Antarctic Science 7 (2): 137–144 (1995)

Hydrocarbons and sterols in marine sediments and soils at Davis Station, Antarctica: a survey for human-derived contaminants

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Abstract: A survey of hydrocarbons and sterols in marine and shoreline sediments was undertaken adjacent to Davis Station in Princess Elizabeth Land, Prydz Bay, Eastern Antarctica to determine the impact of a human settlement, including a sewage outfall on the local marine environment. Soil samples from selected locations onshore were also analysed to ascertain the extent of hydrocarbon contamination emanating from fuel storage facilities and other potential sources. The faecal sterol coprostanol was detected at 13.2 $\mu g\ g^{-1}$ (60% of total sterols) in sediment adjacent to the Davis sewage outfall and up to 5.0 $\mu g\ g^{-1}$ on the shoreline at Davis Beach. These concentrations indicate significant faecal contamination. The absence of coprostanol in faeces from the local wildlife confirms a human origin for this sewage biomarker. Hydrocarbons on the shoreline near Davis were present at up to 5.5 $\mu g\ g^{-1}$ (dry weight of sediment). Biomarker profiles indicate an anthropogenic origin for these hydrocarbons. Onshore, degraded hydrocarbons derived from Special Antarctic Blend distillate were found at relatively high levels in soils at the fuel storage depot (up to 220 $\mu g\ g^{-1}$). The source of these hydrocarbons appeared to be spillage from fuel storage tanks with possible contributions from fuel pipeline leakage and vehicle useage. Concentrations of polycyclic aromatic hydrocarbons in the soils were very low, generally below 1 ng g^{-1} (dry weight of sediment) for individual compounds.

Received 10 January 1994, accepted 26 September 1994

Key words: hydrocarbons, sterols, Antarctica, sediments, environmental impact

Introduction

Davis Station (established in 1957 by the Australian National Antarctic Research Expedition) is located on the shoreline of the Vestfold Hills in Princess Elizabeth Land on Prydz Bay, Eastern Antarctica (68°35'S, 77°58'E). The Vestfold Hills is an ice free area of *c.* 400 km^2 bounded by the Antarctic ice plateau and the Sørsdal Glacier. The proximity of Davis to biological communities, including penguin colonies, geological, glacial and periglacial features, fjords, islands, and a diversity of lacustrine environments make it a key location for Australian Antarctic research. Davis Station is normally occupied over winter by 20–30 personnel. During the austral summer (November–March) the population may reach 100 which includes seasonal scientific parties and summer construction personnel (Antarctic Division 1993). There are a number of sites at Davis which constitute 'point source' contamination risks. These include the sewage treatment plant, the fuel storage depot, refuelling stations and the power generation plant.

All human waste and wastewater from the new station complex at Davis receives primary and secondary treatment before discharge through an outfall pipe into the sea close to the shoreline. The sewage treatment plant was completed in the summer of 1990/91. Prior to 1990, solid waste was disposed of onshore by combustion. The optimum population size served by the installation is *c.* 60 persons (Antarctic Division 1993). There is potential for sewage contamination in Davis Bay due to mechanical breakdowns and the propensity of the system to be overtaxed in summer.

Electrical power at Davis Station is provided by four diesel motors coupled to 125 KVA generators. These are fuelled by Special Antarctic Blend (SAB) distillate which, due to high fuel consumption, constitutes the greatest potential source of hydrocarbon contamination at Davis. The storage capacity of SAB is 10^6 litres and fuel consumption in the past four years has been between 6.6 and 7.5×10^5 l y^{-1}. Other fuels used at Davis include; unleaded fuel and aviation turbine kerosine (helicopters). A range of oils and greases are also used. The use of fuels, oils and greases produces a risk of potential direct release of hydrocarbons into the environment as well as indirectly through incineration and exhaust emissions which are a source of polycyclic aromatic hydrocarbons (PAH).

Cripps (1992a) has reviewed the major marine hydrocarbon pollution incidents in the Antarctic. Although some of these incidents have caused severe localized short-term effects on biota (Kennicutt & Sweet 1992, Eppley 1992), recovery, particularly on high energy shorelines, has been shown to be rapid. Aside from the examination of major pollution events, it is only in recent years that studies have focussed on hydrocarbon and sewage pollution resulting from routine operations at Antarctic stations (Cripps 1992b, Kennicutt *et al.* 1992, Venkatesan & Mirsadeghi 1992, McFetters *et al.* 1993). The aim of this study is to identify, by use of particular hydrocarbon and sterol biomarker compounds, the extent of

existing contamination at the 'point source' risk sites at Davis Station and to provide a basis on which future monitoring of pollutants or assessments of the state of the environment can be based. The study also includes analysis of elephant seal (*Mirounga leonina*) and Adélie penguin (*Pygoscelis adeliae*) faeces for sterols. This was undertaken to more precisely elucidate the source of the faecal sterol coprostanol in the marine environment at Davis Station.

Sampling and methods

Sample collection

Sediment samples were collected in the austral summer of 1992–93 at point sources around Davis Station. Marine sediments were collected adjacent to the sewage outfall at Davis Bay, on a transect from the outfall for 200 m, and at various other locations in the bay and on the shoreline (Fig. 1). The shallow water depth of the nearshore environment at Davis enabled marine sediments to be collected manually with a scoop. A sample of sewage effluent was taken directly from the outlet pipe of the treatment plant. Surface soil samples were collected from the fuel storage depot and at 50 m intervals towards the coast (Fig. 1). The collection area was downwind from the generator plant to detect the presence of any combustion derived hydrocarbons in the environment. All samples were stored in glass jars at -20°C and returned to Australia for analysis.

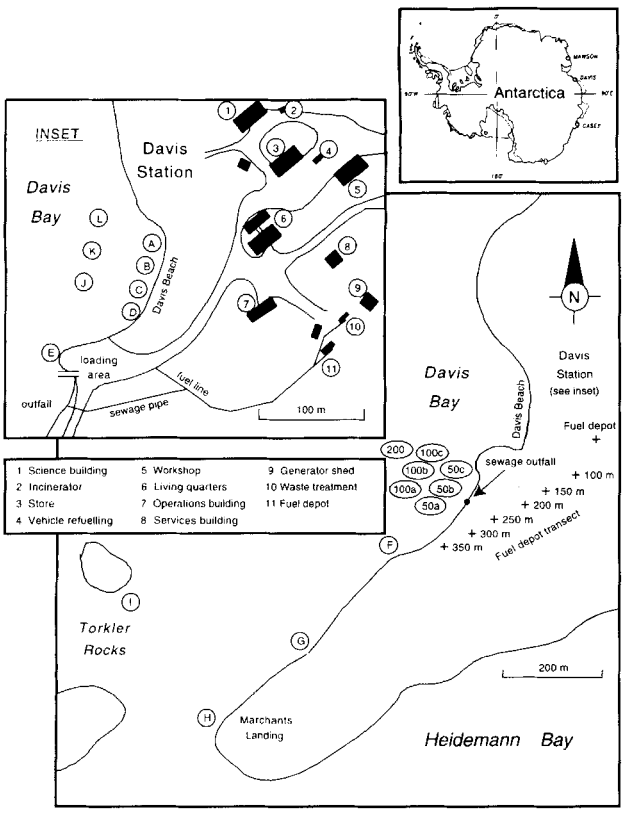

Fig. 1. Map of Davis Station and local area showing sampling locations.

Sample analysis

Samples were extracted by the modified one-phase $CHCl_3$-MeOH Bligh and Dyer method (Bligh & Dyer 1959, White *et al.* 1979). Hydrocarbons were fractionated by column chromatography using silica (2.5 g) and alumina (1 g). The elution sequence was: hexane (35 ml) (aliphatic hydrocarbons) followed by dichloromethane (40 ml) (PAH). The aliphatic fraction comprised alkanes, alkenes, isoprenoids, linear alkyl benzenes (LABs) and hopanes. The PAH fraction contained a range of compounds from the two-ring naphthalenes to six ring compounds such as benzo (ghi) perylene.

An aliquot of the total lipid was saponified to obtain the sterol fraction (Nichols & Espey 1991). Prior to analysis by gas chromatography, sterols were converted to their corresponding trimethylsilyl ethers by treatment with bistrimethylsilyltrifluoracetamide (50 μl, 60°C, 60 min).

Gas chromatography (GC) and GC-Mass spectrometry (GC-MS)

Gas chromatographic analyses were performed with a Hewlett Packard 5890 GC equipped with a 50 m × 0.32 mm i.d. HP1 fused-silica capillary column (0.17 μm film thickness) using splitless injection and flame ionization detection. The initial GC oven temperature was 50°C which, after 1 min, was ramped to 150°C at 30°C min^{-1}, to 250°C at 2°C min^{-1} and to 300°C at 5°C min^{-1}. Hydrogen was used as the carrier gas, and the injector and detector were maintained at 290 and 310°C respectively. Peak areas were quantified using chromatography software (DAPA Scientific Software, Kalamunda, Western Australia). The internal injection standard used was a C_{23} fatty acid methyl ester.

GC-MS analyses were performed on an HP 5890 GC and 5970 Mass Selective Detector (MSD) fitted with an HP1 capillary column and a split/splitless injector operated in splitless mode. The column, injector and chromatography conditions were similar to those described above. Identifications were confirmed by comparison of mass spectra with those of previously reported spectra and by comparison of retention time data with data obtained for commercial and previously identified laboratory standards.

PAH were analysed in selected ion monitoring (SIM) mode and quantified by relating chromatogram peak area to external standard calibration curves (24 component mixture) obtained for standards run in the same batch. The detection limit for individual PAH was 0.1 ng. An internal standard was co-injected with PAH samples to aid in compound identification. This standard was composed of deuterated PAH to prevent co-elution with, and potential masking of, PAH in samples.

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Results and discussion

Sterols

A selection of samples and sediments from near Davis Station have been analysed for sterols primarily to determine the extent of sewage pollution emanating from the outfall into the bay. Sterols such as coprostanol, epi-coprostanol and 5β-ethylcoprostanol can be used as indicators of sewage pollution. The presence of these sterols at different relative concentrations can be diagnostic of mammalian faecal waste (Venkatesan & Santiago 1989). There are three documented sources of coprostanol and epi-coprostanol in the Antarctic marine environment: i) human faeces (e.g. this study and Venkatesan & Mersadeghi 1992); ii) marine mammalian faeces, particularly whales, (Venkatesan & Santiago 1989) and iii) *in situ* formation in reducing environments such as anoxic bottom waters of fjords (Green *et al.* 1992, Nishimura 1989). In addition to coprostanol and epi-coprostanol, other sterols can be used to fingerprint the presence of detrital material from zooplankton and various classes of phytoplankton in sediments.

The highest concentrations of sterols in sediments were found at Davis Beach (up to 119 $\mu g\ g^{-1}$; Table I). The lowest concentration of sterols (0.46 $\mu g\ g^{-1}$; Table II) was at site I, the most distant sample location, 1 km south-west of Davis Station. The sterol content was much higher than concentrations found previously in Antarctica, for example; Bransfield Strait, 0.15–0.42 $\mu g\ g^{-1}$ (Venkatesan *et al.* 1986);

Table I. Sterol content and composition of Davis sewer effluent, Davis shoreline sediments and elephant seal faeces.

Sterol	Common name	Peak number*	Sewage tank	Sewage outfall	Sample sites A	B	C	D	E	Elephant seal faeces	Adélie penguin faeces
Composition (% of total sterols)											
5β-cholestan-3β-ol	coprostanol	2	60.5	60.3	6.3	3.9	4.2	0.5	4.0		
5β-cholestan-3α-ol	epicoprostanol	3	3.7	1.8							
cholest-5-en-3β-ol	cholesterol	5	18.1	13.6	92.3	94.1	95.1	97.0	92.5	> 99	> 99
5α-cholestan-3β-ol	cholestanol	6	2.7	4.1	1.4	1.9	0.7	2.5	3.6	tr	
5β-ethylcholestan-3β-ol	5β-ethylcoprostanol	9	12.4	14.6							
24-ethylcholest-5-en-3β-ol	24-ethylcholesterol	10	2.6	2.6							
Total sterol content ($\mu g\ g^{-1}$)**			1926***	21.8	32.8	52.2	119	43.6	3.80	3900	
Coprostanol content ($\mu g\ g^{-1}$)**			1166***	13.2	2.06	2.04	4.98	0.22	0.15		

* Peak numbers refer to Fig. 2. ** Dry weight of sediment *** $\mu g\ l^{-1}$

Table II. Sterol content and composition of Davis Bay sediment samples.

Sterol	Common name	Peak number*	Sample location 50a	50b	50c	100a	100b	100c	200	F	G	H	I	J	K	L
Composition (% of total sterols)																
24-norcholesta-5, 22E-dien3β-ol	24-norcholesterol	1								1.2	2.1	5.4	tr	tr	1.2	1.2
5β-cholestan-3β-ol	coprostanol	2	2.7	1.8	3.3	3.1	1.4	4.6	3.6	tr	tr	0.3		2.9	4.7	1.5
5β-cholestan-3a-ol	epicoprostanol	3	tr			tr	tr	tr	tr							
cholestα-5, 22E-dien-3β-ol	trans-22-dehydrocholesterol	4	13.9	14.8	14.5	33.6	27.6	27.9	21.2	24.3	13.3	22.8	10.5	13.8	13.1	15.3
5α-cholest-22E-en-3β-ol	trans-22-dehydrocholestanol		5.3	2.7	4.1	6.7	5.2	7.3	4.7	1.5	2.2	1.0	4.4	7.9	8.6	6.1
cholest-5-en-3β-ol	cholesterol	5	31.2	30.8	23.1	8.2	8.0	7.1	10.9	24.8	37.9	36.0	24.0	11.1	13.2	10.8
5α-cholestan-3β-ol	cholestanol	6	9.6	6.2	9.1	5.1	4.4	4.7	5.4	9.1	8.3	2.6	11.1	9.7	10.3	10.6
24-methylcholesta-5, 22E-dien-3β-ol	brassicasterol	7	7.6	9.4	4.7	6.6	5.0	5.8	8.0	4.2	5.1	8.3	10.6	6.1	6.2	6.9
24-methylcholesta-5, 24,28-dien-3β-ol	24-methylenecholesterol	8								6.2	7.0	12.0	9.1	7.1	5.4	5.2
23,24-dimethylcholesta-5,22E-dien-3β-ol			4.7	6.7	9.8	22.6	20.7	13.7	8.6	4.6	2.1	1.1		11.3	10.6	13.7
24-ethylcholest-5-en-3β-ol	24-ethylcholesterol	10	10.3	11.5	12.2	2.4	2.1	3.8	6.7	3.5	5.8	4.0	16.6	12.9	9.7	9.7
4, 23, 24-trimethylcholest-22E-en-3β-ol	dinosterol	11	3.6	2.3	3.1	1.9	1.6	1.6	2.0	0.8	1.6	0.8	tr	2.9	2.2	2.6
Others			11.1	13.9	16.2	9.6	24.0	23.6	29.0	19.8	14.7	5.8	13.8	14.3	14.8	16.5
Total sterol content ($\mu g\ g^{-1}$)**			2.08	2.68	1.94	28.6	28.4	6.48	2.42	12.3	6.10	14.6	0.46	3.06	9.32	4.16
Coprostanol content ($\mu g\ g^{-1}$)**			0.06	0.04	0.06	0.88	0.04	0.30	0.09	tr	tr	0.04		0.08	0.44	0.06

* Peak numbers refer to Fig. 2. ** Dry weight of sediment tr - trace amount

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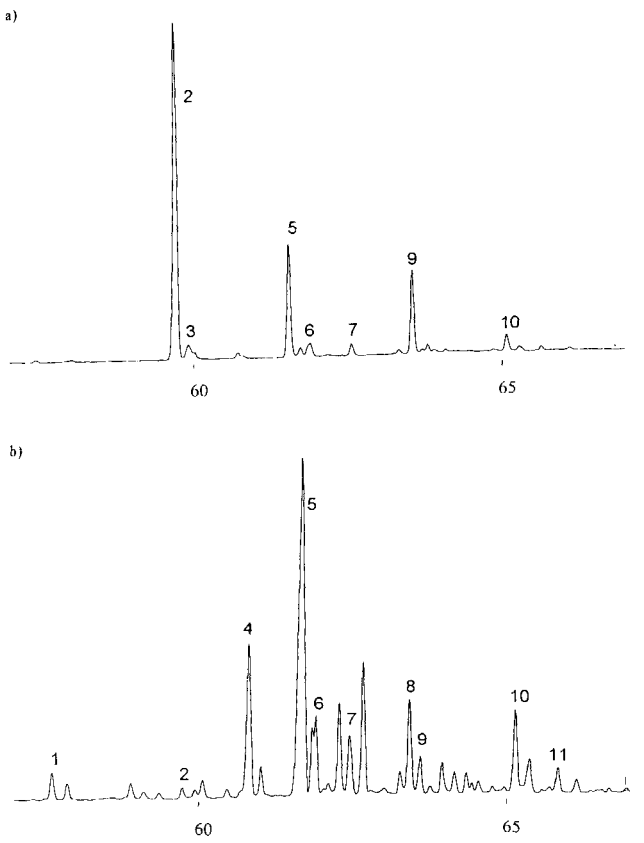

Fig. 2. Partial gas chromatograms (TMSi derivatized sterols) showing: **a.** sterol profile from Davis shoreline sewer outfall sediment sample and; **b.** sterol profile from Davis Bay sediment sample G. Key to sterols: 1. 24-norcholesterol; 2. coprostanol; 3. epicoprostanol; 4. trans-22-dehydrocholesterol; 5. cholesterol; 6. cholestanol; 7. brassicasterol; 8. 24-methylenecholesterol; 9. 5b-ethylcoprostanol; 10. 24-ethylcholesterol; 11. dinosterol.

McMurdo Sound, 0.40–8.0 μg g^{-1} (Venkatesan 1988); Vestfold Hills, 1.0–16.2 μg g^{-1} (Skerratt 1992).

There were two distinct sterol profiles. The first were dominated by coprostanol and/or cholesterol (Table I; Fig. 2a) and were found in sewage outfall sediments, shoreline sediments and faeces from wildlife. The second was found in sediments from Davis Bay and had profiles dominated by algal sterols (Table II; Fig. 2b).

Davis shoreline sites

The sterol composition of sediment at the Davis sewer outfall was similar to that of the sewage digester tank (Table I). The faecal sterol coprostanol was dominant (13.2 μg g^{-1} dry weight). The co-occurrence of epi-coprostanol (1.8%) at the Davis sewer outfall was typical of the amount found in human faecal waste. The sterol 5β-ethyl coprostanol (14.6%; Table I) was also present in human sewage. The concentration of coprostanol in sewage sludge is typically 1000 μg g^{-1}, and in grossly contaminated sediment 9 μg g^{-1} (Nichols & Leeming 1991). The concentration of coprostanol found in this study was much lower than that found at the McMurdo sewage outfall (up to 3000 μg g^{-1}, Venkatesan & Mersadeghi 1992) which represented the impact of raw sewage effluent from about 1000 people. Compared to McMurdo Station, the disposal of sewage at Davis has only occurred since 1991 prior to which it was burnt.

Coprostanol was present at high levels in the shoreline sediment, in particular at site C (5.0 μg g^{-1}, Table I). As coprostanol was not detected in analysis of elephant seal (*Mirounga leonina*) faeces or Adélie penguin (*Pygoscelis adeliae*) faeces, the presence of this stanol on the Davis Station shoreline and at sites up to 1 km from the station, is due solely to human contamination.

At sites A to E from Davis Beach, cholesterol was the dominant sterol (92–97% of total sterols, Table I). The occurrence of cholesterol at high concentrations in the shoreline sediments probably originated from faeces of elephant seals and Adélie penguins. This is supported by analysis of faeces from these animals, both of which have a sterol composition consisting almost entirely of cholesterol (> 99%, Table I).

Davis Bay sediments

The sterol profiles in Davis Bay sediments were dominated by cholesterol, trans-dehydrocholesterol, 23, 24-dimethyl-cholesta-5, 22E-dien-3β-ol, 24-ethylcholesterol and cholestanol (Table II; Fig. 2b). This sterol profile indicated input primarily from algae. The sterols 24-norcholesterol, dehydrocholesterol, cholesterol, brassicasterol, 24-methylenecholesterol, 24-ethylcholesterol and dinosterol have been reported as components in Antarctic sea-ice diatoms (Nichols *et al.* 1989). The small amount of dinosterol in all the samples probably originated from dinoflagellates. Coprostanol was detected in 13 of 14 sediments collected from Davis Bay. The highest concentrations of coprostanol in the bay (0.30–0.88 μg g^{-1}) were found at sites that were 100–200 m distant from the sewage outfall (Table II). The co-occurrence of coprostanol with trace amounts of epi-coprostanol suggested that sewage contamination extended at least 200 m offshore into Davis Bay.

Aliphatic hydrocarbons

The aliphatic hydrocarbon concentrations in sediments from Davis Bay were in the range 0.25–9.0 μg g^{-1} (Table IV). These concentrations were similar to those previously reported for *n*-alkanes in Antarctic marine surface sediments (0.06–9.3 μg g^{-1}; Cripps 1992a) and were lower than a very localized and high level of contamination adjacent to the

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wharf at McMurdo Sound (4500 $\mu g\ g^{-1}$; Lenihan *et al.* 1990). In a study of hydrocarbon contamination at Signy Station, South Orkney Islands, Cripps (1992b) found levels of *n*-alkanes at 0.04–1.7 $\mu g\ g^{-1}$ in marine surface sediments.

There were also differences noted in the aliphatic hydrocarbon profiles. As for the sterols, the shoreline sediments contained compounds attributable to human activity and sediments from Davis Bay were dominated by biogenic compounds.

Hydrocarbons from shoreline sediment

The *n*-alkane series from the Davis shoreline sediments shows a maximum at nC_{17} (Fig. 3a). The *n*-alkane series and presence of the isoprenoid hydrocarbons pristane and phytane in all the shoreline sediments was characteristic of a degraded light fuel.

The hydrocarbons from the shoreline sediment, though at low levels, were probably derived from Special Antarctic Blend (SAB) fuel. SAB is composed mainly of low molecular weight hydrocarbons, nC_8-nC_{16} alkanes. Loss of the *n*-alkanes nC_8-nC_{15} (a major proportion of SAB fuel) from sediment adjacent to the fuel storage depot demonstrates that, in the short term, this fraction of the fuel is almost completely evaporated, even under conditions of extreme cold. A previous study of the degradation of SAB fuel in Antarctica (Green 1992) showed a similar result and demonstrated loss of short-chain hydrocarbons by volatilization within 30 days.

The pristane to phytane ratio in SAB for fuel residues found in soils and sediments at Davis Station was between 3.5 and 6.7 compared to 15 for SAB fuel. This change may be due to preferential degradation of pristane by physical/abiotic processes as previously found in marine sediments (see Barrick *et al.* 1980).

The presence of trace amounts of hopanes in the shoreline sediments was further evidence that petroleum contamination

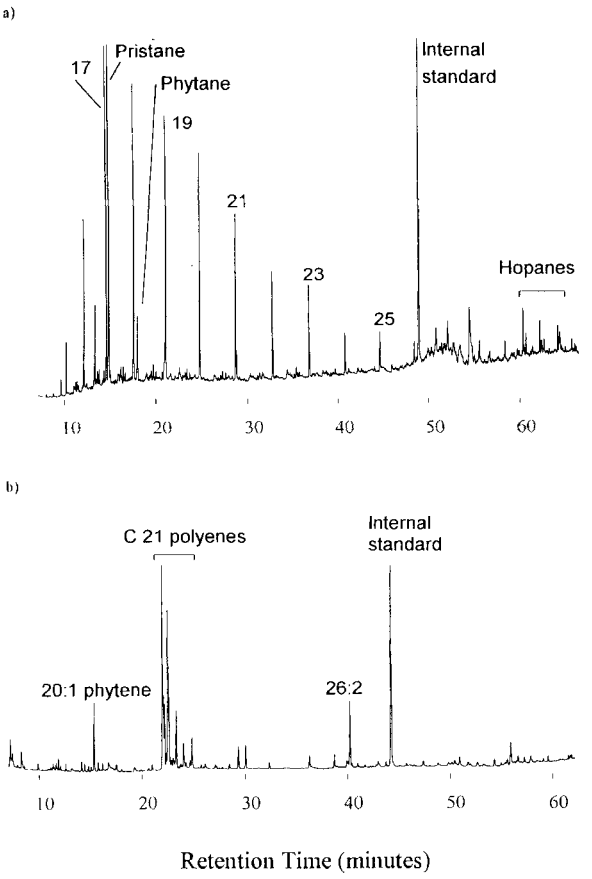

Fig. 3. Partial gas chromatograms showing: **a.** representative aliphatic hydrocarbon profile from Davis Beach sediment sample E and; **b.** representative aliphatic hydrocarbon profile from Davis Bay sediment sample L. Numbers adjacent to peaks indicate alkane carbon chain length.

Table III. Hydrocarbon content and composition of Davis sewer effluent and Davis shoreline sediments.

			Sample				
	Sewage tank	Sewage outfall	A	B	C	D	E
Hydrocarbon content ($\mu g\ g^{-1}$)*	370**	5.46	3.24	1.10	2.69	1.00	1.49
Hydrocarbon composition (%)							
n-alkanes	31.8	30.2	69.0	32.6	30.0	78.9	65.9
linear alkyl benzenes (LABs)	11.3	9.4					
pristane	0.5	3.9	9.2	5.7	8.2	7.9	12.2
phytane	tr	tr	1.8	2.1	2.2	3.4	2.9
pristane/phytane			5.1	2.7	3.7	2.3	4.2
21:2 alkene			0.9	1.3	6.9	tr	
squalene	31.5	37.7		23.7	23.7		
norhopanes	tr	tr	tr	tr	tr	tr	tr
Other compounds	24.9	18.8	19.1	34.6	29.0	9.8	19.0

* Dry weight of sediment ** $\mu g\ l^{-1}$ tr - trace amount

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had occurred at these locations. Hopanes are ubiquitous constituents of crude oil and ancient rock and from these sources occur in thermodynamically stable forms (Barrick & Hedges 1981). Hopanes were identified by the base peak ion (m/z 191) in the mass spectra of these cyclic hydrocarbons (Jones *et al.* 1986). Hopanes and steranes are used as crude oil markers as they are resistant to weathering and bacterial oxidation. The hopane distribution was similar to that of a widely used lubricating oil (Volkman *et al.* 1992).

The source of the hopane series of shoreline sediments at Davis was probably SAB fuel which contains a similar series of hopanes. In both sediments and SAB fuel the hopane trace was weak and steranes were not detected. This indicated that the source of the hopanes was a refined product containing very few residual hopanes. The absence of a significant unresolved complex mixture (UCM) of hydrocarbons in chromatograms from shoreline sediments also suggests that a light fuel rather than an oil was the source of the hopanes.

The hydrocarbons in shoreline sediments may be derived from land run-off or from small spills during ship to shore fuel transfer. Depending upon the sea ice conditions, fuel is transferred ashore either by pipeline or by barge. In recent years the pipeline and its couplings deteriorated to the point where it leaked fuel on many occasions when it was used. Other potential contamination sources were vehicles used for cargo loading and unloading operations, periodic discharge of effluent containing petroleum from the wastewater system and leaching from fuel spills onshore.

The aliphatic profiles indicate that the discharge from the sewerage system is not the predominant source of hydrocarbons on the shoreline at Davis. The aliphatic hydrocarbon distribution for sewage effluent showed the residue of a light fuel. Also present were nC$_{22}$-nC$_{32}$ alkanes associated with a small UCM which was indicative of the presence of fuel oil in the effluent. Squalene, which can be a major component in sewage effluent and is believed to be derived from skin lipids, was the most dominant hydrocarbon in the station sewage effluent (31.5%; Table III). The maximum level of squalene was 37.7% and at two locations on Davis Beach was 23.7% (Table III). Squalene was also found in nearshore sediments (trace-2.2%; Table IV).

Linear alkyl benzenes (LABs with C_{11} to C_{14} side chains) derived from sewage effluent at Davis, were detected in the aliphatic hydrocarbon fraction of the sediment at the sewer outfall site (Σ LABs 9.4%; Table III). LABs have been previously reported in sewage effluent at Davis Station (31% of hydrocarbons; Green *et al.* 1992). LABs are manufactured during the production of the linear alkyl benzenesulphonate surfactants used in commercial detergents (Eganhouse *et al.* 1983). Their appearance in wastes results from incomplete sulphonation of the LABs and they are subsequently found in detergents. The ability of LABs to be preserved in the marine environment for up to 20 years (Eganhouse *et al.* 1983) suggests they are potential tracers for domestic and industrial waste in the marine environment. In Davis Bay, LABs were below the detection limits at all sites remote from the sewage outfall.

Hydrocarbons from Davis fuel storage depot

Compared to sediments from the marine environment, relatively high levels of n-alkanes were detected at the Davis fuel depot (87–220 μg g^{-1}; Table V). These levels were lower than concentrations found at Signy Station, South Orkney Islands in soils heavily loaded with diesel (1220 μg g^{-1}; Cripps 1992b). A study by Kennicutt *et al.* (1992) also found high concentrations of n-alkanes at 4.2–2300 μg g^{-1} in contaminated soils at Palmer Station on the Antarctic Peninsula. Along a transect (350 m to the south-west) from the Davis fuel depot (Fig. 1), hydrocarbon levels in soils were comparitively low (0.24–1.2 μg g^{-1}; Table V) and similar in composition to those detected on the Davis shoreline (Table III). The source of contamination was probably from spillage or leakage from the fuel depot, use of SAB fuel at the station or from leaks in the fuel pipeline. The spread of these hydrocarbons throughout the station soils is probably by melt-water flow during the

Table IV. Hydrocarbon content and composition of Davis Bay sediments.

	Sample													
	50a	50b	50c	100a	100b	100c	200	F	G	H	I	J	K	L
Hydrocarbon content (μg g^{-1})*	0.26	0.39	0.38	9.04	10.1	5.28	1.64	2.02	0.46	0.61	0.25	4.03	6.44	2.51
Hydrocarbon composition (%)														
n-alkanes	24.1	23.3	16.5	tr	tr	tr	tr	8.6	16.2	14.7	9.5	7.8	5.4	8.4
20:1 phytene	1.2	0.7	2.7	3.4	5.5	7.5	4.7	0.9	2.5	0.9	2.4	19.7	34.9	12.5
polyenes (C_{21})	47.1	40.9	32.2	67.8	74.8	69.5	62.8	78.1	57.4	63.1	55.2	27.2	17.8	42.3
$C_{26:2}$ alkene	5.1	3.7	14.6	1.4	1.8	2.2	5.9	1.9	3.1	5.8	3.2	5.7	4.9	7.9
squalene				tr	tr	1.6	1.7					1.8	1.5	2.2
mono aromatic steroid (C_{29})				1.4	1.2	2.8	2.9					2.8	1.6	4.0
Other compounds	22.5	31.4	34.0	26.0	16.7	16.4	22.0	10.5	20.8	15.5	29.7	34.8	33.9	22.7

* Dry weight of sediment tr - trace amount.

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Table V. Hydrocarbons in Davis soil samples.

Sample	Hydrocarbons ($\mu g\ g^{-1}$ dry wt.)	Most abundant *n*-alkane
Fuel depot 1	220	C 17
Fuel depot 2	87	C 16
100 m	0.74	C 18
150 m	0.80	C 18
200 m	0.92	C 18
250 m	1.20	C 20
300 m	1.20	C 20
350 m	0.24	C 18

summer months.

There was a trend of a greater degree of hydrocarbon weathering (loss of low molecular weight compounds) with increasing distance from the fuel depot. This can be seen in the *n*-alkane profile. The dominant *n*-alkanes in soils at the depot were nC_{16}-nC_{17}, whilst towards the coast nC_{18}-nC_{20} were predominant (Table V).

Hydrocarbons in Davis Bay sediments

The dominance of nC_{21} polyenes in sediments from Davis Bay (Table IV; Fig. 3b) was indicative of micro-algal input. Unsaturated odd-carbon numbered alkenes, particularly $nC_{21:6}$ (heneicosahexaene) which was probably derived from the corresponding docohexaenoic acid, predominate in some marine phytoplankton species (Blumer *et al.* 1971). This alkene has previously been found as a major component in Antarctic sea-ice diatoms (Nichols *et al.* 1989).

Other alkenes detected in Davis Bay sediments included a phytene, a C_{26} diene and brace levels of C_{25} isoprenoid alkenes. Phyt-1-ene was detected in most sediments from Davis Bay including at up to 35% of the total hydrocarbons at site K (Table IV). Phytenes are produced from bacterial and chemical degradation of naturally occurring lipids (Volkman *et al.* 1992). The C_{26} diene was detected in all the sediments collected from Davis Bay at levels between 1.4–14.6% of the total alkanes (Table IV). This finding was unusual as, with the exception of $nC_{21:6}$, alkene hydrocarbons reported from algal lipids are generally monounsaturated with carbon chain-lengths in the range C_{15}–C_{21} (Volkman *et al.* 1980). The precise source of the C_{26} diene is not known, however the hydrocarbon and sterol profiles observed suggest marine algae.

Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAH) are generally considered as indicators of contamination from anthropogenic sources. Apart from minor contributions from bacteria and microalgae, PAH are not known to be synthesized by organisms (Saliot 1981). The presence of PAH may be attributed to both petrogenic and pyrogenic sources. Domination of unsubstituted compounds over their alkyl-substituted derivatives suggests a pyrogenic origin for PAH. A petroleum source would be favoured when substituted derivatives dominate (Kayal & Connell 1989). As many PAH are potential carcinogens and mutagens, there is concern about their occurrence in the environment (Smith 1990).

PAH were present throughout the environment at Davis both in soils and marine sediments. The PAH consisted primarily of naphthalenes, fluorenes and phenanthrenes which were also present in trace amounts in SAB fuel. Kennicutt *et al.* (1992) found the same PAH derived from diesel fuel as major contaminants at Palmer Station on the Antarctic Peninsula. The concentrations of PAH in the environment at Davis were very low and close to the limits of detection. Only at the fuel depot and sewage outfall did the concentration of individual PAH exceed 1 $ng\ g^{-1}$. This was in contrast to the findings of Kennicutt *et al.* (1992) who detected up to 51.3 ppm ($\mu g\ g^{-1}$) of naphthalenes in soils at Palmer Station.

The major combustion derived PAH detected in the environment at Davis were benzofluoranthene, fluoranthene, pyrene, benzoanthracene and indenopyrene. These PAH were also present in soils in sub $ng\ g^{-1}$ amounts. The findings indicate that there was no serious contamination from these compounds in soils and sediments sampled at Davis Station. PAH produced by fuel combustion at Davis appear to be well dispersed by aeolian and fluvial processes.

Conclusions

Analysis of coprostanol in sediments, beach sands, and seal and penguin faeces in Davis Bay indicates that human sewage contamination has accumulated to relatively high levels near the sewage outfall. The levels of coprostanol were, however, significantly lower than in sediments in an environment receiving untreated sewage from McMurdo Station. This comparison demonstrates the significance and importance of secondary treatment of effluent in Antarctica. Coprostanol was detected at shoreline sites up to 1 km from the sewage outfall. This work sets background levels from which to gauge any future accumulation of sewage derived material in the marine environment at Davis Station. Anthropogenically derived hydrocarbons were present in soils and the marine environment at Davis, however, levels are lower, particularly for PAH, than in reports for contaminated soils in studies from elsewhere in Antarctica. This finding suggested that the Special Antarctic Blend refined fuel used at Davis contains significantly lower levels of PAH than fuels used in some other areas of Antarctica, and hence is more suitable for use than other fuels in the sensitive and nearly pristine environment of Antarctica.

Measures are currently in place to address the contamination risk from the fuel storage depot at Davis. Containment structures which will hold fuel in the event of a spill are scheduled for installation in 1995. Improved valve functions as well as spill and leak detection facilities are also proposed

(Antarctic Division 1993). The pipeline used for ship to shore fuel transfer has recently been repaired and its condition is now monitored (Antarctic Division 1993). The implementation of management strategies and particularly the installation of containment bunding for fuel storage facilities can only help to minimize possible future contamination at Davis Station.

Acknowledgements

This study was supported by The Antarctic Scientific Advisory Committee (ASAC). Graham Green acknowledges financial support from a University of Tasmania Ph.D. scholarship. Tom McMeekin and Harry Burton are thanked for their initial guidance and continuing support to the project. We thank Jennifer Skerratt, David Nichols and Jo-Anne Cavanagh for help and support with field work; fellow ANARE personnel for their assistance at sea and on base; Andrew Revill, Liz Sikes and Patrick Deprez for comments during manuscript preparation; Geoff Cripps, John Shears and Mahlon C. Kennicutt II for detailed review suggestions. Michael Bessell and Kelvin Michael helped with the preparation of figures.

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