern Ocean

Local sources—biogenic

Aliphatic hydrocarbons are present in the lipid fraction of all marine flora and fauna, and consequently this is the largest potential source in the Antarctic. Natural input from the land to the marine system is very limited due to the sparse terrestrial biota. The source of the relatively high levels of PAH in the particulate fraction of surface water (essentially phytoplankton) is uncertain. Two possibilities are the biosynthesis by bacteria and phytoplankton, or the absorption of compounds originating outside the Antarctic which are not necessarily natural.

Local sources—petrogenic

There is evidence to suggest that the western Weddell Sea and the Ross Sea are likely sites of submarine hydrocarbon reserves (Holdgate & Tinker 1979, Macdonald *et al.* 1988). Hydrocarbon residues have also been found in a sediment core from McMurdo Sound, suggesting that liquid hydrocarbons have migrated through the rock sequence to the ocean floor (Elliot 1988), probably giving rise to the seepage of hydrocarbons into the overlying water, e.g. McIver (1975), Whiticar *et al.* (1985) and Han (1989). As yet there is no evidence that this contributes markedly to concentrations of hydrocarbons in the water, although the possibility is noted by Ventajas (1985).

Local sources—anthropogenic

Local human activity in the Southern Ocean and on land may result in hydrocarbon contamination of the marine environment by spillage, and loss to the atmosphere by evaporation or burning. Most contamination will be restricted, because of the very small scale of human activity, and spillage represents the major source of pollution. This will be associated with permanent research stations and temporary camps, with the use of aircraft, land vehicles and ships (Fig. 1). Ventajas (1985) suggests that the presence of sea-ice may restrict the spread of light fuel or lubricants on the seawater surface, giving rise to local high concentrations, e.g. around a ship which is surrounded by ice for a long time. However, shipping and other sources of liquid hydrocarbon contamination in the Southern Ocean are localized, scarce and widely scattered (see below). Sampling of the sea-surface on transects between New Zealand and the Ross Sea failed to encounter tar balls (the typical traces of large oil slicks) in oceanic Antarctic waters (Gregory *et al.* 1984).

Derelict sites of shore-based whaling pose a significant threat to the Antarctic environment (Headland 1984). The volume of garbage discharged by existing research stations into the Southern Ocean is small, but it is obvious where it does occur. There is now intensive activity to minimize all forms of pollution and optimize the disposal of waste associated with Antarctic research activity.

Global sources—atmospheric

Atmospheric transport of pyrolysis products has been implicated in hydrocarbon contamination of inshore habitats in the Southern Ocean by Platt & Mackie (1981). A contrary viewpoint has been presented by Clarke & Law (1981a,b) who suggest that atmospheric input should result in uniform low levels at all Antarctic sites. Given present data, it is difficult to assess the importance of long-distance atmospheric transport in the total hydrocarbon contamination of the Southern Ocean. There is spatial variability in the hydrocarbon content of seawater and pelagic animals, which might militate against the importance of such input.

So far there has been no work to measure directly the flux of pollutants from the atmosphere to the Southern Ocean, although fluxes of some normal gaseous constituents (e.g. CO_2) have been measured. There is interest in snow and ice cores as means of estimating trends in concentration and distribution of unequivocally anthropogenic compounds such as PCBs, DDE and DDT (Riseborough *et al.* 1976, Peel 1983). The presence of these compounds in the Antarctic environment and food chain has been reported widely. Hidaka & Tatsukawa (1981, 1983) have reviewed the subject and studied the environment adjacent to Syowa station. Chlorinated hydrocarbons have been analysed in air and surface waters (Tanabe *et al.* 1982, 1983), lichen and moss (Bacci *et al.* 1986) and marine phytoplankton (Lukowski& Ligowski 1988). The presence of unequivocally anthropogenic compounds in the Antarctic marine ecosystem indicates the global spread of pollutants, almost certainly by atmospheric transport from outside the area (Alderton & Coleman 1985). Wolff (1990) indicates that Antarctic snow and ice contain an accurate record of global atmospheric changes, although he warns that the key to understanding the data are in improving our knowledge of the atmosphere and the air-snow interface.

Dick & Peel (1985) and Dick (1987) suggest that aerosol transport is the dominant mechanism for input of metals such as lead to Antarctic precipitation. This implies that atmospheric transport is also a feasible route for hydrocarbon input from lower latitudes (Fig. 2). There are four major sources for aerosol material—the oceans, crustal rocks, anthropogenic emissions and extra-terrestrial sources. Except for some exotic elements, these sources are listed in decreasing order of importance. Equatorial atmospheric circulation forms an effective barrier between Northern and Southern Hemispheres for constituents with relatively short residence time in the atmosphere (i.e. particles rather than gases). Thus

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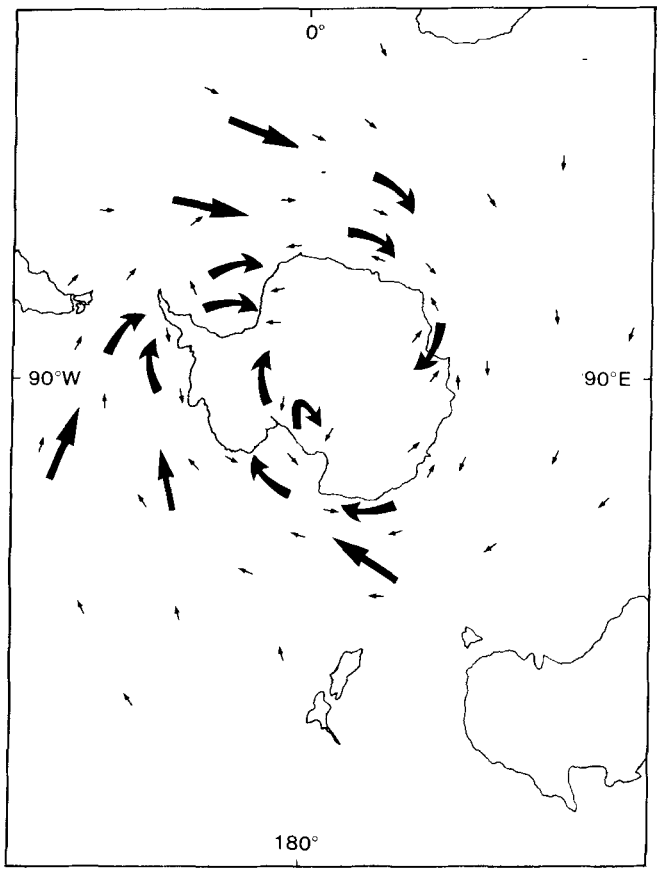


Fig. 2. Wind directions (small arrows) and storm tracks (large arrows) in the Antarctic (after Weyant 1967).

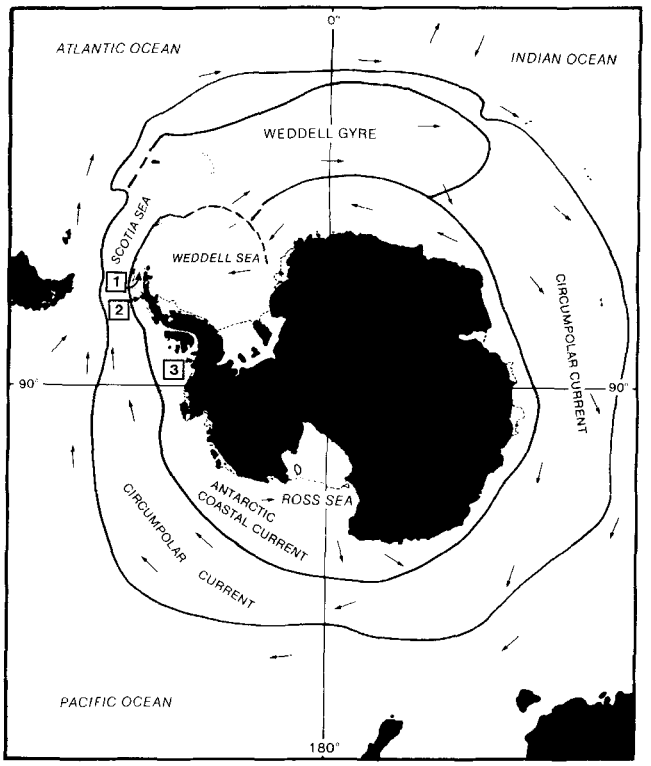


Fig. 3. Surface currents in the Southern Ocean. Numbers indicate sites mentioned in the text - 1. Bransfield Strait, 2. Gerlache Strait, 3. Bellingshausen Sea.

the two hemispheres are effectively isolated from each other with respect to aerosol transport, and the Antarctic is unlikely to receive contamination from the majority of anthropogenic sources which lie in the industrialized Northern Hemisphere (Alderton & Coleman 1985). Forest fires may provide the major source of atmospheric hydrocarbon pollution, including PAH, in the Southern Hemisphere.

Global sources—oceanic

It is difficult to assess the significance of transport of hydrocarbon contaminants in seawater from elsewhere in the world ocean. The sites in the Southern Ocean where exchange takes place are not well defined. The water circulation and hydrological boundaries around Antarctica are illustrated in Fig. 3. Eddy formation in the Drake Passage region of the Southern Ocean suggests that this might be an important area for the transfer of Southeast Pacific Basin Water into the Antarctic Circumpolar Current (see Bryden 1979, 1983, Nowlin & Klinck 1986). However it seems unlikely that this area of the Pacific Ocean will be unusually affected by hydrocarbon contamination. The convergent nature of the Antarctic Polar Frontal Zone will limit southerly mass transport into the circumcontinental Southern Ocean.

Pollution incident and biological effects

Human activity in the Antarctic has already resulted in local pollution incidents. Of all current activities, shipping in poorly charted waters presents the major risk. The wreck of the *Bahia Paraiso* released between 500 and 600 m^3 of oil, primarily diesel and aviation fuel, into the sea and the shoreline of all the islands of Arthur Harbour and Biscoe Bay had been contaminated within a few days. This was one of the worst ever spillages experienced in the Antarctic, but not the only one in recent years (Fig. 4). The *Nella Dan* released 270 m^3 of light marine diesel into the sea after running aground at Macquarie Island in 1987. A Russian tanker which ran aground at Grande Terre, Iles Kerguelen, spilt 850 m^3 of petroleum (Jouventin *et al.* 1984). A number of spills of petroleum products have occurred on land but it is not clear how much has reached the marine environment. Two recent instances were a leak of 90 m^3 of petroleum at Casey Station, and a spill of 250 m^3 of fuel at Williams Field on the Ross Ice Shelf (Greenpeace 1990). Fortunately the spill at Casey was contained in a natural rock depression and the local environment was otherwise unaffected (ANARE 1990).

These spills have provided almost the only opportunity to assess the responses of the marine biota to hydrocarbon pollution. The *Bahia Paraiso* spill proved lethal for a wide

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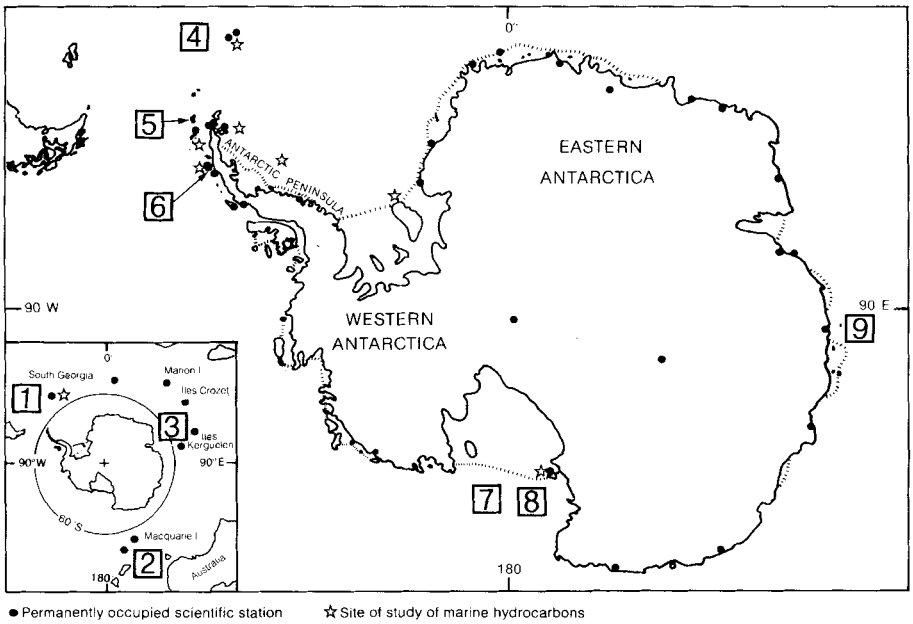


Fig. 4. Map showing the location of studies of hydrocarbons, permanently-occupied research stations, and selected incidents of pollution in the Antarctic marine ecosystem. Numbered squares indicate pollution incidents - 1. Derelict whaling stations with leaking oil tanks at South Georgia. 2. Shipwreck of the *Nella Dan* at Macquarie Island. 3. Shipwreck of a Russian tanker, Iles Kerguelen. 4. Oil leak from research bases, South Orkney Island. 5. High density of research bases on King George Island. 6. Shipwreck of the *Bahia Paraiso*, Anvers Island. 7. Shipwreck of the *Southern Quest*, Ross Sea. 8. Airstrip spill and polluted harbour at McMurdo Base. 9. Fuel spill, Casey Station.

range of biota—algae, intertidal limpets (*Nacella concinna*), blue-eyed shags (*Phalacrocorax atriceps*) and Adélie penguins (*Pygoscelis adeliae*) (Penhale 1989). Natural variability in breeding success of some Antarctic species can make their response to pollution difficult to assess. For instance the breeding failure of south-polar skuas (*Catharacta maccormicki*) was reported as an indirect effect of the spill by Eppley & Rubega (1989). Trivelpiece *et al.* (1990) reported a simultaneous breeding failure at a skua colony 400 km distant from Palmer (Cape Crozier, King George Island), which they attributed to low food availability. They suggested that the birds at both locations were starving and the chicks at Palmer would have died anyway (see also Anderson 1991). Kennicutt (1990) reports that immediate effects of the spill were restricted to within 5 km and that limpet populations subsequently showed a substantial recovery within six weeks.

Oiling of seabirds has occurred elsewhere in the Antarctic with varied severity. Croxall (1987) cites three documented incidents: Jehl *et al.* (1979), Wilson (1980) and Williams (1984)—outside the geographic scope of this review. Croxall points out that penguins will be particularly vulnerable to such pollution, although cases vary in severity from a few oiled birds (Wilson 1980) to a small oil slick on subantarctic Marion Island which killed hundreds of southern rockhopper penguins, *Eudyptes chrysocome* (Williams 1984). The oil from the *Bahia Paraiso* killed about 300 seabirds. Following the *Nella Dan* spill thousands of marine invertebrates were washed up dead along 2 km of shore. Penguins and seals were largely unaffected (Pople *et al.* 1990).

More minor incidents are not uncommon. For example, contamination was observed in 1987 at South Georgia from fuel oil and bituminous tar leaking from derelict whaling stations and a military base (Table XII). The shoreline of the fjords, where the whaling stations are situated, was contaminated, oiled king penguins and elephant seals were also noted (Cripps 1989b). However the pollution was very localized and was undetectable further than 2 km away. An inspection of the sites at Stromness Bay and King Edward Cove in 1990 showed the pollution to be similar to that reported in 1976 (Platt 1980). Most of these sources have since been removed or secured. The marine sediment at Winter Quarters Bay, McMurdo Sound, has been highly modified by human activities and apparently may require decades to recover. Robillard & Busdosh (1981) describe a petroliferous-smelling sediment with a depleted biota and a bed of dead clam shells. Analysis by Lenihan *et al.* (1990) found that the sediment alongside the McMurdo Sound wharf had levels of hydrocarbons greater than for most polluted harbours in other parts of the world. The contamination was very localized, and concentrations decreased from 4500 to <1 mg kg^{-1} within a few hundred metres of the wharf.

As with seabird species in other parts of the world,

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Table XII. Aliphatic and polycyclic aromatic hydrocarbons (PAH) in potentially polluting materials found in the Antarctic.

	Total n-alkanes	Pristane	Phytane	Total PAH (mg kg^{-1})	Ref
Bituminous tar Stromness	5717	316	427	402	1
Beached tar Stromness	2409	139	147	18	2
Beached tar Grytviken	2080	85	64		3
Fuel oil Grytviken	49360	1551	1715	3300	4
Whale oil Grytviken	9	323	1	1	4

References
(1) Cripps, unpublished result, Stromness Whaling Station, South Georgia.
(2) Cripps, unpublished result, Stromness Bay , South Georgia.
(3) Mackie *et al.* (1978), King Edward Cove, South Georgia.
(4) Platt & Mackie (1979), Grytviken Whaling Station, South Georgia.

hydrocarbons in the form of plastics and related materials also present a hazard to Southern Ocean species. Ingestion of material at sea (Prince 1980, Bourne & Imber 1982) and from waste around research stations (Stonehouse 1965, Johnston 1971) are documented. Floating debris may present a further physical hazard to animals. Bonner & McCann (1982) and Croxall *et al.* (1990) have documented the entanglement of fur seals at South Georgia by discarded plastic netting and banding material. The expansion of fishing in the Southern Ocean will increase such impacts on shore-breeding seabirds and seals if stricter controls on the discarding of these materials are not introduced.

The response to the recent hydrocarbon spillages has emphasized the fact that few data are available on the impact of anthropogenic hydrocarbons in the Antarctic environment, their natural degradation or the effects on the biota. Following the *Bahia Paraiso* accident, the National Science Foundation of the United States organized a research team to identify and determine the fate of hydrocarbons, study their microbial degradation and record the reaction of flora and fauna to the oil spill (Penhale 1989). Initial studies suggest that the population density of indigenous hydrocarbon-oxidising bacteria is very low compared with temperate zones (Kennicutt 1990). A long term programme will monitor the recovery of the ecosystem, but this will lack baseline data pre-dating the incident. The only previous relevant work was by Delille & Cahet (1984) and Cahet *et al.* (1986) who have studied the degradation of crude oil in the Subantarctic environment of Iles Kerguelen. They found that the existing microflora was able to adapt to hydrocarbon utilisation, and recorded the development of specialized heterotrophic bacteria. Recently, Delille & Vaillant (1990) have reported that the introduction of hydrocarbons to the marine environment induces rapid increases in bacterial numbers. The rate of degradation of hydrocarbons depends on the amount of bacteria present, which in turn is seasonally variable. Konlechner (1985) studied two controlled spills of crude oil at Cape Byrd, Ross Island and found low hydrocarbon bacterial activity in mineral soil and none in ornithogenic soil.

There is a need for data on the effects of these pollutants on the biota. The only experimental study on the toxicity of hydrocarbons to Antarctic marine biota (Ogrodowczyk 1981) looked at the effects of crude oil on *Euphausia superba* and on *Notothenia rossii*. Krill proved to be especially sensitive to oil pollution. Apart from some casual observations from the effects of spillage incidents, there is no other information on the likely impact of a major hydrocarbon pollution incident, and none on the effects of possible gradual increases in environmental concentrations on ecosystems. However a large body of data exists for temperate biota. Non-Antarctic species may have acquired higher resistance to hydrocarbons, having been exposed to greater levels over a longer period of time. Accumulation of PAH in an animal can progress from a sub-lethal to a lethal effect, and polycyclic aromatic hydrocarbons and their metabolites are considered to be carcinogenic (Harvey 1985).

In contrast to the Antarctic there already exists a large body of information on the Arctic. This has been prompted largely by oil exploration activities. A substantial proportion of the data has resulted from two studies, the Beaufort Sea Project (Percy & Mullin 1975, Bunch & Harland 1976, Wong *et al.* 1976) and the Baffin Island Oil Spill Project (BIOS) (Hodgson 1987). These projects made extensive studies of the background hydrocarbon levels in the environment, flora and fauna in the oil drilling area of the South Beaufort Sea and a remote 'pristine' location. The latter was the site of an experimental stranding of crude oil on a beach and release of chemically dispersed oil into the sea. There were two main conclusions from the BIOS project (Sergy & Blackall 1987):

(a) that there was no compelling ecological reasons to prohibit the use of chemical dispersants on oil slicks in nearshore areas, and
(b) that there is no strong ecological reasons for the clean up of oil stranded on shorelines.

Discussion

Although we have noted some serious deficiencies in existing data on hydrocarbons in the Antarctic marine ecosystem, certain key facts emerge. Overall, the Antarctic seas and

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their biota appear to contain very low levels of those hydrocarbons likely to be of anthropogenic origin. In most cases, the natural (biogenic) hydrocarbons can be identified but the several conventional indices of biogenic versus pollutant hydrocarbons do not give consistent indications. Local pollution, both recent and within a short historical period, can be identified from alkane and PAH distribution.

However, there remain compelling reasons for collection of further data on hydrocarbons in the Antarctic marine ecosystem (Weller *et al.* 1987). There is a demonstrable need to establish a baseline in one of the few areas of the world which is sufficiently uncontaminated to act as an indicator for global change. Hydrocarbon analyses carried out on zooplankton and fish samples from the Ross Sea (Nachman 1985), Croker Passage (near Anvers Island) (Reinhardt & Van Vleet 1986a,b) and the Bransfield Strait (Cripps 1990) identify the biogenic compounds which comprise the natural hydrocarbon pool of the Southern Ocean ecosystem. Levels of hydrocarbons in the Antarctic are similar to or lower than values for the open ocean worldwide (Table XI). Antarctic PAH levels are particularly low. Molluscs, regarded as indicators of pollution were found to be especially low. Likewise the values for Antarctic phytoplankton are an order of magnitude lower than those for the Arctic and the rest of the world.

Before defining the criteria for a suitable monitoring programme we will first list the limitations of existing data:

(i) There has been little systematic sampling.
(ii) Identification of pollutant hydrocarbons against the natural background is inadequate.
(iii) The methodologies employed have been inconsistent, both for sample manipulation, analysis and the reporting of the data.
(iv) Present baseline data are very limited.

No systematic survey of the Southern Ocean environment (Fig. 4) has been carried out and most of the samples described above are serendipitous, associated with other biological and oceanographic sampling. There has been no planned spatial coverage, and negligible repeat visits to sampling stations or studies of variability between seasons. A bias towards coastal areas has already been noted (Fig. 4).

Analytical methods and the processing of results are in many cases inconsistent. The instrumentation used is less varied. For alkanes, gas chromatography (GC) is used in all the work cited. PAH were usually analysed using fluorescence spectroscopy as 'total PAH' except for GC/MS (Desideri *et al.* 1989); GC (Sanchez-Pardo & Rovira 1987) and HPLC (Cripps 1990,1989b, Danyushevskaya *et al.* 1989). These techniques make the identification of individual PAH possible. For brevity, in this review only total PAH and n-alkanes are quoted. Inconsistency in methods is a worldwide problem and not confined to the Antarctic, and often makes comparisons between different authors' data impossible. Few authors provide any estimate of analytical precision or natural sample variability. This is of critical importance, especially where a monitoring programme is designed to assess differences between samples or sites.

Composition of the hydrocarbon content has been used to determine what is 'natural' (ie. biogenic or autochthonous) and what represents environmental contamination. For instance, n-alkanes have been characterized by the proportion of odd- and even-carbon numbers: a preponderance of odd-carbon compounds being associated with biogenic material. Until recently there has been very little information available which addresses this problem in the Antarctic. Seawater from the Bransfield Strait region showed a predominance of odd-even ratios less than one, whereas most animals examined from the same area had higher odd-even ratios close to unity (Cripps, 1990). Clarke & Law (1981a) and Platt & Mackie (1981) indicate an odd-carbon number preference in animals from Signy Island and South Georgia, whilst Nachman (1985) and Reinhardt & Van Vleet (1986*a*) found that even-carbon compounds predominated in their samples from McMurdo Sound and Croker Passage respectively. Nachman (1985) indicates that the odd-even ratio may not be a suitable indicator of allochthonous contamination in the Southern Ocean where unusual biochemical pathways may operate and give rise to novel hydrocarbon compositions. Furthermore, Cripps (1989b) shows that odd-to-even ratio and similar indices are at best ambiguous. Thus, methods which compare hydrocarbon distribution patterns are preferable to those which use indices. This requires the establishment of extensive baseline data, with which subsequent analyses can be compared.

Proposed monitoring programme

Global monitoring

The ideal sites for monitoring change in global hydrocarbon concentrations are oceanic, and could be visited on an annual basis by research vessels on their supply visits to Antarctic stations. Such voyages also provide the opportunity for meridional transects sampling pollutant gradients between low and high latitudes. Recent unpublished work (GCC) shows there to be overall consistency in the hydrocarbon content of the water bodies of the South Atlantic and South-East Pacific Sectors of the Southern Ocean. Any routine sampling from shore bases must be preceded by detailed reconnaissance of the area to identify a site which is, and will remain, unaffected by local activity.

At present, coverage of much of the Southern Ocean is poor. A broad range of samples is needed, but seawater and particulates would form the core of the sampling. A more elaborate sampling campaign would include animal samples which would provide a means of integrating hydrocarbon input to the system over a longer time-scale. Commercial fishery in defined areas could provide a means of collecting

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Table XIII. Comparison of hydrocarbon data for filtered seawater (depth 10 m) from water bodies in the Bransfield Strait as defined by Heywood in Hunt *et al.*(1990) for the austral summers of 1985 and 1989 (Cripps, 1990 and unpublished data).

	1985			1989		
Water mass	n	Total n-alkanes* ± σ (μg l^{-1})	Odd to even ratio*	n	Total n-alkanes* ± σ (μg l^{-1})	Odd to even ratio*
Bellingshausen Sea	12	9.65 ±5.7	0.84	3	12.3 ±14.0	0.71
Gerlache Strait	1	5.4	0.87	6	5.7 ±5.8	0.56
Mixed Water+	15	4.1 ±2.6	0.77	8	3.3 ±3.3	0.75
South Eastern Pacific Basin	4	3.0 ±1.3	0.84	4	8.9 ±3.6	0.84
Weddell Sea	14	4.2 ±2.7	0.66	5	6.6 ±3.2	0.80
Whole area	46	5.5 ±4.3	0.77	26	7.7 ±5.1	0.71

n - number of samples
σ - Standard deviation
* - evaluated for C_{15} - C_{30} n-alkanes
+ - Water body resulting from the mixing of Bellingshausen Sea and Weddell Sea water

Table XIV. Comparison of aliphatic hydrocarbon data for filtered seawater (depth 10 m) from the area of South Georgia between austral summers of 1985 and 1989, (Cripps, unpublished data).

	Mean value ± standard deviation (μg l^{-1})			
Year	*1985*	*1986*	*1988*	*1989*
Number of samples	2	6	14	5
Total Alkanes *	1.6	5.0 ±2.4	3.8±1.7	6.6 ±4.0
Pristane		0.1 ±0.1	0.1 ±0.1	0.2 ±0.1
Phytane		0.1 ±0.1	0.2 ±0.3	0.1 ±0.2
Squalene	0.2	0.4 ±0.2	0.8 ±0.4	0.9 ±0.5
Odd to even alkane ratio*	0.8	0.7	0.7	0.7

* - evaluated for C_{15} - C_{30} n-alkanes.

animals. In all cases, the species selected would need to satisfy the following criteria:

(i) They must be indigenous, accumulating all of their hydrocarbon load within the Southern Ocean.
(ii) They should be easily identified. The FAO species identification guide (Fischer & Hureau 1985) provides a convenient means of doing this. Commercially-caught species such as krill and fish would be convenient subjects for global monitoring, provided that no contamination was introduced in the fishing or processing. For large animals such as fish, a conveniently recognized and dissected tissue such as somatic muscle should be specified.
(iii) The biogenic hydrocarbon complement should either be very low or easily and consistently identifiable. Where this is known to vary within a species, for instance with age or sex, animals should either be segregated into groups or a large bulk sample should be analysed in order to circumvent this problem.
(iv) The species should be relatively long-lived, accumulating hydrocarbons over a long period of time. Hydrocarbons should not be metabolized or excreted, but retained to provide an integration over time which complements the more instantaneous measurements derived from analysis of water and particulates.

For global monitoring, regular and consistent sampling is needed. At present, there is no information on the longitudinal variation in global hydrocarbon transport. A restricted data base for hydrocarbons in seawater exists for the Bransfield Strait and the South Georgia region (Tables XIII & XIV). There is still a requirement for data on interannual and seasonal variation in hydrocarbon levels in water and particulates before baseline levels can be assessed.

Local monitoring

Local pollution may be a single acute event, such as a major

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spill, or more gradual pollution. A baseline or background is also required here, but must be specific to particular areas at risk. Those sites with a history of pollution may provide a useful case study in the effects and extent of local pollution. In order to meet the contingency of further hydrocarbon contamination in the Antarctic marine ecosystem, there is also a need, covered separately below, to investigate the effects of hydrocarbon pollution on key members of the biota and on ecosystem structure.

Three categories of site can be defined. First, to quantify and map hydrocarbon pollution in the event of environmental contamination the background reference may be provided not by 'pre-pollution' samples but by kindred unpolluted sites. Second, sites deemed to be at risk of pollution might be investigated and subsequently monitored as part of an Environmental Impact Assessment. Third, the small number of polluted sites around the Antarctic provide areas where the fate of hydrocarbons in the environment can be monitored now. The effects of continuous low-level input to the ecosystem may differ markedly from the impact of a single event. All of these sites are likely to be coastal, as this is where human activity is concentrated and where any traces of pollution are likely to remain.

For specific incidents sediment and benthic organisms would provide the most appropriate indicators of local pollution. When establishing a baseline for risk assessment, an intensive systematic sampling programme is required in order to establish the nature and magnitude of spatial, temporal and inherent random variability in the samples - from this it must be possible to define the level of contamination that can be resolved.

Existing contaminated sites can be used to determine the fate of pollutant hydrocarbons along gradients away from the site of contamination.

Conclusion

Investigations into the Antarctic so far reveal that anthropogenic input is both very limited and localized in comparison to the rest of the world. Thus the Antarctic is perhaps the last region of the Earth to offer the opportunity to monitor changes in global hydrocarbon levels. Local pollution may also need to be assessed. For this monitoring to be effective, several requirements must be met:

(i) An accurate baseline founded on a wide range of samples and sites and with defined limits of variability must be provided;
(ii) Analytical methods should be standardized, and where possible intercalibrated;
(iii) Sampling should be systematic and designed specifically to detect temporal change against a background of spatial, sample and analytical variability;
(iv) Monitoring should be based on measurements of concentrations of individual compounds, not on poorly-defined hydrocarbon classes or on summary indices.

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