Composition and Biodegradation of a Synthetic Oil Spilled on the Perennial Ice Cover of Lake Fryxell, Antarctica

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A helicopter crashed in January 2003 on the 5 m-thick perennial ice cover of Lake Fryxell, spilling synthetic turbine oil Aeroshell 500. Molecular compositions of the oils were analyzed by gas chromatography–mass spectrometry and compared to the composition of contaminants in ice, meltwater, and sediments collected a year after the accident. Aeroshell 500 is based on C_{20}–C_{33} Pentaerythritol triesters (PET) with C_5–C_{10} fatty acids susbstituents and contain a number of antioxidant additives, such as tricresyl phosphates. Biodegradation of this oil in the ice cover occurs when sediments are present. PETs with short fatty acids substituents are preferentially degraded, whereas long chain fatty acids seem to hinder esters from hydrolysis by esterase derived from the microbial assemblage. It remains to be seen if the microbial ecosystem can degrade tricresyl phosphates. These more recalcitrant PET species and tricresyl phosphates are likely to persist and comprise the contaminants that may eventually cross the ice cover to reach the pristine lake water.

Introduction

Increasing tourism, scientific traffic, leaking tanks, and oil transport increase the risk of hydrocarbon spills in Antarctica (*1*). Oil spills in cold regions are more viscous than in warm regions usually leading to a decrease in distribution, dissolution, diffusion rates, and degradability of the contaminating fluid, the latter of which is caused by freezing of some of its components (*2*). In the largest Antarctic ice-free region, the McMurdo Dry Valleys (MCM), there are increasing concerns about hydrocarbon contamination of soils adjacent to research bases (*3, 4*).

On January 17, 2003, a Bell 212 helicopter crashed on the 5 m thick perennial ice cover of Lake Fryxell in Taylor Valley spilling ~730 L of aviation diesel fuel (JP5-AN8) as well as a total of ~27 L of hydraulic fluid MIL-5605 and synthetic

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turbine oil Aeroshell 500. Cleanup efforts, initiated four days after the accident, recovered no more than 45% of the spilled fluids (*5*). Environmental impacts from such spills is minimized by immediate cleanup, but this is possible only early in the field season, from September to early November, while the ice is solidly frozen. Later in the Austral summer, spilled fluids can penetrate deeper in the ice cover via melt pools and are difficult to remove or contain (*6*). The crash occurred during a warm period when the lake ice was isothermal at 0 °C and partly covered by large melt pools, the worst possible scenario for a successful cleanup.

The few studies of accidental hydrocarbon releases and their impacts in the MCM focus only on the effects on soil biogeochemistry as most incidents occurred on land (*4, 7, 8*). Conclusions derived from these soil-based studies indicate that hydrocarbon contaminants in cold desert environments can persist for many years and profoundly affect microbial diversity and geochemistry. However, results of those studies cannot be directly extrapolated to the ice cover, which has significantly different physical, chemical, and biological characteristics.

Composition and natural attenuation of the spilled aviation diesel fuel are discussed in Jaraula et al. (*9*). Here, we compare the initial chemical composition of the synthetic turbine lubricant Aeroshell 500 spilled on Lake Fryxell ice with that of residues in the ice cover collected a year later. We are presenting evidence for biodegradation of the synthetic oil in the cold oligotrophic conditions of the ice cover. This manuscript present the detailed composition of such a pentaerythritol triester (PET) based oil and for the first time notes the differential biodegradation of PETs as a function of their fatty acid substituents carbon number. We also discuss the potential for the spilled oils to reach the lake water by penetrating the 5 m perennial ice cover.

Lubricants are formulated from mineral or synthetic oils. Whereas mineral oils are readily available and affordable, synthetic oils have superior properties such as increased thermal stability, large temperature range of application, low volatility at high temperature, and decreased susceptibility to oxidation (*10, 11*). These advantages led to widespread adoption of synthetic oils by the lubricant industry as the worldwide demand for synthetic oils is estimated to have increased 5–7% annually since the 1980s (*12*). Exceptional thermal and oxidative stability of PETs made these the base of choice for lubricants used in military jet fighters and helicopters. Lubricants are now regulated and tested for toxicity, potential for bioaccumulation, and biodegradability (*13*). Laboratory and field investigations show that synthetic oils are more extensively and rapidly biodegraded than mineral oils (*14–16*).

Materials and Methods

Study Site. The MCM, the coldest and driest desert on our planet, is the site of a long-term ecological research (LTER) program. The climate, limited nutrients, and slow-growing biological communities make the MCM ecosystem extremely sensitive to climatic changes and human impact (*17, 18*). At the site of the helicopter crash (77°36′41.098″ S, 163°06′47.228″ E; see map in the Supporting Information (SI)) the ice cover was 5.3 m thick (*5*). Average annual ice-cover thickness is a balance between ~30 cm y^{-1} of freezing of lake water at the bottom and 15–60 cm y^{-1} of ablation loss at the surface via sublimation. Together, these processes, in combination with a fully floating ice cover, generate ~30 cm y^{-1} of net average upward movement of the ice. Aeolian sand embedded in or covering the ice has a lower heat capacity than the sur-

rounding ice (19), inducing the formation of melt pools as wide as and as deep as 1.5 m during the austral summer.

Average annual air temperatures are between −15 and −30 °C (20); however, the accident occurred during the austral summer. From January 1 to 11 of 2003, maximum daytime air temperatures were above 0 °C daily and reached as much as 5.5 °C (LTER, temperature database http://www.mcm-lter.org), although the average summer air temperatures is ∼−3 °C (1). From January 12 to 18 the air temperatures dropped below zero; however, from January 20 to 25 average air temperatures were above zero and as high as 3.3 °C. Thermistors deployed near the accident site to monitor the ice cover temperature showed that, in January, the ice cover between 0.5 and 2.5 m deep was isothermal at 0 °C (5). Ice temperature at 0.25 and 0.5 m dropped below 0 °C on February 14 and 16, respectively, about a month after the accident. The isothermal temperature of the ice indicates that the ice cover was saturated with liquid water, explaining the presence of large melt pools and subsurface chambers prior to the crash.

Sediments also melt into the ice and leave trails of liquid water in their wakes (19). Some of the sediments collect in pockets and accumulate in the summer at the bottom of cavities in the porous ice. Fritsen et al. (21) referred to a layer of sediment at ∼0.5 m depth in the Lake Fryxell ice as an "aquifer" because it contains liquid water from November to February. At the height of summer, the volume of liquid water in the ice cover can be as much as 40% (21). Hydrostatic level in the ice is ∼65 cm from the ice surface.

Sample Collection. Raytheon Polar Services provided samples of Aeroshell 500 collected from the stock used for the crashed helicopter. Meltpool waters and sediments were collected at five locations near the accident site (see SI). The uppermost 80 cm of seven ice cores were logged for ice structure, presence of sediments, and fluorescence under ultraviolet light. Subsamples were cut in ice layers where the ice character changed, sediments were present and/or UV fluorescence was observed (9) using a methanol-cleaned band saw in a −22 °C walk-in freezer. Volatile hydrocarbons were extracted using solid-phase microextraction (SPME) from 2000 μL water samples, or melted ice as described in Jaraula et al. (9). For this report the fluid used for SPME was extracted three times with 1 mL of hexane and 1 mL of dichloromethane to obtain data in nonvolatile contaminants. The extracts were dried under N_2, weighed, diluted with cyclohexane (100 μL mg^{-1}), and analyzed by gas chromatography−mass spectrometry.

In this report we present data for the cores and melt pools samples where PETs were observed. All other sampled sites did not contain PET contamination.

Ice core 12, recovered ∼7 m south of the crash site, contains fluid-filled bubbles that fluoresce under ultraviolet light. Using a syringe, 15 μL of yellowish fluid was recovered from one of the bubbles. From this fluid, 1.0 μL was dissolved in 1999 μL ultrapure water (9) and was extracted following the procedure described above.

Gas Chromatography−mass Spectrometry (GC−MS). A HP-6890 GC coupled to a HP-5973 mass selective detector used in electron ionization mode (70 eV) with helium as a carrier gas. The mass range (40−650 amu) was scanned every 3 seconds. The capillary GC column used was a HP-5MS (30 m, 0.25 mm i.d., 0.25 μm film).

Aeroshell 500 was diluted in cyclohexane (100 μL mg^{-1}) and 0.5 μL was injected in splitless mode. The GC oven was programmed to increase in temperature from 60 °C (1.5 min) to 130 at 20 °C min^{-1}, and then at 4 °C min^{-1} to 300 °C (52.5 min).
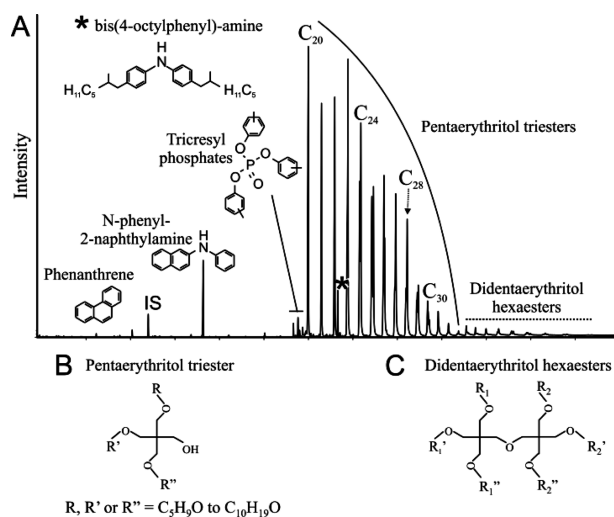

FIGURE 1. Total ion current trace of turbine oil Aeroshell 500. Total carbon number is indicated above the pentaerythritol triester peaks. Structures of (B) pentaerythritol triesters and (C) didentaerythritol hexaesters. IS: 3,3-diethylheptadecane.

Results and Discussion

Synthetic Oil Aeroshell 500. Under the U.S. military specification MIL-PRF-23699F STD, the synthetic lubricant Aeroshell 500 (1.083 g mL^{-1} at 4 °C) is used in gas turbine engines. The helicopter had flown only 15 min after a full service when it crashed. It is estimated that the spilled oil was minimally altered compared to new Aeroshell 500 turbine oil.

This lubricant contains C_{20} to C_{33} Pentaerythritol triesters of C_5 to C_{10} fatty acids (MW 388 to 556 amu; Figure 1A), C_{20} being the most abundant, and minor amounts of didentaerythritol hexaesters (Figure 1A and B). Additives include the antioxidants phenanthrene (and traces of methyl- and dimethyl-phenanthrenes), N-phenyl-2-naphthylamine, tricresyl phosphate isomers (*ortho*, *meta*, and *para*-cresyl), and *bis*-(4-octylphenyl)-amine.

The PETs were tentatively identified based on mass spectral data (Figure 2). On the mass spectra of the C_{20} PET (Figure 2A), the molecular ion M$^+$ 388 is present in low intensity (<1%). The fragment ion m/z 371 ([M−17]$^+$; 4%) corresponds to the loss of the hydroxyl substituent. The fragment ion m/z 85 (100%; $[C_5H_9O]^+$) corresponds to fragmentation α to the carbonyl group of a fatty acid substituent. The absence of other large fragment ion suggests that pentaerythritol has three C_5 fatty acids substituents. Similarly, on the mass spectra of a C_{21} PET (Figure 2B), the molecular ion is less than 1%, but the fragment ion ([M−17]$^+$ is more preponderant (4%). The presence of the fragment ions m/z 85 (100%) and m/z 99 (33%) indicate the presence of two C_5 and one C_6 fatty acid substituents on the C_{21} pentaerythritol.

PETs having at least 22 carbon atoms have multiple isomers as various combinations of fatty acid substituents occur (Figures 2C and 3). Determination of the carbon number of these susbstituents can be done by mass chromatography of fragment ions m/z 85, m/z 99, m/z 113, m/z 127, m/z 141, and m/z 155. For example, the C_{25} PET has three abundant isomers (Figure 2C). The first eluting isomer (**I**) forms a peak in the mass chromatograms of fragment ions m/z 85, m/z 113, and m/z 127, indicating the presence of C_5, C_7, and C_8 fatty acid susbstituents, respectively. C_{25} isomer **II** forms a peak in the mass chromatogram of the fragment ion m/z 85, m/z 99, and m/z 141, indicating the presence of C_5, C_6, and C_9 fatty acid susbstituents, respectively. C_{25} isomer **III** has a C_{10} and two C_5 fatty acid substituents. The mass spectra of the C_{25} PET isomers are provided in the
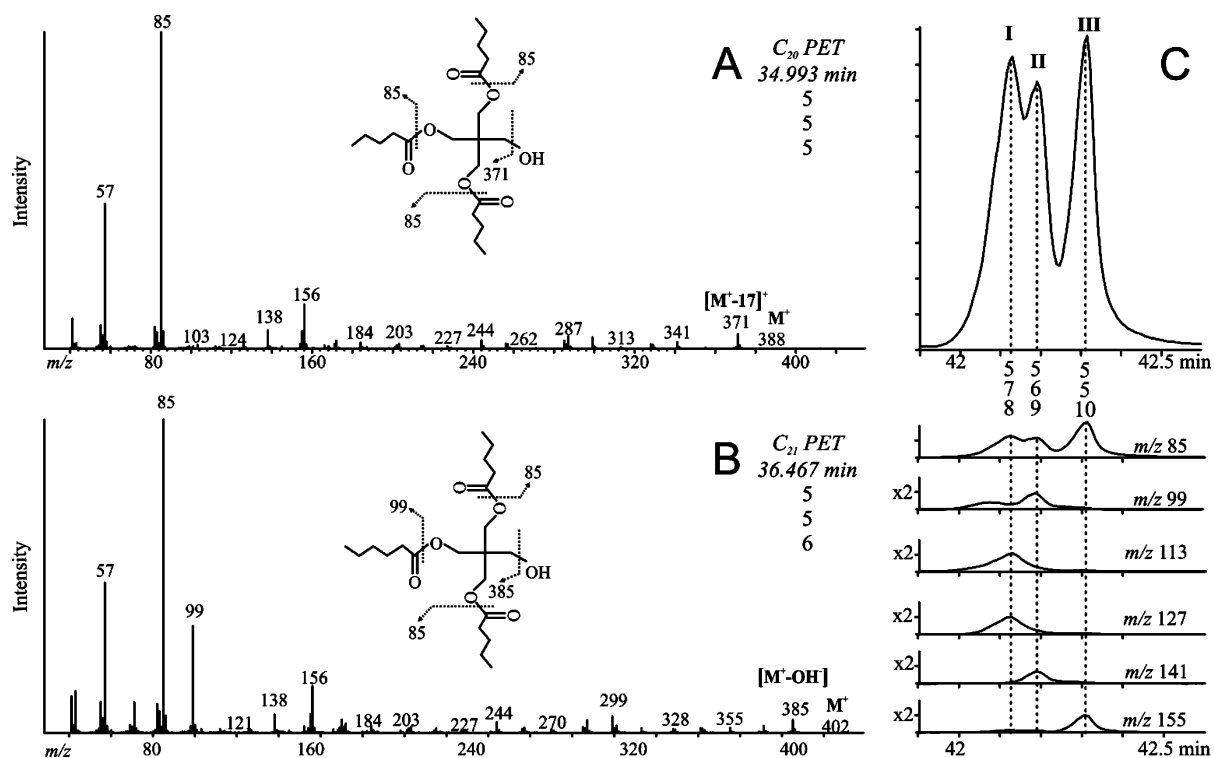
FIGURE 2. Mass spectra and tentative structures of (A) C_{20} pentaerythritol triester (PET) and (B) C_{21} PET. (C) Partial total ion current and partial mass chromatogram of fragment ions m/z 85, m/z 99, m/z 113, m/z 127, m/z 141, and m/z 155 of Aeroshell 500 showing the distribution the fatty acid subtituents of C_{25} PET. Peak I, II, and III are C_{25} PETs with C_5–C_7-C_8, C_5–C_6-C_9, and C_5–C_5-C_{10} fatty acids substituents, respectively.

SI. It is noteworthy that the isomer with the longest fatty acid substituent elutes last.

Degradation Potential of Spilled Contaminants. Aeroshell 500 consist entirely of high molecular weight (HMW) compounds (>388 amu) and will not evaporate unless heated. Photodegradation is not expected because PETs do not absorb radiation in the UV and VIS region, but laboratory experiments have shown that synthetic tri- and tetraester-based lubricants are biodegradable at ~20 °C (22–26). These studies concur in indicating that in the presence of carboxyl esterase, Pentaerythritol esters will release easily degradable fatty acids and pentaerythritol, a C_5 compound with a quaternary carbon and four hydroxyl groups, which is water-soluble but probably poorly biodegradable (22). Carboxyl esterase is generally involved in the primary degradation of organic matter (23, 24) and is a relatively common enzyme in microorganisms. Carboxyl esterase preferentially hydrolyzes triglycerides with fatty acids shorter than C_6. The longer fatty acids probably impose steric hindrance of the carboxyl group (23). Hence, the length of the fatty acid substituents in PET should influence the biodegradation potential of Aeroshell synthetic esters. PET bearing two or three C_5 fatty acids will be more easily biodegraded than those bearing longer chain ones, resulting in the biodegradation of the lower molecular weight PETs. However, synthetic oil, containing aliphatic esters up to C_{34} was still present in sediments 10 years after a spill at a helipad in Bunger Hills, East Antarctica and even in the surface sediments, there was no evidence for biodegradation (27). In absence of biological activity, these hindered esters will persist. Thus, their degradation in the ice cover of Lake Fryxell should be limited to sediments, ice layers, and melt pools where biological activity, with esterase capacity, may occur during the summer melt season.

The additives phenanthrene and methylated phenanthrenes are more susceptible to photodegradation and biodegradation than evaporation (28). Tricresyl phosphates are not volatile, relatively insoluble in water, and have low hydrolysis potential, although they are rapidly biodegraded or ingested by living organisms (29, 30). *N*-phenyl-1-naphthylamine, similar to *N*-phenyl-2-naphthylamine, is lipophilic, therefore it can accumulate preferentially in cell membranes and disrupt photosynthetic reactions (31). *N*-phenyl-1-naphthylamine is biodegradable in sewer and lake water although at slow rates (32). This additive does not hydrolyze, but sorbs onto sediment and organic materials and its ultraviolet absorption spectrum indicates that it should degrade photochemically in air. No data are available on the biodegradation of *bis*(4-octylphenyl)amine in aquatic systems (33), but this compound is extremely hydrophobic and thus unlikely to be easily biodegraded.

GC–MS Analysis of Field Samples. Three of the melt pools, sites 20 (~10 m northwest of the crash site), site 38 (~7 m northeast of the site), and site 24 (~10 m southwest of crash site), contain residues of Aeroshell 500 (Figure 4). Two other melt pool samples (samples W and E), which were collected more than 19 m away from the accident site, do not contain synthetic oil, consistent with the 19-m limit of reported extent of contamination determined during the initial crash investigation by Alexander and Stockton (2003). Only one out of nine ice cores analyzed (cores 12; see the SI) has synthetic ester residues. PETs were only observed in the yellowish fluid encased in an air bubble, though nine other ice subsamples of core 12 and one sample for core 6 were analyzed.

The extract of meltpool waters from site 38 contains C_{20} to C_{32} PETs, among which C_{23} and C_{26} triesters are the most abundant (Figure 4A). A much lesser abundance of PET was observed in the meltpool water of site 20 (chromatogram in the SI), though the distribution of PET was similar to that observed in waters of site 38. Melt pool sediments at site 38 contains *n*-alkanes from C_{12} to C_{22} with a mode at *n*-C_{15} (Figure 4B) derived from helicopter JP5-AN8 contamination (9). The extract also contains PET, with a different distribution to
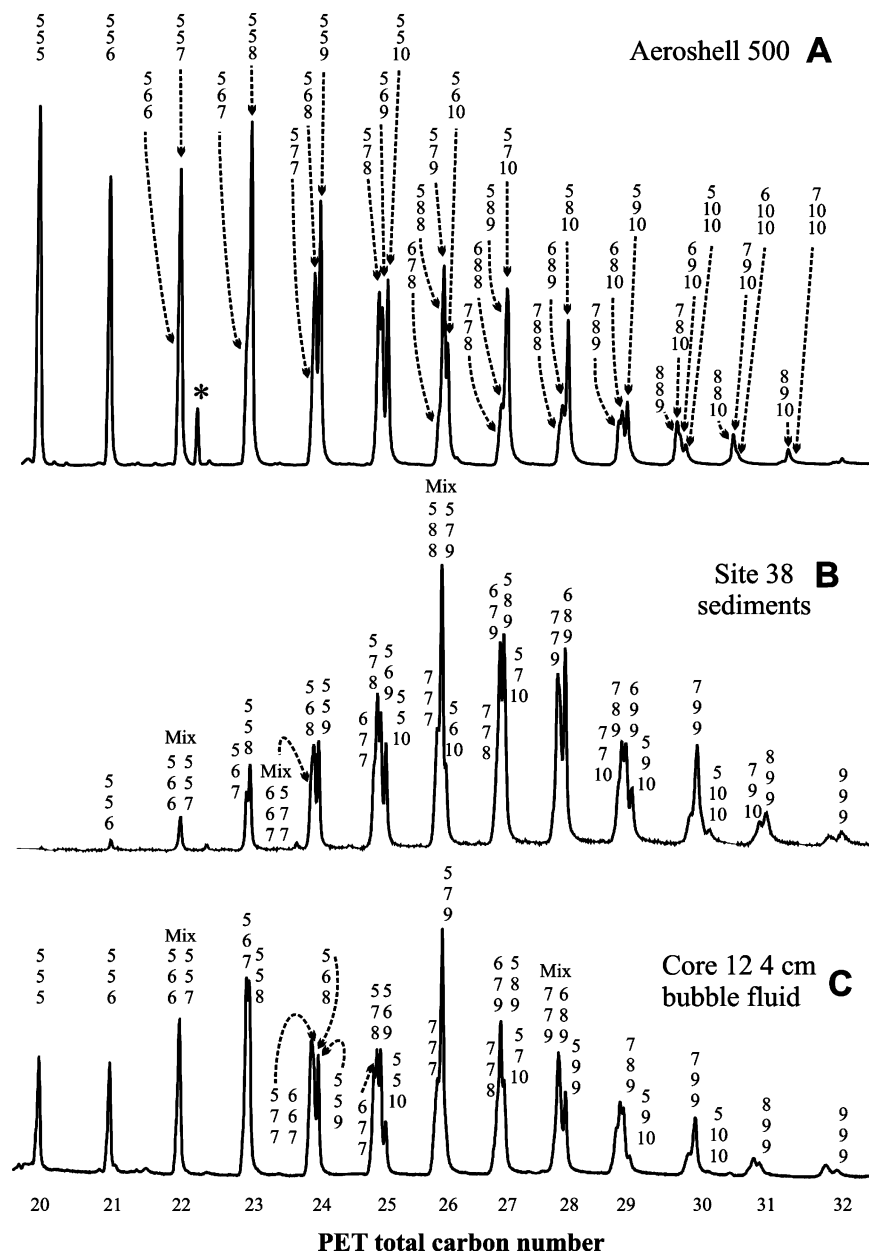
FIGURE 3. Partial total ion current of pentaerythritol triesters (PETs) showing the carbon number of the fatty acid substituents in (A) Aeroshell 500, (B) Site 38 sediments, and (C) Core 12 bubble fluid. The total carbon numbers of the PETs is indicated on the *x*-axis, corresponding to the sum of carbon atoms in the acid substituents plus five carbon atoms from pentaerythritol. * Indicates the antioxidant additive *bis*(4-octylphenyl)-amine.

that observed for Aeroshell 500 (Figure 3A and B). The $C_{20}-C_{25}$ triesters are significantly less abundant than the C_{26} triesters, indicating preferential loss of low molecular weight (LMW) PETs. The same distribution of PET was observed in the melt pool sediments collected at site 20 and 24 (see the SI). Weathering of the PET is not due to evaporation nor photooxidation as these triesters are not susceptible to such processes, but likely the effect of biodegradation. It is noteworthy that the presence of C_{20} PET in melt pool waters suggests limited biodegradation in melt waters. This observation is consistent with the biodegradation of diesel fuel spilled on the ice cover, which was shown to occur mostly in sediment bearing ice layers and meltpool sediments (9).

The carbon chain length of the fatty acid substituents of the PETs detected in the sediments of meltpool 38 and in the bubble of core 12 was determined (Figure 3B and C). Isomers with C_5 and C_6 substituents were depleted relative to their distribution in Aeroshell 500 (Figure 3A). In site 38 sediments, the C_{20} PET containing three C_5 fatty acids ($C_5-C_5-C_5$) is

now present only in trace amounts. In both the meltpool sediments of site 38 and the bubble fluid of core 12, the $C_5-C_5-C_9$ isomer of the C_{24} PETs, dominant in Aeroshell 500, is in equal abundance or less abundant than the C_{24} $C_5-C_6-C_8$ and $C_5-C_7-C_7$ isomers. The percentage of the contribution of C_5 substituents to all substituents in all PETs as determined by integration of the mass chromatogram of the fragment ion m/z 85 versus mass chromatography of m/z 85 + 99 + 112 + 127 + 155 is much lower in site 38 meltpool water (48%) and meltpool sediments (45%), as well as in the bubble fluid of core 12 (49%) than in Aeroshell 500 (62%; Figure 5). In contrast, the contribution of C_7 substituents to the whole pool of PET substituents increase from 8% in Aeroshell 500 to 16% and 17% in meltpool water and meltpool sediments of site 38, respectively, and to 17% in the bubble fluid of core 12 (Figure 5). For all PETs, isomers carrying one or two C_5 isomers are preferentially removed, concordant with the previous observation that esterase preferentially hydrolyzes triglycerides with fatty acids shorter than C_6 (23).
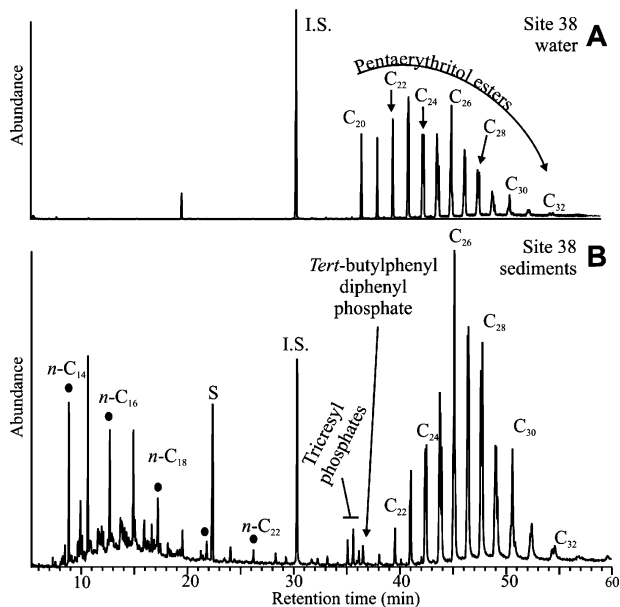
FIGURE 4. Total ion current trace of meltpool (A) waters and (B) sediments collected at site 38, showing the distribution of contaminants derived from Aeroshell 500, and aviation diesel. I.S.: Internal standard (n-C$_{24}$).

Thus, the selective loss of isomers with short fatty acid substituents is likely due to degradation via esterase activity (22, 25). It is noteworthy, that biodegradation in this fluid-filled bubble is also supported by the preferential loss of n-alkanes versus branched alkanes and by the presence of naphthalenones (9) that are known byproducts of naphthalene biodegradation (34).

The antioxidant additives tricresyl phosphates were detected only in the meltpool sediments, consistent with their low solubility in water (Figure 4A and SI). These antioxidants are more abundant than the LMW PETs, suggesting that these compounds are not easily biodegraded. Biodegradation usually changes the relative abundances of the three tricresyl phosphates isomers (35). The relative abundances of the three isomers is identical in Aeroshell 500 and in the meltpool sediments, suggesting that these compounds are not degraded in the ice cover.

Tert-butylphenyl diphenyl phosphate elutes just after the tricresyl phosphates (Figure 4B). This compound was not initially detected in the Aeroshell 500 due to its low concentration and perfect coelution with the very abundant C$_{20}$ triester. This additive can be metabolized by fungi (36, 37), which are probably present in the ice cover as these organisms are common in cryoconites (38), which are cylindrical water-filled melt holes common on glacier surfaces in the Dry Valleys. Thus, this additive is not expected to persist in the ice cover where sediments are present.

Bis-(4-octylphenyl)amine and *N*-phenyl-2-naphthy-lamine, major antioxidants in Aeroshell 500 (Figure 1), were not detected in the samples that contained Aeroshell residues. It is likely that both additives were weathered, although byproduct of their biodegradation were not observed.

Lateral and Vertical Transport in the Ice Cover. Aeroshell 500 behaves as a dense nonaqueous phase liquid (DNAPL) and, as a result, occurs more abundantly at the bottom of melt pools, usually in association with sediments (Figure 4B). The minor fraction of the PETs dissolved in the melt pool waters (Figure 4A) can be transported laterally in the summer when the ice is porous and an aquifer develops in the ice cover (21). The bulk of the Aeroshell oil residue, however, and the recalcitrant additives tricresyl phosphates preferentially sorb onto sediments. This association with sediments favors natural attenuation because biodegradation
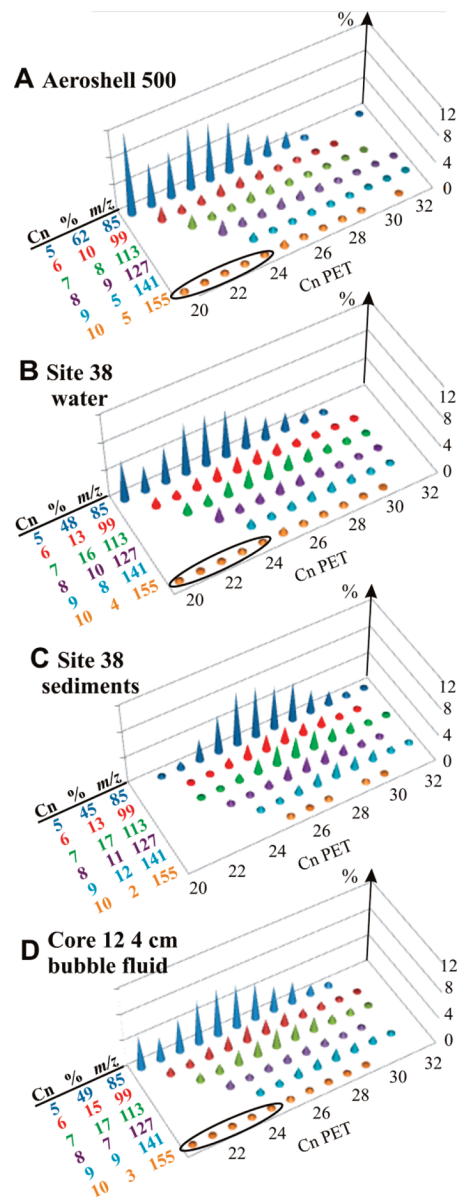

FIGURE 5. Contribution in % of C$_5$ to C$_{10}$ fatty acids to the pool of PET substituents for (A) Aeroshell 500, Site 38 meltpool (B) sediments, (C) water, and (D) bubble fluid from core 12. The data are derived from the integration of the mass chromatogram of fragment ions m/z 85, m/z 99, m/z 113, m/z 127, m/z 141, and m/z 155. The percentages on the left of the plots correspond to the summed percentage contribution of each substituent (C$_5$–C$_{10}$) to all substituents in the corresponding sample. The circled peaks for m/z 155 do not indicate the presence of C$_{10}$ fatty acid derivatives but are the result of a fragment ion couplet m/z 155 and m/z 156.

occurs mostly in sediment layers. DNAPLs that sorb onto sediments and are not biodegraded may melt their way into the aquifer in the ice. The net upward movement of the ice cover will limit the descent of DNAPLs across the ice cover into the water column. However, discrete conduits in the ice that connect the aquifer to the lake water (6, 21), may hasten the transfer of sorbed contaminants into the pristine lake waters.

Acknowledgments

Note Added after ASAP Publication

Due to a production error Figures 4 and 5 were switched in the version of this paper published ASAP March 5, 2009; the corrected version published ASAP March 10, 2009.

Supporting Information Available

Location map; Mass spectra of C_{25} pentaerythritol triester isomers; Total ion current of nonvolatile contaminants in Site 20 water and sediments. This material is available free of charge via the Internet at http://pubs.acs.org.

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ES802655S