

# Petroleum–hydrocarbon contamination and remediation by microbioventing at sub-Antarctic Macquarie Island

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## Abstract

Natural attenuation of petroleum hydrocarbons in polar and subpolar soils is limited by low nutrients, low temperatures, and water availability. This study investigated three sites contaminated with diesel fuel and the use of aeration to remediate one of the sites at sub-Antarctic Macquarie Island. These sites were of differing ages and had different soil–water regimes. The most recent spill (New Main Power House) occurred in 2002 and resulted in ~180 metric tons of highly-contaminated (~7000 mg kg<sup>-1</sup>), moderately-drained, sandy soil. An older site (<1994; Old Main Power House) comprised ~100 metric tons of moderately-contaminated (~2800 mg kg<sup>-1</sup>) water-saturated peaty soil. A third spill (<1994; Fuel Farm) contained approximately 600 metric tons of low- to moderately-contaminated (~800 mg kg<sup>-1</sup>) sandy soil. Using a hydrocarbon distribution model (NAPLANAL) we determined that non-aqueous phase liquid droplets start to form in these soils at concentrations 50–1000 mg kg<sup>-1</sup> mostly depending on organic carbon fraction. An in-field treatability evaluation with an air sparge port to increase oxygen concentration in the soils proved unsuccessful because the shallow water table and thin soil cover led to channel development. However, an easily-installed ‘microbioventing’ system, comprising many small air injecting rods, successfully aerated a wide area of soil. Field estimates of biodegradation rates under unamended aerobic conditions were ~10–20 mg kg<sup>-1</sup> d<sup>-1</sup>. When considered with results from a nutrient optimisation respiration experiment [Walworth, J., Pond, A., Snape, I., Rayner, J.L. and Harvey, P.M., 2007-this issue. Nitrogen requirements for maximizing petroleum bioremediation in a sub-Antarctic soil. Cold Regions Science and Technology, In Press.], we conclude that *in situ* bioremediation for these sites should treat the soil to a target concentration of ~200 mg kg<sup>-1</sup> in approximately 1–2 years of continual operation at ambient temperatures. This simple methodology could have useful application in the summer treatment of other waterlogged tundra soils.

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**Keywords:** Petroleum hydrocarbons; Air sparging; Bioremediation; Sub-Antarctic; Tundra

## 1. Introduction

Petroleum contamination of soil is a widespread and well recognized global environmental issue. In cold

region soils, oil and fuel spills are among the most extensive and environmentally damaging pollution problems constituting potential threats to human health and ecosystems (Snape et al., in press). There is evidence that spills are more damaging in cold regions, and that ecosystem recovery is slower than in warmer climates (AMAP, 1998; Det Norske Veritas, 2003). In

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this environment the rate of natural attenuation is very slow, and the rate of off-site migration is often relatively fast (Gore et al., 1999; Snape et al., 2006a).

Remediation of petroleum contaminated soils is much more expensive in polar and subpolar regions than in developed temperate regions. Dig-and-haul and offsite treatment is particularly expensive, with cost estimates from Antarctica being around US\$4000/metric ton, and up to US\$450/metric ton in Alaska (Filler et al., 2006; Snape et al., 2005). Such treatment is also environmentally damaging because the soil that is removed is essentially destroyed, and the underlying permafrost can be degraded. Low-cost, on-site remediation alternatives have not been widely adopted in these regions, largely because problems such as remote access, high energy costs and environmental factors must be managed to achieve accelerated clean-up. Environmental factors include low temperatures, spatially- and temporally-variable water distributions, low nutrients and soil heterogeneity. Unlike some sites closer to the poles, (Ferguson et al., 2003a,b; Walworth et al., 1999), many subpolar or polar tundra sites are primarily limited by excess rather than lack of water. Soils with high water contents typically have low oxygen diffusivities and associated low oxygen levels which, when coupled with other limitations such as low temperatures and low nutrient availability, can reduce natural biodegradation to nearly negligible rates.

Few studies have evaluated the effects of increased aeration on hydrocarbon contaminant degradation in Arctic soils, and we are aware of none in the Antarctic. Although their studies did not directly evaluate soil aeration, Reynolds et al. (1998) observed that longer hydrocarbon half-lives were associated with areas of a Fairbanks (Alaska, USA) landfarm that tended to remain saturated for longer periods after rain, indicating that poor aeration may have limited bioremediation. Similarly Yeung et al. (1997) found that the half-life of crude oil in contaminated soil was reduced from 248 to 182 days by providing aeration to a bio-treatment cell in Alberta, Canada. Research quantifying the relationship between soil oxygen levels and hydrocarbon biodegradation in cold region soils is lacking, however several studies (such as those cited above) indicate that rates of degradation may be increased by aerating oxygen limited soils. Research on biodegradation of naturally occurring organic material (NOM) in northern soils also demonstrates that degradation of these materials in wet environments is limited by lack of oxygen and can be accelerated by providing aeration (Shaver et al., 2006).

As part of a regional survey of fuel-contaminated soils in Australian Antarctic Territory and the Australian

sub-Antarctic islands, the Australian Government Antarctic Division (AGAD) has been evaluating the nature of fuel contamination and determining the remediation potential of on-site techniques. Here we report the results of our field evaluation for sub-Antarctic Macquarie Island and discuss the results of a remediation technique using ‘microbioventing’ that could benefit other subpolar contaminated sites and wet tundra soils.

## 2. Background

Macquarie Island is a World Heritage sub-Antarctic area located in the Southern Ocean approximately 1500 km south of Tasmania (Fig. 1). It is an important breeding ground and terrestrial habitat for migrating mammals and birds. Temperatures range from 3 to 8 °C. It has strong winds and an annual rainfall of 920 mm over 326 rain days. A research station is situated on a narrow isthmus at the northern extremity of the island and has an elevation < 10 m above sea level. Soils on the isthmus are derived from basalts and dolerites and are principally medium- to coarse-grained sand with little fine material.

The AGAD has maintained a permanent station on Macquarie Island since 1948. For station operations there is a need to supply and store fuel (Special Antarctic Blend, SAB) and lubricants, and a number of spills in the range ~1000–10 000 L have occurred. In 1994, Deprez et al. conducted a preliminary assessment of contaminants at Macquarie Island. Their survey comprised soil samples from the surface and composite bulk samples, but with little depth information to delineate the vertical extent of contaminated soil. Two contaminated sites identified by Deprez et al. (1994), the Main Power House (MPH) and the Fuel Farm (FFM), are examined in detail here. An additional site from a recent spill adjacent to the culvert to the south of the powerhouse is also examined. To distinguish the two MPH sites they are referred to as the Old MPH and New MPH sites respectively.

The soils associated with areas of fuel contamination are variable. To the southeast of the powerhouse at the Old MPH spill, soil has high organic matter content; it is overlain with tussock grass and is periodically saturated with water. More generally, there is a perched water table 10–20 cm below the soil surface that is recharged by almost daily rain and subsurface runoff from Wireless Hill to the east. Soil to the south and southeast of the powerhouse at the New MPH site is sandy; it is without tussock covering and is moderately free-draining. The water table fluctuates, but typically occurs

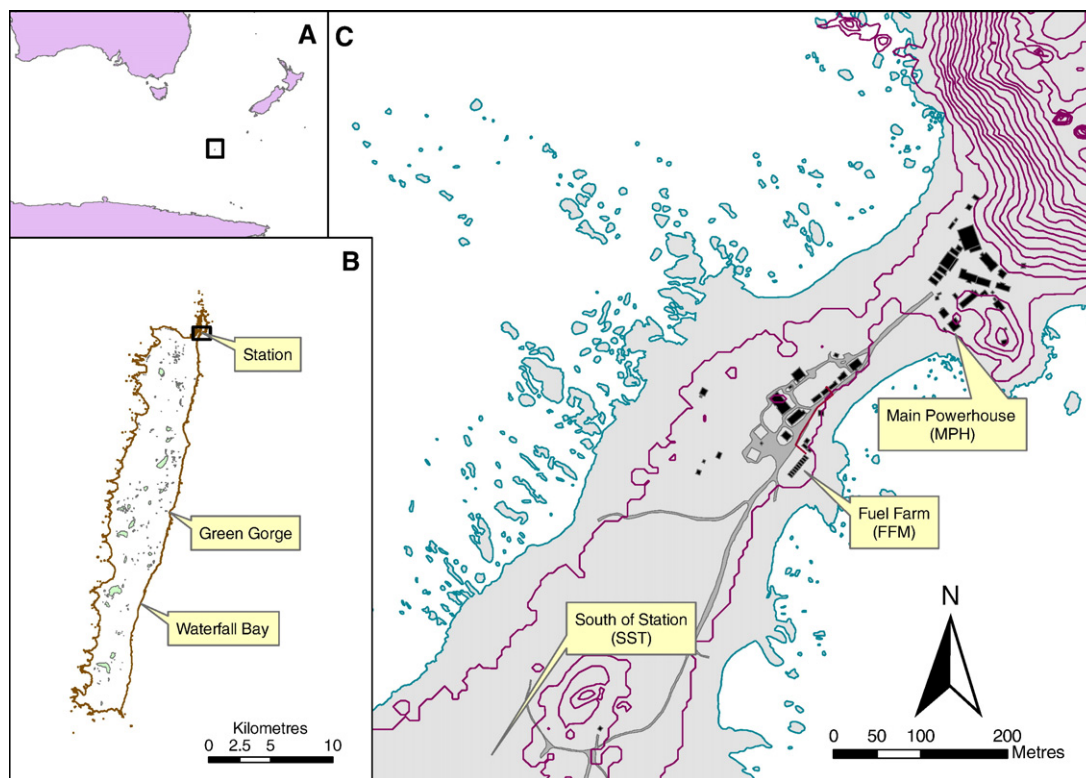


Fig. 1. A, location of Macquarie Ocean in the Southern Ocean; B, location of Macquarie Island Station and reference sample sites south of the station (SST); C, location of the contaminated areas investigated at the Main Powerhouse and Fuel Farm.

at depths of 20–30 cm. Water can sometimes be seen to discharge at the break in slope to the SE onto the beach. Soil surrounding the FFM is sandy fill and is largely devoid of vegetation. It is highly free-draining but is shallow and underlain by impermeable bedrock. A discontinuous spring line occurs at the bedrock-soil/overburden interface.

To date there has been no active remediation of fuel spills and any reduction of fuel concentrations has been achieved by natural attenuation through runoff, dissolution and biodegradation.

### 3. Materials and methods

#### 3.1. Sample collection and handling

Soils were collected in March 2003 from two sites corresponding to the recorded fuel spills at the Old MPH and New MPH (Fig. 2). A third site, the FFM, was also sampled (Fig. 3). Uncontaminated reference samples were collected from 500 m to the south of the station buildings (SST) and from Green Gorge and Waterfall Bay, 15 and 20 km away respectively (Fig. 1, inset B).

Soil samples were collected from pits and soil cores. Cores were retrieved in 50 mm (i.d.) polycarbonate sleeves which were driven into the ground inside a steel casing with a 50 mm diameter stainless steel cutting shoe. A one-way ball valve at the top of the piston maintained recovery, and soil core compaction (5–25% mean=9%) was measured by the difference between the depth of the hole and the length of the core. Samples from pits were collected by digging an open pit (~40×40 cm) with a spade and taking samples from the pit face with a stainless steel spoon.

Samples from MPH1–10 (Fig. 2) were taken by core; MPH11–17 were from soil pits; MPH18 was a piezometer installation installed with an auger. Coring was not possible in the region of MPH11 to MPH17 due to large cobbles in the profile and the close proximity to gentoo penguins. Sites FFM1–6 and FFM13 were collected by core (Fig. 3). All other samples were taken from soil pits.

Water samples were collected from multiport samplers, piezometers, soil pits, and seeps using a 50 mL glass syringe. Samples for chemical analysis were frozen until analysed on return to Australia.

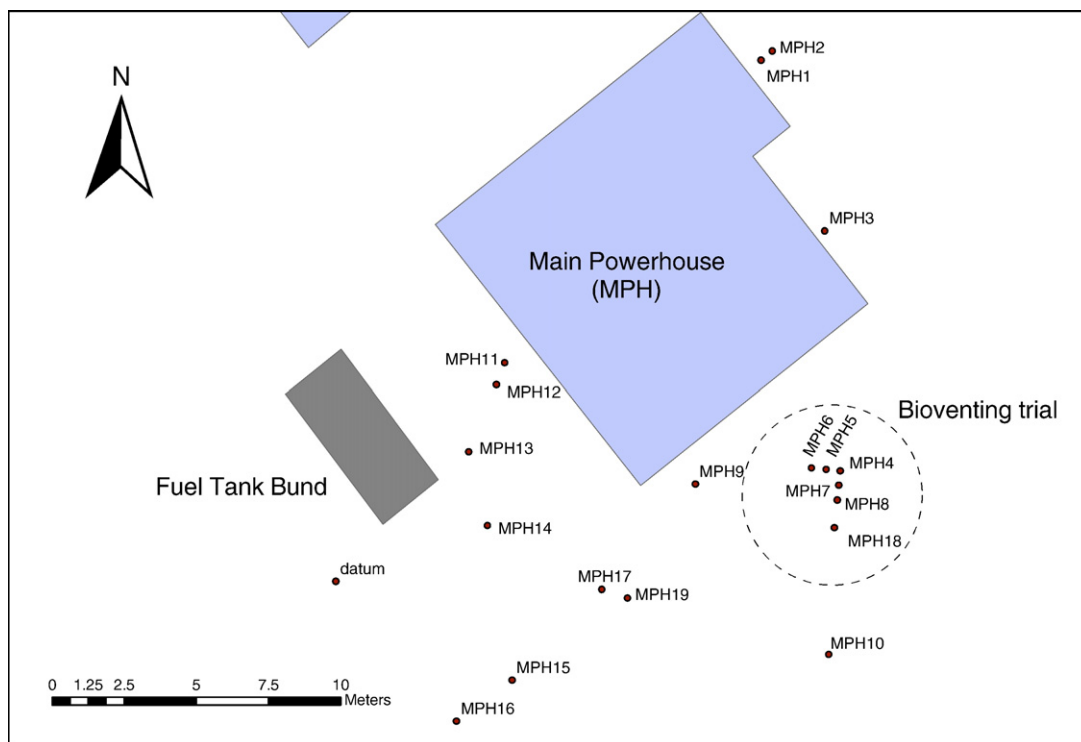


Fig. 2. A Contour Map of the area surrounding the Main Powerhouse. The locations of the monitoring arrays are indicated by dashed circle.

### 3.2. Physical analysis

Cores were cut into 5-cm sections, sub-sampled for chemical analysis, and the remaining soil oven dried to constant weight at 105 °C to determine gravimetric water content. The core barrels were cleaned and dimensions measured with callipers to determine the volume for estimates of soil bulk density and porosity (results available on-line at [www.aadc.aad.gov.au](http://www.aadc.aad.gov.au)).

### 3.3. Chemical analysis

Sub-samples were taken from 5-cm core sections with a 6 mm diameter stainless steel mini-corer. The soil was extruded from the mini-corer into a 40 mL screw top vial with a stainless steel pushrod. Four sub-samples were taken from each 5 cm core section to give a mass of soil for extraction of  $10 \pm 1$  g. A 0.5-mL volume of internal standard solution containing  $1000 \text{ mg L}^{-1}$  cyclo-octane,  $100 \text{ mg L}^{-1}$   $d_8$ -naphthalene,  $100 \text{ mg L}^{-1}$   $p$ -terphenyl and  $1000 \text{ mg L}^{-1}$  1-bromoeicosane dissolved in hexane was added to the soil, followed by the addition of 10 mL of water and 10 mL of hexane. The vials were then tumbled end over end (50 rpm) overnight, centrifuged at  $110 \times g$ , and the hexane layer transferred into a 2 mL vial for Gas

Chromatography-Flame Ionisation Detector (GC-FID) analysis.

The GC-FID was a Varian 3800 fitted with 30 m capillary column (BP-1, 0.22 mm i.d., 0.25  $\mu\text{m}$  film thickness, supplier SGE). The injector temperature was 270 °C and 1  $\mu\text{L}$  of sample was injected at a split ratio of 1:32. The carrier gas used was helium and GC oven conditions were 35 °C for 2.5 min, ramped at 25 °C  $\text{min}^{-1}$  to 310 °C and held isothermally for 1.5 min, giving a total run time of 15 min. The detector temperature was 260 °C.

Calibration was carried out by dissolving SAB in hexane and using an identical extraction and analytical procedure to that outlined above. Standards were run at the start, middle, and end of each batch of 35 samples. Blank hexane and hexane with internal standard were run with each batch to allow for correction of baseline drift and column bleed. The concentration of fuel, which is mostly aliphatic, was determined by integrating all peaks between 5 and 15 min with the Varian Star software (Version 5.3) and subtracting the internal standards.

Water samples with a high particulate content were extracted as two parts: an aqueous phase and a combined particulate and aqueous phase. For the

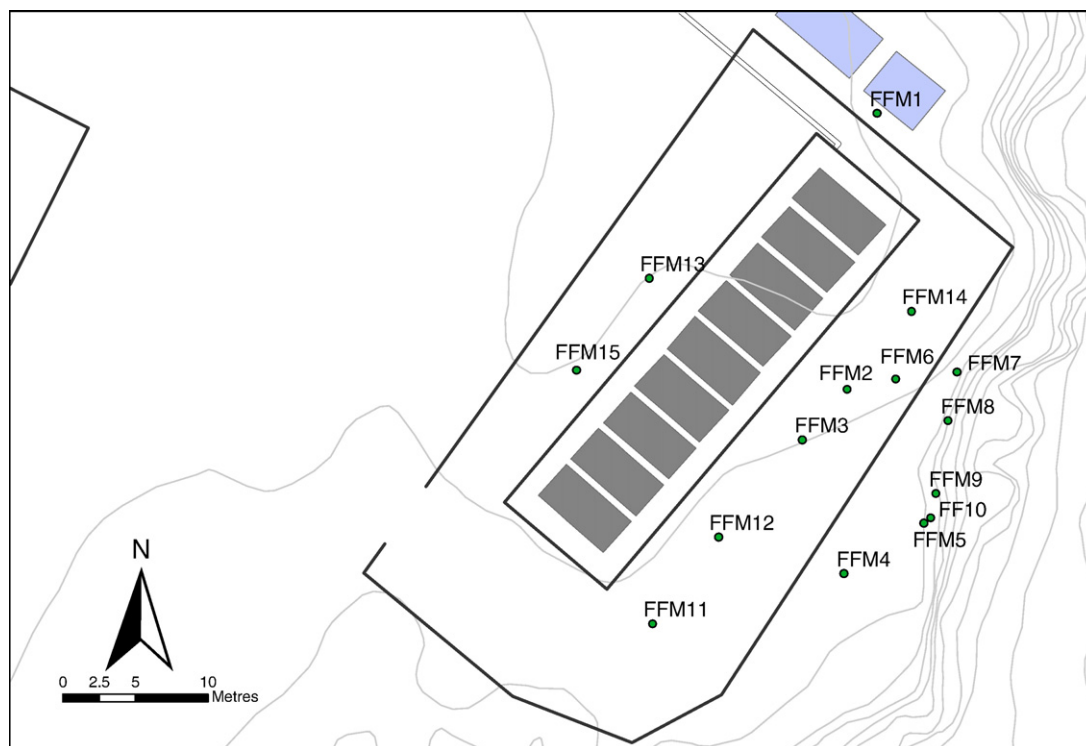


Fig. 3. A Contour Map of the area surrounding the Fuel Farm.

aqueous phase, a spike of D<sub>8</sub>-toluene was added to approximately 200 mL of sample. This was allowed to equilibrate for 30 min. Then 7.5 mL dichloromethane was added, mixed end over end for 16 h, and centrifuged. When an emulsion formed this was broken by the addition of salt (NaCl).

The solubility of SAB in water was determined by equilibrating 30 mL of SAB with 1 L of MilliQ water in a separating funnel, and mixing on a rotary shaker (100 rpm) at 20 °C. After equilibrating for 50 days water samples were collected from the bottom of the funnel before being centrifuged to remove any microdroplets, and extracted as described above.

Samples taken from the cores were sent to Analytical Services Tasmania for analysis of ammonium (NH<sub>4</sub><sup>+</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), potassium (K) and phosphorous (P) using standard methods.

The organic matter profile from core samples was determined to assess how fuel distribution coincides with organic matter, and to allow more accurate calculation of air filled porosity given the density differences between organic and inorganic soil constituents. Organic matter contents were determined by loss on ignition (Dean, 1974). Approximately 10 g soil was put into a crucible, precisely weighed, then oven dried at 105 °C for 24 h to determine dry weight. The crucible was placed in a

muffle furnace at 550 °C for 24 h and weighed, and the organic matter content determined by difference.

### 3.4. In-situ measurements

*In-situ* oxygen concentrations were measured at the FFM and Old MPH sites with electrochemical sensors connected to a data logger (Datataker DT500, Datataker Pty Ltd). At the FFM, the sensors were placed on a single string at location FFM6 at depths of 0.20, 0.40 and 0.60 m (Fig. 3); at the Old MPH site 4 strings were used (MPH5, 6, 7 and 8) at depths of 0.40 m and 0.60 m below ground level (Fig. 2). Aqueous samples collected from multilevels and piezometers were measured with an oxygen probe (model WP-81, TPS). Soil temperatures were measured with thermometers at 4 depths, 4 times per day by the Bureau of Meteorology at a location between the fuel farm and the powerhouse (detailed data available at [www.bom.gov.au](http://www.bom.gov.au)).

### 3.5. Aeration trials

Compressed air was introduced into the subsurface at a flow rate of ~100 L min<sup>-1</sup> and a delivery pressure between 7 and 15 KPa. Start-up pressure was usually 5 to 10 KPa higher prior to the displacement of water from the soil.

Three sparging configurations were used. Two single point schemes were tested at two locations and one micro-injection scheme, using 9 injection points, was trialled in the same area as the two single injection locations. The single point sparge well was made of 40 mm PVC, slotted over the bottom 0.20 m. Two sparge sites were trialled at the Old MPH, one at MPH4 and the other at MPH4a (Fig. 2). The depth of sparging slots at MPH4 was 0.40 to 0.60 m, while at MPH4a it was 0.55 to 0.75 m. The position was changed to MPH4a after the initial installation failed to increase oxygen at the in-ground sensors at MPH4. This was because the air quickly developed channels to the surface (discussed below). The sparge point at MPH4 was installed on 13 March 2003 and at MPH4a on 19/3/03.

On the 21 March 2003, 9 micro-sparge points consisting of 1.20-m long, 6-mm diameter copper tubing with multiple 2.5-mm holes drilled into the bottom 0.20 m were installed. The points were installed at a 45° angle to maximise air distribution. To make best use of the existing monitoring array, the sparge points were installed 0.5 m apart in a 1 m grid overlaying the monitoring points previously used for the single point injection experiment.

### 3.6. Calculation of field respirometry rates

Respirometry tests were conducted by aerating the soil profile and then halting this process to measure the rate of oxygen consumption. Consumption rates are determined from the slope of the oxygen depletion

Table 1

Physical and chemical properties of Equivalent Carbon Number (ECN) fractions as defined by the TPH working group (Gustafson et al., 1997) as used in the NAPLANAL model

ECN	MW g mol <sup>-1</sup>	Density Kg L <sup>-1</sup>	H unitless	Henry's law K atm L mol <sup>-1</sup>	Solubility mg L <sup>-1</sup>	K <sub>oc</sub>
<i>Aliphatics</i>						
5 to 6	81	0.679	34	833.68	28	794
6 to 8	100	0.726	51	1250.52	4.2	3980
8 to 10	130	0.733	82	2010.64	0.33	31600
10 to 12	160	0.76	130	3187.6	0.026	251000
12 to 16	200	0.766	540	13240.8	0.00059	5010000
16 to 21	270	0.78	640	15692.8	0.000001	1E+09
<i>Aromatics</i>						
Benzene	78	0.877	0.23	5.6396	1780	79.4
Toluene	92	0.867	0.27	6.6204	520	251
8 to 10	120	0.871	0.49	12.0148	65	1580
10 to 12	130	0.904	0.14	3.4328	25	2510
12 to 16	150	1.02	0.054	1.32408	5.8	5010
16 to 21	190	1.23	0.013	0.31876	0.51	15800
21 to 35	240	1.28	0.00068	0.016674	0.0066	126000

Table 2

Special Antarctic Blend (SAB) mass fractions for Equivalent Carbon Numbers as determined by the TPH working group (Gustafson et al., 1997)

ECN	Mass fraction
<i>Aliphatics</i>	
5–6	0
6–8	0
8–10	0.095
10–12	0.358
12–16	0.343
16–21	0.00187
<i>Aromatics</i>	
Benzene	0
Toluene	0
8–10	0.024
10 to 12	0.0981
12–16	0.083
16–21	0.00012
21–35	0

profile. Utilising the oxygen consumption rate ( $O_r$ ), along with the air filled porosity ( $\theta_a$ ) and bulk density ( $\rho_b$ ), that were determined from the soil cores taken at the time of oxygen sensor installation, and using hexane as a model hydrocarbon, hydrocarbon degradation rates can be estimated by Eq. (1) (Hinchee and Ong, 1992):

$$D_h = \frac{O_r \theta_a}{RT \rho_b} \frac{MW_h 1000}{9.5} \quad (1)$$

In Eq. (1),  $D_h$  is the hydrocarbon degradation rate (mg hexane kg soil<sup>-1</sup> day<sup>-1</sup>),  $R$  is the universal gas constant (8.206 × 10<sup>-5</sup> m<sup>3</sup> atm K<sup>-1</sup> mol<sup>-1</sup>),  $T$  the temperature (K) and  $MW_h$  the molecular weight of hexane (g mol<sup>-1</sup>).

### 3.7. Fuel partitioning, natural attenuation and dispersal

An important consideration in the distribution of fuel spills at Macquarie Island is the occurrence of free phase

Table 3

TPH concentrations (mg kg<sup>-1</sup>) at the New MPH spill

Depth	MPH11	MPH12	MPH13	MPH14	MPH15	MPH16
	(1.0 m)	(1.5 m)	(4.5 m)	(6.5 m)	(11.5 m)	(13.0 m)
0.10	24 990	7930	–	310	<200	5700
0.20	–	12 410	10 820	<200	–	–
0.30	17 990	14 880	–	510	6030	4600
0.40	–	13 810	13 810	1900	590	3840
0.50	–	–	–	8510	–	–
0.60	–	11 790	–	–	–	3780

Note: the number in brackets ( ) is distance from spill; '–' indicates no sample taken.

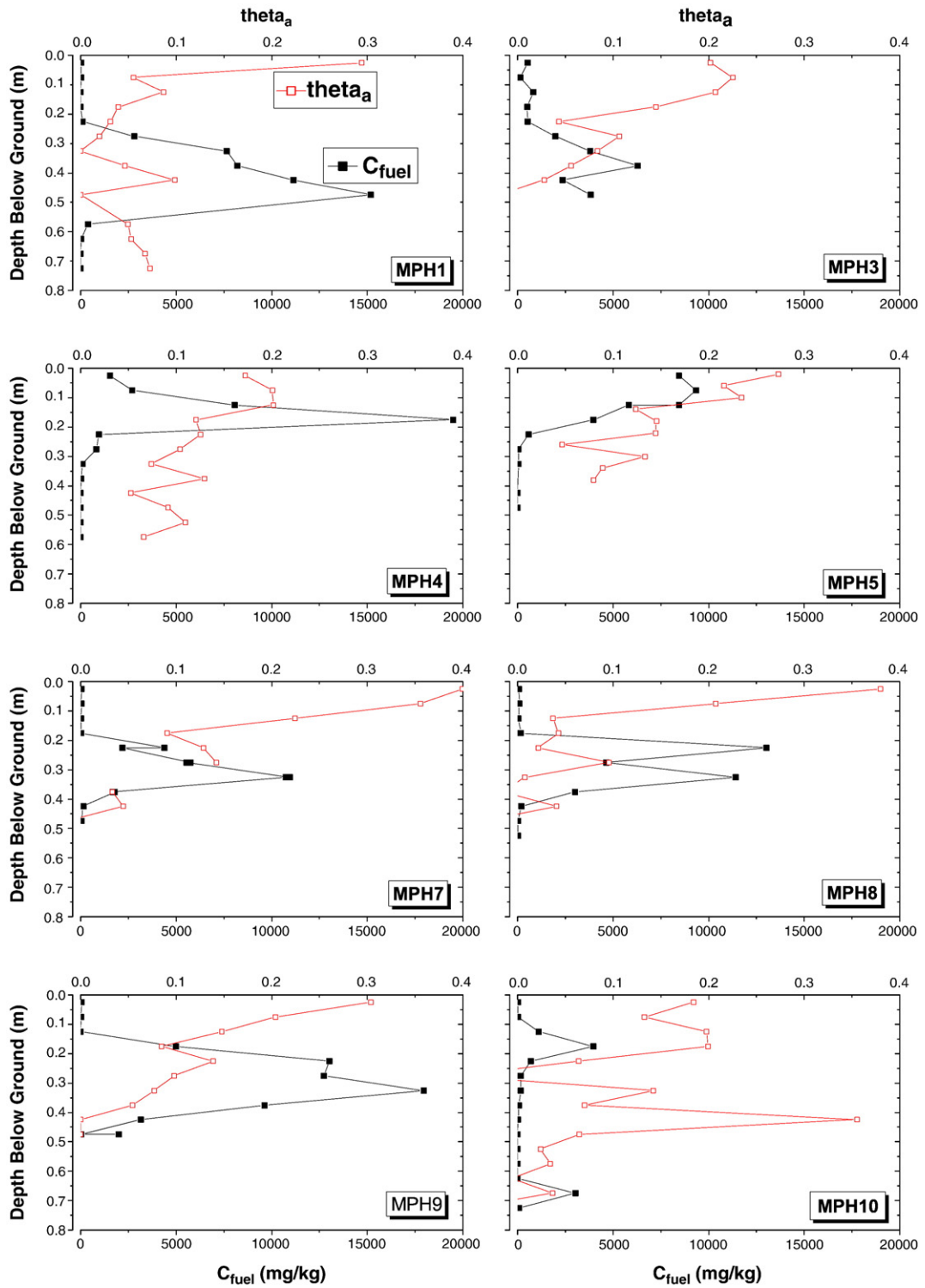


Fig. 4. Fuel and volumetric air contents for cores retrieved from the Old MPH site.

fuel, referred to as non-aqueous phase liquid (NAPL). The presence of NAPL indicates a source of hydrocarbon contamination which will continue to partition into the gaseous, aqueous and solid phases, but also has the ability to directly impact surface water quality. Mariner et al. (1997) developed a NAPL saturation algorithm to predict the occurrence of NAPL from soil core samples. The algorithm firstly considers NAPL in a three phase system of air, water, and solid. Eq. (2) calculates the aqueous solubility of individual compounds. Here  $C_{w,i}$  is the aqueous phase concentration of component  $i$ ,  $C_{t,i}$  is the total concentration of  $i$  in the sample,  $\theta$  is porosity,  $\theta_w$  is the volumetric water content,  $K_{H,i}$  is the dimensionless Henry's constant,  $f_{oc}$  is the mass fraction of organic carbon within the soil matrix and  $K_{oc,i}$  is the organic carbon to water partition coefficient for component  $i$ .

$$C_{w,i} = \frac{C_{t,i}}{\theta_w + K_{H,i}(\theta - \theta_w) + f_{oc}K_{oc,i}(1 - \theta)} \quad (2)$$

If the summed concentration of all compounds in the water phase is greater than the solubility of those compounds, then NAPL is calculated to be present.

To simplify the composition of the fuel for modelling purposes, compounds are grouped into fractions according to their Equivalent Carbon Number (ECN) (Gustafson et al., 1997). This approach is a reasonable approximation because there is less than an order of magnitude difference in the physical and chemical properties between constituents within a particular fraction (Table 1). The TPH mass fractions used in the model were estimated from summed peak areas for the particular ECN based on Special Antarctic Blend analysis by GC-FID. The mass fractions for particular ECNs are listed in Table 2.

The model can be used to predict the mass distribution of fuel components in different phases for different soil types by varying the porosity, water content, and fraction of organic carbon. The purpose of modelling here was to evaluate at what concentrations free phase fuel (NAPL) might be produced when Special Antarctic Blend fuel interacts with a range of soil types on Macquarie Island. The model does not account for trapping or mobility of NAPL within the soil matrix, but rather when NAPL may be present based on partitioning.

## 4. Results

### 4.1. Extent of fuel distribution

#### 4.1.1. Soil

By carefully matching reference fuel profiles with chromatograms from the samples it was possible to

distinguish between naturally occurring organic matter (NOM) and fuel-contaminated soil. Reference sites have few hexane-extractable natural hydrocarbons and concentrations were typically  $\ll 200$  mg 'diesel range organics'  $\text{kg}^{-1}$  ( $\sim n\text{-C}_{10-28}$ ).

It is extremely difficult to estimate the areal extent of contamination at the three spill sites. All sampling locations at the old and new spills in the vicinity of the MPH were contaminated to some extent, whilst approximately half the sampling sites at the FFM were contaminated. The most recent spill at the MPH has the highest average fuel concentration, containing up to  $24\,990$  mg fuel  $\text{kg}^{-1}$  (Table 3). The site of the Old MPH spill is also highly contaminated, with 75% of the cored sites having soil horizons with  $>10\,000$  mg fuel  $\text{kg}^{-1}$  (Fig. 4). Fuel contamination in the soil at the FFM is much less than at the MPH spill sites; concentrations at the FFM site peaked at  $1000\text{--}5000$  mg fuel  $\text{kg}^{-1}$  (Table 4; Fig. 5).

Cored soil profiles taken from the Old MPH spill site (Fig. 4) indicate the fuel is concentrated at a depth of 0.20 to 0.50 m and this coincides with a decrease in volumetric air content to  $<10\%$ , as a result of the increase in soil water content.

The spill which occurred at the New MPH site reflects contamination dominated by one spill emanating from the culvert and chemical compositions closely match recent batches of SAB reference fuel (data not shown). Fuel distribution reflects a single point source, with concentrations decreasing 4-fold over the 13 m length of the sampled plume. The older spills have different compositions reflecting older SAB and mixtures of diesel. Soil profiles sampled from pits at the New MPH spill site were contaminated through the entire depth sampled, and for the full length of the sampled transect.

Table 4

Estimates of fuel spill area and volume, mass of contaminated soil and volume of fuel remaining in-ground

Site	Area of spill ( $\text{m}^2$ )	Depth (m)	Mass of soil (Tons)	Average conc. fuel ( $\text{mg kg}^{-1}$ )	Volume fuel (L)	Maximum conc. fuel ( $\text{mg kg}^{-1}$ )
MPH New	220	0.50	180	7000	1400	24 990
MPH Old	110	0.55	100	2800	300	28 770
FFM	760	0.55	600	800	600	4700
Total	1090		880		2300	

Area and volume estimates were derived from limited along-axis judgmental sampling. The boundaries of the spills were estimated from the surface topography and likely flow path. More extensive core sampling was not possible in 2003.

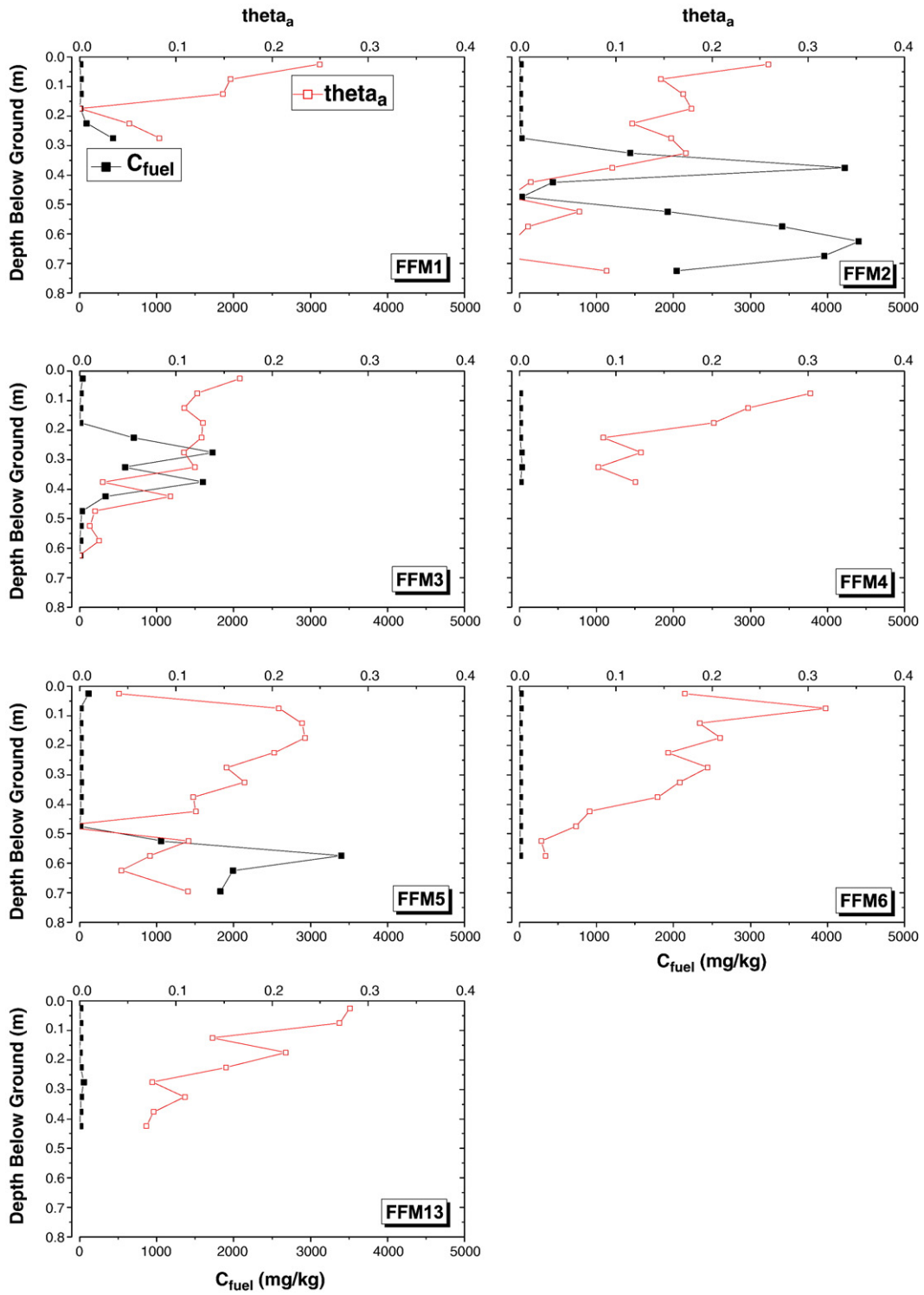


Fig. 5. Fuel and volumetric air contents for cores retrieved from the FFM site.

Table 5

Water samples analysed for TPH collected from the station background, seawater and two fuel spill areas

Purpose/location	Site	Date	TPH (mg L <sup>-1</sup> )±SD
Background	Seawater	26/3/05	<1
	SST1	23/3/05	<1
	SST2	23/3/05	<1
	SST3	23/3/05	<1
FFM	FFM9	26/3/05	<1
New MPH	MPH12	6/3/05	388±39
	MPH13	6/3/05	305±30
	MPH15	6/3/05	<1
	MPH16	6/3/05	134±13

Note: DPIWE investigation level is 0.600 mg/L (DPIWE, 2004).

#### 4.1.2. Water

Water samples were taken from the SST site as a reference. The single FFM sample had fuel concentrations at or below the limit of detection of 1.0 mg L<sup>-1</sup> (Table 5) (Tasmanian investigations levels in water are 0.6 mg L<sup>-1</sup> (DPIWE, 2004)). Water samples taken from the New MPH spill had fuel concentrations ranging up to ~390 mg L<sup>-1</sup>; while those at the Old MPH spill were less, ranging up to 69 mg L<sup>-1</sup>, but still appreciably more than remediation trigger values and remediation levels (see discussion below). The solubility of SAB in water was measured in the laboratory to be 7 mg L<sup>-1</sup>. This indicates that samples with greater concentrations likely have free phase fuel present, or fuel sorbed to particulate matter. Sheen was evident on ponded water at the powerhouse, and on water at a spring line adjacent to the beach at the fuel farm.

#### 4.2. Nutrients

Inorganic nitrogen (N) concentrations in soil (extracted by 2 M KCl) at the MPH and FFM sites were low and extremely variable with the average total available N being <20 mg L<sup>-1</sup> (Table 6). Observed

Table 6

Summary of soil nutrient concentrations from cores removed from MPH, FFM and control sites (SST)

Site	Number of samples	Average Concentration (mg kg <sup>-1</sup> )±SD (range)			
		N-NH <sub>4</sub>	N-NO <sub>3</sub> +NO <sub>2</sub>	P	K
MPH	15	18±31 (<1–110)	1.2±0.7 (<1–47)	227±125 (91–490)	85±28 (48–140)
FFM	10	7.5±17 (<1–57)	6.1±8.0 (<1–20)	121±128 (37–450)	84±33 (32–1300)
SST	4	111±213 (1–430)	165±180 (<1–360)	370±180 (130–540)	100±69 (47–200)

concentrations of P are not likely to be limited to biodegradation (cf. Mills and Frankenberger, 1994).

#### 4.3. TOC

Background levels of TOC (Fig. 6) varied markedly depending upon sampling location and the proximity to vegetation. Core SST1 had up to 20% (w/w) TOC in the top 0.25 m and then very little until 0.70 m below

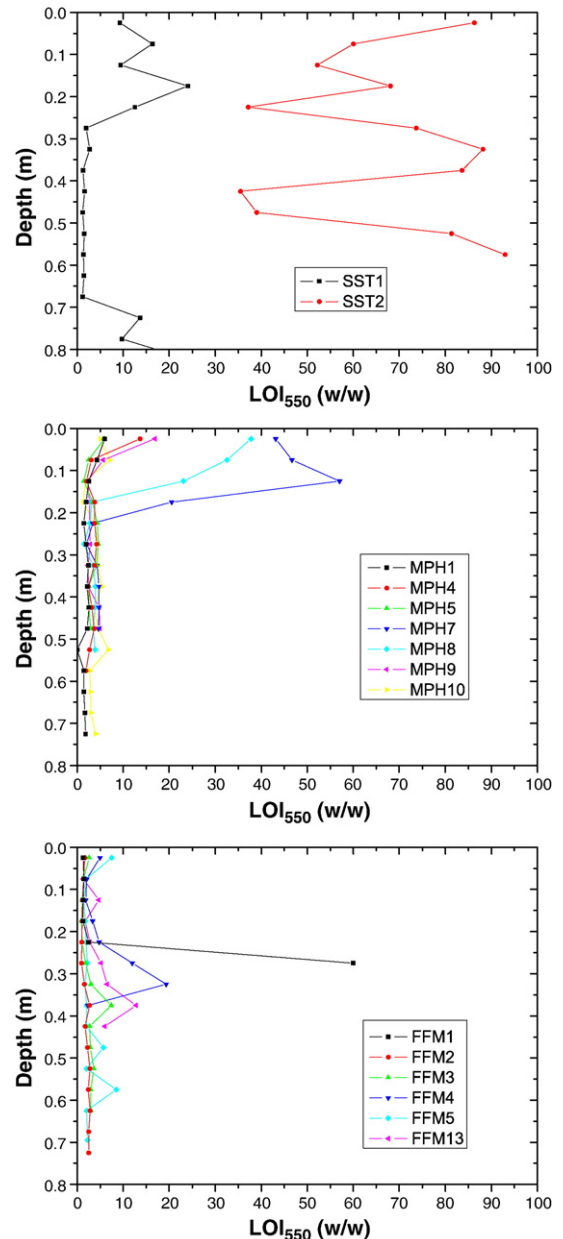


Fig. 6. Organic matter measured by loss on ignition (LOI<sub>550</sub>) for cored soil samples taken from the control (SST), MPH and FFM sites.

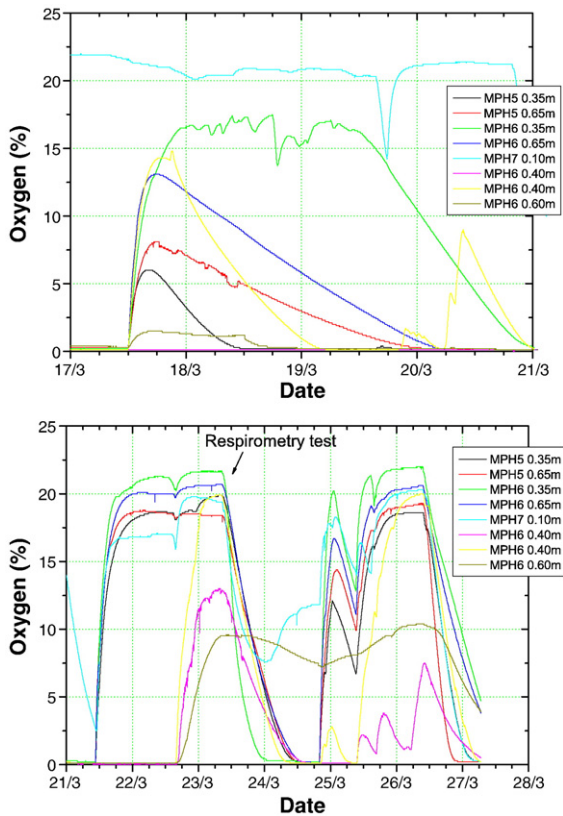


Fig. 7. Soil oxygen partial pressures measured at the Old MPH site during aeration trials. Top graph is single point venting, bottom graph is multiple point venting.

ground level, where TOC increased again, possibly representing a buried surface horizon. Core SST2 had >50% (w/w) TOC which is indicative of a peaty soil.

TOC at the Old MPH site was up to 50% (w/w) in the top 0.20 m and then decreased with depth. The fuel in the soil is concentrated below this depth and appears to coincide more with low volumetric air contents than high TOC (Figs. 4 and 6). The average TOC below 0.20 m was 3.2%, and relatively uniform (standard deviation=1.2).

At the FFM, most of the TOC in the profile was between 0.25 m and 0.40 m below ground level. It is thought that this represents a relic surface horizon which has been buried by fill for siting the tanks. Fuel does not appear to be associated with the distribution of TOC (Figs. 5 and 6).

#### 4.4. Oxygen distribution and air sparging

The background oxygen status of the soil at the contaminated sites, the effectiveness by which oxygen could be introduced into the system by injecting it under

pressure, and the rate of oxygen consumption once air injection ceased were determined by buried oxygen sensors.

Continuous oxygen concentrations were measured for 15 days at the Old MPH site (Fig. 7) for a variety of aeration conditions. Oxygen concentrations were at atmospheric levels prior to installation and then dropped to zero over a period of about 30 h. Seven out of 8 sensors which were located between 0.10 and 0.65 m in depth were initially anoxic. One sensor at 0.1 m initially behaved erratically. We suspect that this was because it was installed to only a shallow depth and there may have been leakage to atmosphere.

Single-well air injection failed to oxygenate much of the soil due to the shallow installation depth and rapid desaturation of the soil causing the development of air channels and ‘short-circuiting’ of air to the atmosphere. Two attempts at this were trialed in separate injection wells (MPH4 and MPH4A, Fig. 2) and both failed to provide adequate aeration (Fig. 7).

The placement of 9 microventing points throughout the soil provided a better means of delivering oxygen as seen by the immediate positive response of 5 sensors and a delayed response some 30 h later of the remaining 3 sensors (see Fig. 7). The soil was fully aerated by this technique at 6 out of 8 locations, with the two deeper probes at MPH7 and MPH8 measuring oxygen levels between 30 and 50% of atmospheric content.

The effect of air injection on the concentration of fuel in the water phase was measured by collecting water samples from piezometers at the start and end of aeration, covering a period of 12 days (Table 7). It appears that each of these sites were within the radius of influence of aeration from the sparge points. Dissolved oxygen levels increased in the water samples (data not shown), and in most samples the concentration of fuel in water was reduced by a factor of between 2 and 10, with only one sample from MPH6 showing a small increase from 3 to 7 mg L<sup>-1</sup>. Two main processes are likely to be responsible for the reduction: partitioning of fuel from

Table 7  
Water samples from the Old MPH site before and after aeration

Site	Before aeration (14/3/05) TPH (mg L <sup>-1</sup> )±SD	After aeration (26/3/05) TPH (mg L <sup>-1</sup> )±SD
MPH5	69±7	5±1
MPH6	3±0	7±1
MPH7	24±2	8±1
MPH8	43±4	17±2
MPH9	11±1	9±1
MPH10	1±0	<1

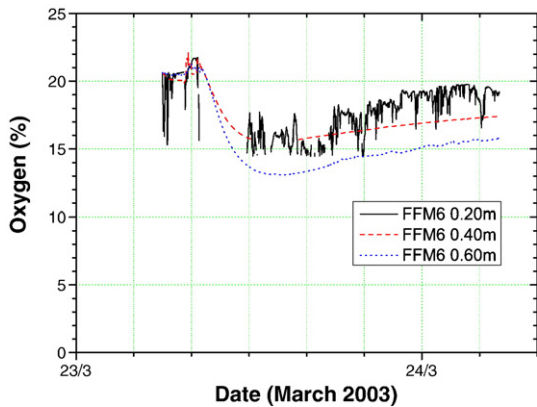


Fig. 8. Soil oxygen partial pressures measured at the FFM site under natural conditions.

water into the air phase and elevated microbial degradation from increased oxygenation.

The soil at the fuel farm appears oxygenated down to a depth of at least 0.60 m (Fig. 8). The shallowest sensor at 0.20 m appears to be fluctuating erratically, possibly as a result of water in the sensor tip or a poor electrical connection. There is a near-linear decrease in the vertical distribution of oxygen with depth indicating there is respiration occurring within the profile. This profile can be used to estimate zero-order oxygen consumption rates based on the model developed by Ritchie (1977). Oxygen consumption rates for the fuel farm are one to two orders of magnitude less than those calculated for the Old MPH site during the micro bioventing trial (discussed below).

#### 4.5. Estimation of respiration rates

Respiration rates were estimated by measuring oxygen depletion during cessation of air injection at

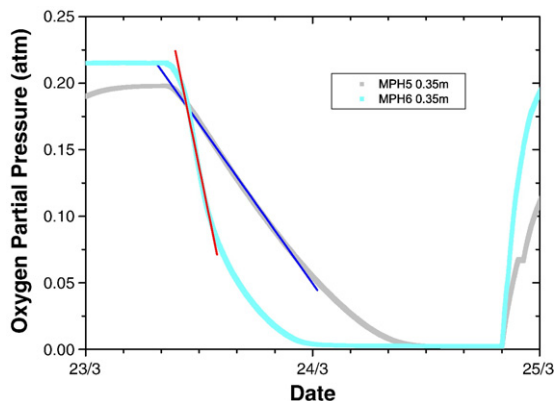


Fig. 9. Oxygen depletion curves and linear fits for two sensors at the Old MPH site after halting aeration.

Table 8

Biodegradation rates estimated from oxygen sensors which showed significant oxygen depletion during the cessation of aeration

Site	Depth (m)	$\theta_a$	$\rho_b$ (kg m <sup>-3</sup> )	$O_r$ (atm day <sup>-1</sup> )	$D_{phc}$ (mg kg <sup>-1</sup> d <sup>-1</sup> )
MPH5	0.35	0.14	1452	0.24	9.21
	0.65	0.08	1477	0.19	4.06
MPH6	0.35	0.13	1585	0.78	25.41
	0.65	0.13	1585	0.25	8.25
MPH7	0.1	0.1	1741		
	0.4	0.4	1523	0.17	17.87
MPH8	0.4	0.05	1740	0.24	2.79
	0.6	0.01	1574		

the Old MPH site. Example curve fits for two sensors are presented in Fig. 9 and the resulting analysis is in Table 8. All sensors could be analysed except the two which did not fully respond. If it is assumed that all oxygen consumption is attributable to hydrocarbon degradation, then estimates indicate hydrocarbon degradation rates of between 3 and 25 mg kg<sup>-1</sup> d<sup>-1</sup>, with an average rate of ~10 mg kg<sup>-1</sup> d<sup>-1</sup>. Sensors were located below the highest fuel concentrations and are therefore likely to represent slower rates than would occur in the more contaminated layers.

#### 4.6. Fuel partitioning, natural attenuation and dispersal

The NAPL saturation algorithm was used on five soil types chosen to cover the range of water and organic carbon contents found at Macquarie Island. Organic carbon contents selected were 1%, 5%, 20% and 60%, while volumetric water contents were 0.07 and 0.35, representing water saturations of 20 and 100%. The results shown in Fig. 10 indicate that for wet or dry soils

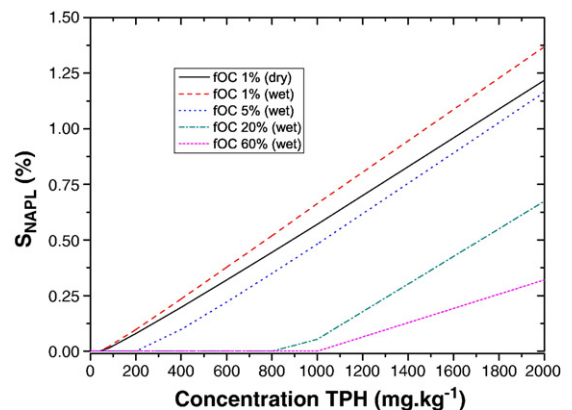


Fig. 10. Concentration of TPH versus NAPL saturation determined by the model NAPLANAL (Mariner et al., 1997).  $f_{OC}$  is the fraction of organic carbon, dry and wet represent volumetric water contents of 0.2 and 0.35.

with relatively low organic carbon (1%), NAPL is present when the TPH concentration exceeds 50 mg kg<sup>-1</sup>. For wet soils with organic carbon contents of 5%, 20% and 60%, the concentration of SAB fuel required to generate NAPL is 200, 800 and 1000 mg kg<sup>-1</sup>, respectively.

## 5. Discussion

The type and extent of the various spills on Macquarie Island are typical of petroleum contamination associated with small research stations in the Antarctic or sub-Antarctic (e.g. see Snape et al., *in press*, and references therein). Average fuel concentrations in Macquarie Island soils were ~2800 and 7000 mg fuel kg<sup>-1</sup> at the Old and New MPH site respectively, which would be regarded as moderate to high levels of contamination. The guideline threshold values in Tasmania are 65 mg fuel kg<sup>-1</sup> for C<sub>6</sub> to C<sub>9</sub> compounds and 1000 mg fuel kg<sup>-1</sup> for C<sub>10</sub> to C<sub>36</sub> (DPIWE, 2004). Hot spots with up to 24990 mg fuel kg<sup>-1</sup> at the New MPH spill are very high. NAPL presence is predicted for the measured concentrations and soil properties using a partitioning model, and dispersal is observed at these sites. Average contaminant concentrations were lower at the FFM (800 mg fuel kg<sup>-1</sup>), but because organic carbon fraction is lower, NAPL is also predicted to be present in the soil, and sheen was observed at a spring line near the beach. There is insufficient temporal sampling from the Macquarie Island sites to be able to accurately estimate a typical natural spill half-life, but persistent high concentrations and largely unweathered fuel signatures a decade or more since spillage suggests that the half life is of the order of tens to hundreds of years.

Given the high rainfall and relatively organic soils, we hypothesized that the main reason for the long natural half-life is because the soils are water-saturated and anaerobic. To test this hypothesis, we successfully developed a microbioventing system that enabled pervasive *in situ* air injection. Using an interrupted venting test, we observed significant increase in soil respiration and a rapid decrease in fuel concentration in water. If all the respiration was attributable to petroleum hydrocarbon degradation, degradation rates were 3 to 25 mg fuel kg<sup>-1</sup> d<sup>-1</sup>. However some degradation of naturally occurring organic material (NOM) was also likely. In this study it was not possible to separate the two sources. However, Shaver et al. (2006) measured CO<sub>2</sub>-C evolution during NOM degradation from a wet Alaskan sedge tundra soil with moisture and vegetation characteristics similar to those at the Old MPH site.

They obtained values from drained (well-aerated) soil incubated at 7 °C of 1.3 mg kg<sup>-1</sup> d<sup>-1</sup>. A similar proportion might reasonably be attributed to NOM degradation in our study. Additional validation of our hydrocarbon degradation estimates is provided by laboratory incubation experiments conducted on well-aerated soil from the Old MPH site. In this study petroleum hydrocarbon losses, measured by mass loss during incubation, ranged from 20.3 to 30.3 mg fuel kg<sup>-1</sup> d<sup>-1</sup> in unfertilized and fertilized soil, respectively (Walworth et al., 2007-this issue). The range observed in the field trial (3 to 25 mg kg<sup>-1</sup> d<sup>-1</sup>) in this study is possibly an underestimate because sensors were placed in the soil horizons where contamination was relatively low (see Fig. 4).

Another significant reason that natural attenuation is slow in these soils is because they are N-limited (Walworth and Ferguson, *in press*). Background average concentrations of N at the uncontaminated reference sites (SST) were one to two orders of magnitude higher than at the contaminated sites. This might be related to a closer proximity to seal wallows and bird nesting sites, but the lower concentrations in the fuel spill sites are more likely to be a consequence of N consumption during biodegradation of the fuel spills. This is also indicated because P is not as depleted as N in these sites (see Table 6; cf. ref., which is consistent with N:P consumption ratio in fuel biodegradation of ~5–10:1. The optimum N concentration for biodegradation of fuel in these soils was determined in a laboratory respirometer system to be about 750 mg N kg<sup>-1</sup> soil water (Walworth et al., 2007-this issue). Whereas the soil N at the spill sites, when expressed as soil water, does not exceed 100 mg N kg<sup>-1</sup> soil water. These observations strongly indicate that N is limiting fuel biodegradation and that amending the N regime to 750 mg N kg<sup>-1</sup> soil water would greatly increase degradation rates.

There is currently no environment specific clean-up criteria for the sub-Antarctic islands. Preliminary results from a risk-based study indicate that trigger values for the fresh fuel might be approximately 200 mg fuel kg<sup>-1</sup> based on the likelihood of NAPL dispersal and observed ecotoxicology response in contaminated soil (Schafer et al., 2006; Snape et al., 2006b,c).

By aeration alone the site may take ten to twenty years to remediate to concentrations of ~200 mg fuel kg<sup>-1</sup>. The addition of 125 mg kg<sup>-1</sup> N combined with aeration (as reported by Walworth et al., 2007-this issue), would substantially improve the remediation time. For the bulk of the soil at moderate to high levels of contamination (~5000 mg fuel kg<sup>-1</sup>) we estimate that *in situ* microbioventing with nutrient amendment

could achieve such a target fuel concentration in approximately 1–2 years of continual, or 3–5 summer seasons. The more highly contaminated spots, with up to 25000 mg fuel kg<sup>-1</sup>, would take appreciably longer, and it might be necessary to remove those areas for *ex-situ* treatment in a heated bioreactor to accelerate remediation.

## 6. Conclusions

Two fuel spills identified in 1994 and a third which occurred in 2002 were investigated to determine the distribution of petroleum contaminants, the fuel distribution within soil representative of Macquarie Island and limitations to biodegradation.

The New MPH spill had ~180 metric tons of highly contaminated soil (average 7000 mg kg<sup>-1</sup>) which had spread at least 13 m down gradient from the source. The Old MPH spill had ~100 tons of contaminated soil on the eastern and southern sides of the MPH. The FFM had approximately 600 tons of soil with relatively low levels of contamination although this is difficult to estimate due to the spill being widely dispersed across the site. Hydrocarbon sheen can be seen on surface water flowing from all three sites. A simple hydrocarbon distribution model (NAPLANAL, Mariner et al., 1997) indicates that in soil typical of those contaminated by fuel at Macquarie Island may generate NAPL at fuel concentrations between 50 and 1000 mg kg<sup>-1</sup>.

Biodegradation is limited at the Old MPH site by anaerobic conditions and low N concentrations. The fuel farm has adequate soil oxygen concentrations, which reflect the lower fuel and soil organic carbon concentrations, but it is also highly depleted of N. Nitrogen and oxygen contents were not measured in the New MPH spill although N is likely to be low due to the coarse texture of the soil and high fuel loading. Oxygenation is likely to be better because the soil is coarser and more free-draining. In pilot aeration tests at the Old MPH spill site, single-well aeration was found to be ineffective in achieving any significant oxygenation of the soil profile. A microbioventing technique using nine small injection rods spaced 0.50 m apart achieved a much more uniform distribution of oxygen. This technique removed considerable quantities of hydrocarbon from the water fraction, and greatly increased biodegradation.

The proximity to wildlife and logistic constraints associated with bulk earth removal make *in situ* remediation an attractive option. We estimate that in the bulk of the contaminated soil at Macquarie Island (where concentrations are ~5000 mg kg<sup>-1</sup>), fuel concentrations could likely be reduced to <200 mg

kg<sup>-1</sup> in 1–2 years by continual operation of a microbioventing array at ambient soil temperatures (~5 °C). The soil would also need to be augmented with N. Hotspots of contamination might need to be removed for *ex situ* treatment to achieve a reasonable rate of remediation.

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