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The rate of removal and the compositional changes of diesel in Antarctic marine sediment

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ABSTRACT

Diesels and lubricants used at research stations can persist in terrestrial and marine sediments for decades, but knowledge of their effects on the surrounding environments is limited. In a 5 year *in situ* investigation, marine sediment spiked with Special Antarctic Blend (SAB) diesel was placed on the seabed of O'Brien Bay near Casey Station, Antarctica and sampled after 5, 56, 65, 104 and 260 weeks. The rates and possible mechanisms of removal of the diesel from the marine sediments are presented here.

The hydrocarbons within the spiked sediment were removed at an overall rate of 4.7 mg total petroleum hydrocarbons kg^{-1} sediment $week^{-1}$, or 245 mg kg^{-1} $year^{-1}$, although seasonal variation was evident. The concentration of total petroleum hydrocarbons fell markedly from 2020 ± 340 mg kg^{-1} to 800 ± 190 mg kg^{-1}, but after 5 years the spiked sediment was still contaminated relative to natural organic matter (160 ± 170 mg kg^{-1}). Specific compounds in SAB diesel preferentially decreased in concentration, but not as would be expected if biodegradation was the sole mechanism responsible. Naphthalene was removed more readily than *n*-alkanes, suggesting that aqueous dissolution played a major role in the reduction of SAB diesel. 1,3,5,7-Teramethyladamantane and 1,3-dimethyladamantane were the most recalcitrant isomers in the spiked marine sediment.

Dissolution of aromatic compounds from marine sediment increases the availability of more soluble, aromatic compounds in the water column. This could increase the area of contamination and potentially broaden the region impacted by ecotoxicological effects from shallow sediment dwelling fauna, as noted during biodegradation, to shallow (<19 m) water dwelling fauna.

1. Introduction

Antarctica has long been considered a pristine environment (Kennicutt et al., 1992). Interest in the continent is increasing both in the scientific community and the wider public due to its unique environment, importance to the study of climate change and expanding ecotourism. Consequently, there is an increase in the number of people visiting Antarctica and an increased risk of fuel spills. Furthermore, years of exploration in Antarctica have created a legacy of petroleum product pollution from spills and run off from abandoned waste disposal sites that can last for decades (Gore et al., 1999). The main petroleum products contributing to this are diesel fuels and lubricating oils (Snape et al., 2001a, 2001b). The petroleum products that are the most likely to cause hydrocarbon contamination in Antarctica are Special Antarctic Blend diesel and lubricants used in transport vehicles and other machinery. Hydrocarbons from these oils and heavy metals from their storage containers can have major environmental impacts when mobilised by the meltwater that runs through the land fills and spill sites during the warmer seasons (Snape et al., 2001a, 2001b; Woinarski et al., 2006). The most significant levels of hydrocarbons are found near occupied stations and the surrounding bays where disposal sites are or were located (Powell et al., 2003).

A previous series of investigations examined the effects of contaminants from landfills in cold climates, the depth of interaction and the residual toxicity of these contaminants. It was found that sediment contamination, in particular hydrocarbon contamination, in Brown Bay, east of Casey Station, had a significant effect on biological communities (Stark et al., 2003). Some Antarctic micro-organisms have been shown to degrade oils (Golyshin et al., 2003; Powell et al., 2004; Yakimov et al., 2004). Different components are removed and degrade at different rates within oils by a variety of methods such as dispersion, migration and dilution or dissolution, biodegradation and evaporation (Table 1).

In 2001 a long term multidisciplinary experiment was set up by the Australian Antarctic Division to investigate the effects of SAB diesel

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Table 1
Possible processes of removal of SAB diesel in Antarctic marine sediments. MN = methylnaphthalene; DMN = dimethylnaphthalene; EN = ethylnaphthalene.

	Expected changes in compound isomer ratios	Expected changes in compound concentration	General expectations from published data
Particle dispersion	Isomer ratios remain unchanged.	Compounds with high carbon sorption decrease in concentration. The concentration of other compounds remains relatively constant.	Can occur from physical disturbance during deployment or in a non-sheltered bay and would result in an observed loss of overall sediment.
Migration	Isomer ratios remain unchanged.	Compounds with low carbon sorption decrease in concentration.	Migration of hydrocarbons through the sediment is possible
Dilution	Isomer ratios remain unchanged.	Aromatic and aliphatic hydrocarbons decrease in concentration to the same degree.	Sediment traps measure the rate of sedimentation and therefore estimate dilution of contaminated sediment to be ~0.8–5.3 g m^{-2} day^{-1} (A. Palmer, 2010, personal communication) over the 5 year period. Therefore, ~0.7–19.7 g of sediment over the 5 year period may have been due to sedimentation.
Biodegradation	Ratios change by relatively well known systematic degradation patterns	Overall concentration will reduce.	• *n*-alkanes > branched alkanes > low molecular weight aromatics > cyclic alkanes (Atlas et al., 1981). • 2MN > 1MN > 2,7-, 1,7-, 1,6- DMN > 1,4-, 1,5-DMN > 1,2- DMN > 2,3- DMN, 1-EN > 2-EN > 1,8-DMN. (Greenwood et al., 2008).
Dissolution	Low molecular weight aromatic hydrocarbon isomer ratios remain constant, compound ratios differ. Higher molecular weight aromatic hydrocarbon isomer ratios remain constant. Compound ratios differ and compound ratios relative to low molecular weight aromatic hydrocarbons change e.g. *n*-alkanes relative to naphthalene.	Low molecular weight aromatic hydrocarbons decrease in concentration. Higher molecular weight aromatic hydrocarbons also decrease in concentration relative to aliphatics hydrocarbons.	Water samples could be taken and analysed for non-indigenous organic compounds. Aqueous solubilities increase with temperature and decrease with salinity and increased molecular weight as shown by McAuliffe (1979).

on marine sediment and the biota (macro-, meio- and micro-fauna) (Powell et al., 2005; Thompson et al., 2006). Here we present detailed removal patterns of the SAB diesel to establish the rate and major process of removal of the fuel from marine environments over five years.

2. Methods and materials

2.1. Location

Casey Station (66°17′05″S, 110°31′26″E) is located on the Bailey Peninsula, Antarctica (Fig. 1). O'Brien Bay, on the southern side of Bailey Peninsula, is surrounded by ice cliffs and snow banks from ~10–30 m high and covered by sea ice for 11 months of most years. This location was chosen as the experimental site because it is close to Casey Station but is outside the region of station impacts (Thompson et al., 2006), although there was still increased current and water flow during the Antarctic summer months when the sea ice melted.

2.2. Sample preparation and collection

Experiment details have been described by Thompson et al. (2006) for equivalent lubricant treatments. Sediment spiked with SAB diesel was deployed in separate trays (34 × 23 × 12 cm), at the same time as the lubricant and control treatments, in the same 24 block (3 m × 3 m) design. In brief, in the Antarctic summer during November 2001, divers collected fine marine sediment consisting of 70% silt, 28% sand and 2% clay from O'Brien Bay, site 1 (Fig. 1) in 15 L polyethylene buckets from water depths of 16–19 m. Both the sediment defaunation and the gravel removal was achieved using a 500 μm sieve, with the fine sediment left to settle overnight while the temperature and salinity were maintained and monitored. Before the addition of SAB diesel, excess water was removed and the sediment stirred into a slurry for 2 min. SAB diesel was added over a 5 min period, whilst the sediment was stirred continuously, to an approximate ratio of 150 mL SAB to 35 L of wet sediment (47 kg wet weight) to give an approximate concentration of 4000 mg kg^{-1}. This mixture was left to settle for 24 h before deployment. Overlying water was removed to minimise slick formation directly on post-deployment. Although the oxygen concentration was not measured the stirring aerated the sediment and equalised the oxygen initial concentration throughout the sediment in the trays.

The spiked sediment was transported to O'Brien Bay, site 2 (Fig. 1) and transferred to 24 trays which were placed into 3 m × 3 m randomised blocks at depths of 15–18.5 m. Each block was 2 m apart on the sea floor and each tray within the block was 1 m apart. Samples were taken from the trays before the sediment was placed on the bay floor (pre-deployment) and again after 5, 56, 65, 104 and 260 weeks. Four trays were sampled at each time and two replicates were taken from each tray. The samples were collected *in situ* by pushing two polycarbonate tubes vertically into each tray, collecting ~80 mm of sediment. Each tube was capped on the upper end by divers underwater, then the core was retrieved and the bottom capped once on the surface. The samples in the polycarbonate tubes were bagged, frozen at −20 °C and shipped to Tasmania, Australia. At each collection time, including pre-deployment, a treatment control sample of sediment was taken from the same (3 m × 3 m) plot as the SAB-spiked samples to test for background levels of hydrocarbons and any possible cross contamination of samples. These control samples also allowed testing for contaminant migration.

2.3. Solvent extraction

Based on the method of Thompson et al. (2006) the surface 10 mm slice of frozen sediment from each 80 mm core was thawed. Light coloured sediment was visible in the surface 0–10 mm getter darker through the core, indicative of a decreasing oxygen profile. A homogenised sub-sample of the 0–10 mm aerobic sediment (5–10 g) was extracted with a mixture of 10 mL of deionised water, 9 mL of dichloromethane and 1 mL of dichloromethane containing 1 mg L^{-1} cyclooctane, 1 mg L^{-1} bromoeicosane, 0.25 mg L^{-1} 1,4-dichlorobenzene, 0.25 mg L^{-1} deuterated tetracosane and 0.1 mg L^{-1} *p*-terphenyl (internal standards; IS). The sample/solvent mixture was left to tumble overnight (~30 turns min^{-1} at 20 °C) in Teflon capped 40 mL vials. The samples were then centrifuged for 10 min at 3000 rpm at 10 °C. After the dichloromethane extract was decanted into Teflon capped vials, the remaining sediment in the vials