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POLYCYCLIC AROMATIC HYDROCARBONS IN FUEL-OIL CONTAMINATED SOILS, ANTARCTICA

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ABSTRACT

Where fuel oil spills have occurred on Antarctic soils polycyclic aromatic hydrocarbons (PAH) may accumulate. Surface and subsurface soil samples were collected from fuel spill sites up to 30 years old, and from nearby control sites, and analysed for the 16 PAHs on the USEPA priority pollutants list, as well as for two methyl substituted naphthalenes, 1-methylnaphthalene and 2-methylnaphthalene. PAH levels ranged from 41-8105 ng g^{-1} of dried soil in the samples from contaminated sites and were below detection limits in control site samples. PAH were detected in surface soils and had migrated to lower depths in the contaminated soil. The predominant PAH detected were naphthalene and its methyl derivatives. © 1999 Elsevier Science Ltd. All rights reserved

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INTRODUCTION

Antarctica is one of the largest and most pristine wilderness areas left on earth. The main human activities in this area are scientific research, tourism and fishing, and all of these activities require fuels for transport and energy. As marine and ice-free regions are considered particularly vulnerable to oil contamination, petroleum hydrocarbons are potentially the most likely source of pollution in the Antarctic [1]. While there have been a number of investigations of hydrocarbon contamination in marine ecosystems in the Antarctic [2, 3, 4] very little is known about the impact of hydrocarbons on land.

Accidental fuel spills on land occur mainly near scientific stations where storage and refuelling of aircraft and vehicles can result in spills [1]. Fuel spills have been reported at McMurdo Station [5], Marambio Base [6] and Faraday Research Station [4]. Oil contamination of soil was also a consequence of the Dry Valley Drilling Project [7]. Generally the areas contaminated by terrestrial fuel spills are localised; however runoff, from soil has contaminated sub-tidal sediments [8]. Petroleum hydrocarbons have been detected in soil from McMurdo Station [5], Scott Base, the former Vanda Station and the old Marble Point camp site within the McMurdo Dry Valley Region (Figure 1) [9], and in soil from around the H. Arctowski Polish Station [10] and Palmer Station on the Antarctic Peninsula [8]. The more toxic polycyclic aromatic hydrocarbons (PAH) have been shown to accumulate in soils from Palmer Station [8] and Grytviken Whaling Station [1] in the Antarctic Peninsula Region.

Chemical characterisation of the hydrocarbon contaminants in soils from Scott Base has identified both *n*-alkanes and aromatic compounds with less than three rings [9]. In this study we determined the PAH content of fuel oil-contaminated soils and nearby control soils from three locations within the McMurdo Dry Valley Region (Figure 1): around Scott Base, Marble Point and the Wright Valley near Lake Vanda.

MATERIALS AND METHODS

Soil collection

Soil samples for PAH analysis were selected from around an operational scientific research station, Scott Base and the site of two former facilities at Marble Point and the Wright Valley near Lake Vanda (Figure 1). Soils in the Scott Base area have been impacted as a result of establishment and habitation of the base. Two hydrocarbon-contaminated sites were sampled: a storage area for drums of engine oils, and an area beneath the generator room. At Marble Point, the soil sampled was situated near the old Marble Point camp [11] which was inhabited from 1957 to about 1963. Oil stains were visible on the surface of the soil and it is assumed that they have been there for over 30 years. The surface soil samples selected for analysis from the Wright Valley came from the site of the former Vanda Station [12], where oil stains were visible on the soil surface. Descriptions of the soils are given in Balks et al. (1998) [13]. Using a sterile trowel, soil samples were taken from a range of depths at Scott Base and Marble Point and from the surface at the Vanda station site. In addition, control surface soil samples were collected at least 30 m from contaminated areas. For PAH analyses approximately 50 g of soil was placed in tin cans, and stored at room temperature until analysis in New Zealand.

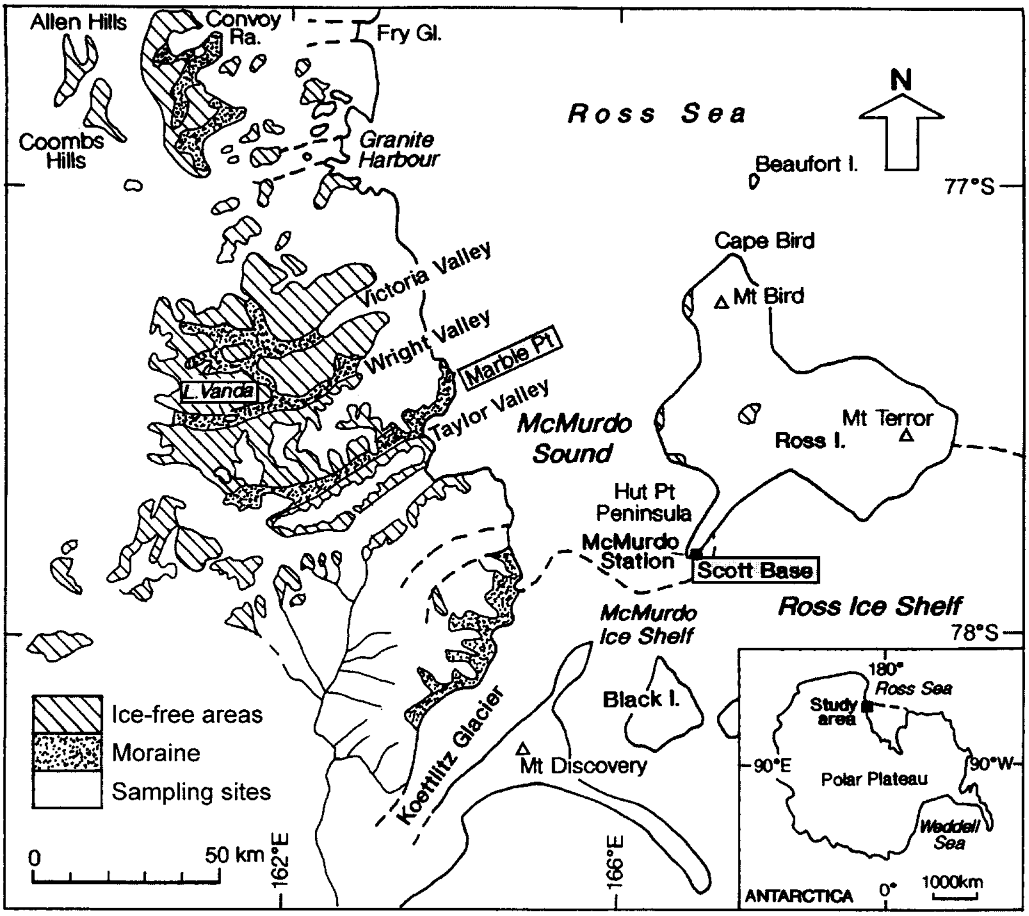

Figure 1. Map of the McMurdo Sound - Dry Valley Region of Antarctica

Polycyclic Aromatic Hydrocarbon Determination

Soil samples (10 g) were weighed and placed into cleaned 22 mL stainless steel extraction vessels and spiked with a range of deuterated PAH surrogate standards. Extractions were performed using a Dionex ASE-200 Accelerated Solvent Extractor (ASE™) . Approximately 25mL of acetone:hexane (1:1) was used for each sample with the method allowing for a heating period of 5 minutes followed by a static extraction of 5 minutes at 1500 psi and 150°C. After this cycle, fresh solvent was added to the cell and a second static extraction was initiated to complete the extraction. Total time for a single sample was about 30 minutes. Extracts were loaded onto a 5 g silica chromatography column and rinsed with hexane then eluted with hexane:dichloromethane (1:1).

The final volumes of the extracts were reduced under controlled conditions using a Zymark Turbovap™ concentrator at a temperature of 38°C and using a clean dry nitrogen gas supply. A recovery spike of d_{10}-Anthracene was added just before analysis by gas chromatography-mass spectrometry (GC/MS).

GC/MS analyses were carried out on a Hewlett Packard (HP5890 II GC, HP5972 Mass Selective Detector) system equipped with a J&W DB5-MS capillary column (30 m, 0.25 mm I.D. 0.25 μm film thickness). A splitless injection of 2μL was performed with an injector temperature of 270°C and an initial helium pressure of 15 psi. The oven temperature program was 50°C for 2 min, heating to 130°C at 45°C min^{-1} then 270°C at 15°C min^{-1}. Transfer line was set at 290°C. A constant flow of 1.0 mL min^{-1} was maintained throughout the run. MS data was acquired over the range 40 to 450 amu.

Identification of the PAH and alkylated PAH was carried out using authentic PAH standards and comparing their retention times and the response of characteristic quantification and confirmatory ions. Quantification of the amounts of PAH contained in the samples was calculated against standard calibration curves constructed for each of the PAH reported and the recoveries of the surrogate PAH compounds relative to the d_{10}-Anthracene recovery spike.

Moisture contents of the soil samples were determined by drying the soil samples to constant weight in an oven at 105°C.

RESULTS AND DISCUSSION

Analyses of soil samples confirm that polycyclic aromatic hydrocarbons accumulate in Antarctic soils where fuel oil spills have occurred. PAH levels were elevated at all the contaminated sites but were below detection limits at control sites (Table 1). The concentrations of the PAH in the soils sampled vary due to differences in the mixtures of hydrocarbons spilt, the amount spilled and the time since spillage. At the contaminated sites, PAH levels ranged from 41 to 8105 ng g^{-1} of dried soil. These levels are significantly higher than those reported for Davis Station where concentrations of PAH in soil were generally below 1 ng g^{-1} [14], and either comparable with or significantly less than those detected in Antarctic soils at Palmer Station [8] and Grytviken Whaling Station [1]. PAH were detected in surface soils and had migrated to lower depths in samples analysed from Scott Base and Marble Point. At Scott Base levels of PAH were higher in subsurface soil at both sites sampled. At the drum storage site 362 ng g^{-1} were detected in the 0-2 cm surface soil layer compared with 8105 ng g^{-1} in the 2-10 cm depth and 2543 ng g^{-1} in the 20-30 cm depth. By contrast, levels of PAH in the subsurface soils were less than that of the surface soil in the Marble Point sample. Naphthalene and the methylnaphthalenes predominated in all samples, as has been observed previously for most soils analysed around Palmer Station [8]. Eleven of the 16 PAH on the USEPA Priority Pollutant List were detected in soil from Scott Base and the Wright Valley. No samples contained the high molecular weight PAH benzo(k)fluoranthene, benzo(a)pyrene, indeno(123cd)pyrene, dibenz(ah)anthracene or benzo(ghi)perylene. However, the known carcinogens benz(a)anthracene and fluoranthene were detected [15].

Table 1: PAH content of soils (oil-contaminated and nearby control sites) collected in the Ross Dependency, Antarctica.

Location	**Scott Base**						**Marble Point**				**Wright Valley**		
Site Details	**Control Site**	**Drum Storage Site**			**Generator Site**		**Control Site**	**Former Base**			**Control Site**	**Vanda Station Spill Sites**	
Soil Depth	0-5 cm	0-2 cm	2-10 cm	20-30 cm	0-2 cm	5-15 cm	0-2 cm	0-2 cm	5-10 cm	20-30 cm	0-5 cm	0-5 cm	0-5 cm
PAH[a] (ng g^{-1} dry weight)													
1-Methylnaphthalene	<30	125	803	404	306	2820	<30	<30	<30	<30	<30	<30	299
2-Methylnaphthalene	<30	160	804	442	370	3015	<30	53	<30	<30	<30	<30	436
Naphthalene	<30	235	6858	2310	551	3571	<30	127	53	41	<30	46	244
Acenaphthylene	<30	<30	43	39	<30	43	<30	<30	<30	<30	<30	<30	137
Acenaphthene	<30	<30	203	84	52	87	<30	<30	<30	<30	<30	<30	69
Fluorene	<30	39	154	70	143	206	<30	<30	<30	<30	<30	<30	286
Phenanthrene	<30	89	113	40	425	232	<30	<30	<30	<30	<30	<30	1052
Anthracene	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	121
Fluoranthene	<30	<30	161	<30	352	38	<30	<30	<30	<30	<30	<30	482
Pyrene	<30	<30	416	<30	223	42	<30	<30	<30	<30	<30	<30	851
Benz(a)anthracene	<30	<30	38	<30	39	<30	<30	<30	<30	<30	<30	<30	59
Total of 16 USEPA Priority Pollutants	0	362	8105	2543	1844	4220	0	127	53	41	0	46	3398

[a] Levels of benzo(k)fluoranthene, benzo(a)pyrene, indeno(123cd)pyrene, dibenzo(ah)anthracene, and benzo(ghi)perylene were <30 ng g^{-1} dry weight of soil in all samples analysed.

The levels of some of the PAH detected in the soils were above the target values for the Dutch clean-up standards which range from 15-45 ng g^{-1} dry weight [16]. These target values indicate the level at which the risks of adverse effects on soil functional properties are considered to be negligible. The use of these values to indicate risks in Antarctic soils is questionable. This is because Antarctic soils occur in an environment of low precipitation and severe cold, with unique biological communities [17] and as a consequence it is difficult to predict the adverse effects PAH may cause in these soils.

When deposited on soil, PAH have a number of possible fates including volatilisation, photooxidation, bioaccumulation, leaching and microbial degradation [15]. The fate of PAH or hydrocarbons in general in Antarctic soils has been little studied. Volatilisation was considered the major mechanism for removal of fuel oil after application to an Antarctic beach [2]. As the authors measured loss of hydrocarbons from surface soils the significance of leaching of hydrocarbons into subsurface soils as a mechanism for loss may have been underestimated. We have detected PAH (Table 1) and petroleum hydrocarbons in subsurface soils [13]. Microbial degradation was not considered a major mechanism for removal of hydrocarbons from the beach sands by Green et al. (1992) [2]. However, we have detected higher numbers of hydrocarbon-degrading microbes in oil-contaminated samples when compared with control soils [9, 13], and hydrocarbon mineralisation activity has been demonstrated in fuel oil-contaminated soils from Scott Base [9] and Marble Point (unpublished). These observations provide indirect evidence that microbial degradation processes *in situ* may be a mechanism for removal of hydrocarbons, including PAH from contaminated Antarctic soils.

In addition to PAH, preliminary data (not shown) indicates that anti-icing agents were present in solvent extracts from fuel-contaminated soils. They were identified by GC/MS as either ethylene glycol or diethylene glycol monoethyl ether but not quantified.

CONCLUDING REMARKS

In conclusion, PAH can accumulate in Antarctic soils and migrate into the subsurface. Given the physical constraints of the Antarctic environment it is difficult to predict their fate. In on-going studies we will evaluate the environmental significance of contaminants in fuel-oils on Antarctic soils by determining how the biological, chemical and physical properties of Antarctic soil are modified following fuel oil spills.

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