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Biomarker assessment of organic matter sources and degradation in Canadian High Arctic littoral sediments

Brent G. Pautler · Janice Austin · Angelika Otto · Kailey Stewart · Scott F. Lamoureux · Myrna J. Simpson

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Abstract Carbon stocks in the High Arctic are particularly sensitive to global climate change and the investigation of the variation in organic matter (OM) composition is beneficial for improved understanding of OM vulnerability. OM biomarker characterization of solvent–extractable compounds and CuO oxidation products of littoral sedimentary OM in the Canadian Arctic was conducted to determine OM sources and decomposition patterns. The solvent–extracts contained a series of aliphatic lipids, steroids and one triterpenoid of higher plant origin as well as the low abundance of *iso*- and *anteiso*-alkanes originating from *Cerastium arcticum* (Arctic mouse-ear chickweed), a native angiosperm. The carbon preference index (CPI) of the *n*-alkane, *n*-alkanol and *n*-alkanoic acid biomarkers suggests relatively fresh lipid material in the early stages of degradation. The CuO oxidation products were comprised of benzenes, lignin-derived phenols and short–chain diacids and hydroxyacids. A high abundance of these terrestrial biomarkers at sites close to the river inlet suggests soil-derived fluvial inputs are an important source of OM delivered to the littoral sediments. The high lignin-derived phenol ratios of acids to aldehydes suggest that lignin degradation is in a relatively advanced oxidation stage. The absence of ergosterol, a common fungal biomarker also suggests that lignin-derived OM may be preserved in soil OM and transported to littoral sediments. This representative OM characterization suggests that Arctic sedimentary OM is a mixture of recently deposited and/or preserved lipids in permafrost melt and oxidized lignin-derived OM that may become destabilized from external influences such as climate change.

Keywords Organic matter · Biomarkers · Littoral sediments · Lignin · Lipids · *Iso*-alkanes · *Anteiso*-alkanes

Abbreviations

OM	Organic matter
GC-MS	Gas-chromatography-mass spectrometry
MAGs	Monoacylglycerols
CPI	Carbon preference index
Ad/Al	Acid/Aldehyde

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B. G. Pautler · J. Austin · A. Otto · M. J. Simpson (✉)
Department of Physical and Environmental Sciences, University of Toronto, 1265 Military Trail, Toronto, ON M1C 1A4, Canada
e-mail: myrna.simpson@utoronto.ca

Present Address:
A. Otto
Forschungsinstitut Senckenberg, Sektion Palaeobotanik, Senckenberganlage 25, 60325 Frankfurt/Main, Germany

K. Stewart · S. F. Lamoureux
Department of Geography, Queen's University, Kingston, ON K7L 3N6, Canada

V	Vanillyl monomers
S	Syringyl monomers
C	Cinnamyl monomers
3,5-DHBA	3,5-Dihydroxybenzoic acid

Introduction

Arctic landscapes are characterized by highly diverse ecosystems with a large variation in plant species, litter biochemistry and biogeochemical cycling rates due to the functionally distinct microbial communities that differentially alter naturally occurring organic matter (OM) as it resides or is transported throughout the ecosystem (Zak and Kling 2006). To date, Arctic regions have not been studied to the same extent as those in temperate regions, yet the northern permafrost ecosystems are estimated to contain 25–33% of the world's stored carbon (Oechel and Vourlitis 1995), 12% of which is stored in the tundra regions alone (Billings 1987). Recent findings estimate as much as 191.2 Pg of carbon is stored in the top 30 cm of Arctic soil, 495.8 Pg in the top 100 cm, and as much as 1024 Pg in the top 300 cm (Tarnocai et al. 2009). There is growing concern that climate warming could release this vast amount of carbon as greenhouse gases to the atmosphere (Trumbore et al. 1996; Hossain et al. 2007), however the molecular-level composition of Arctic OM has yet to be analyzed which would aid in the understanding of OM turnover mechanisms. Assessment of the decomposition of OM is a challenging task because it is highly heterogeneous and consists of numerous chemical components, from simple molecules, such as small solvent-extractable compounds, to extremely complex aggregates and associated compounds such as humic substances (Simpson et al. 2002). Previous studies emphasize the need for accurate quantification of labile OM, such as carbohydrates and proteins, because they are thought to be more sensitive to degradation at elevated temperatures than refractory components such as the alkyl and lignin-derived compounds and can be a major source for increased CO_2 emissions to the atmosphere (Schlesinger and Andrews 2000). However, Feng et al. (2008) found that the degradation of lignin, a major component of soil OM, derived from terrestrial plants, also accelerates under soil warming conditions. This highlights the need for assessing the response of both labile and refractory OM fractions to future global warming. Such research is of particular interest for OM in Arctic regions where the carbon balance is more sensitive to environmental change than in lower latitude areas (Oechel et al. 1993; Boddy et al. 2008; Ping et al. 2008).

In this study, solvent-extractable lipid and lignin-derived phenol OM biomarker composition and concentrations were measured and quantified using solvent extraction, chemolytic methods and gas chromatography–mass spectrometry (GC–MS) to investigate the input source and degradation stage of littoral sedimentary OM along the edges of a Canadian Arctic lake. The objective of this study is to examine the nature of the current OM composition of Arctic littoral sediments because they are representative of recent inputs and molecular-level OM alterations. An understanding of the nature and composition of Arctic OM will assist in understanding and predicting the potential responses to future disturbances, vulnerability, and biogeochemistry of OM in the Canadian High Arctic.

Materials and methods

Littoral sediment samples

Four Arctic littoral sediment sample locations were chosen from the Cape Bounty Arctic Watershed Observatory (http://geog.queensu.ca/cbawo/index.htm) on the south central coast of Melville Island Nunavut, in the western Canadian High Arctic (74°55′ N, 109°35′ W, Fig. 1). The landscape is characterized by simple drainage patterns, sparse tundra vegetation and continuous permafrost (Cockburn and Lamoureux 2008). The active layer depth varies between 0.5 and 1 m, with surface detachments and gullies along the river channels (Lamoureux et al. 2006). Vegetation cover is heterogeneous and varies from sparse polar desert to dense, localized sedge meadows consisting mostly of patchy dwarf prostate shrub tundra where water sources are sustained during the summer, such as below perennial snow banks (Walker et al. 2005). Mean summer (June, July, August) and winter (December, January, February) temperatures at Rea

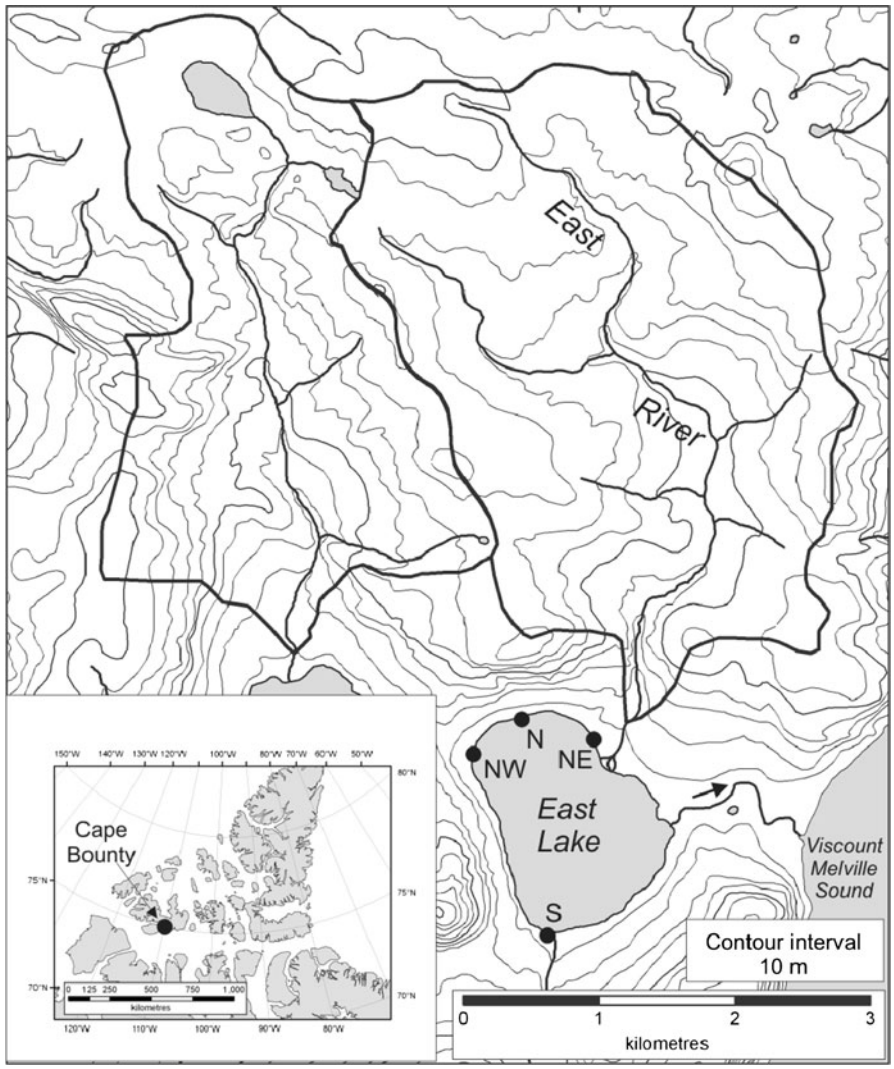

Fig. 1 East Lake littoral sample locations, Cape Bounty Arctic Watershed Observatory, Melville Island, Nunavut, Canada. Note that the indicated watershed boundary of the East River is based on the location of a long term hydrometric guagin site (data not used in this study). Lake input is dominated by the East River with a small ephemeral water track on the south edge with limited flow from the slopes around the lake only during the snow melt period, and the output is indicated by an arrow

Point (105 km northeast of Cape Bounty, 1969–1985) are 1.9 and −32.2°C respectively (Cockburn and Lamoureux 2008).

Cape Bounty contains two adjacent watersheds—referred to as West (8.0 km^2) and East (11.6 km^2) watersheds, which drain into similar small lakes. Flow into the East Lake is dominated by the East River that drains the 11.6 km^2 catchment. Discharge is typical of Arctic nival systems, with a short period of high flow during the snow melt period, followed by low flow during the summer recession. In most years, discharge is limited to a 2–3 month period, and flow ceases during the remainder of the year (Cockburn and Lamoureux 2008). Water tracks from the south drain the slopes around the lake and are highly ephemeral, with limited flow typically only during the snow melt period. Littoral sediment samples were collected at the East Lake littoral margin and East River channel. Several sub-samples that were free of vegetation were collected by hand at each site and placed in a single Whirl-pak to generate one homogenized sample from each location. Samples were kept dark and frozen for the remainder of the field season (ca 2 weeks). After sampling, the four East Lake littoral sediment samples were freeze-dried and stored at −20°C prior to analysis. Four locations were selected for sampling (Fig. 1). N and S were chosen to compare the OM along the north (N) and south (S) shores while NW (north west) and NE (north east) were chosen for the evaluation of the

impact of fluvial delivery on the OM composition in littoral sediments.

Carbon content

Carbon contents were determined using an Analyzer Vario EL III (Hanau, Germany) C, H, O, N, S elemental analyzer. Samples were ground to a fine powder and milligram quantities were analyzed in duplicate for C. Inorganic carbon, such as carbonate, was measured with the method of Bundy and Bremner (1972) and was not detected in any of the littoral sediments. Consequently, elemental carbon values represent the amount of organic carbon (OC) in the sediments.

Sequential extraction of OM biomarkers

Sequential chemical extractions (solvent-extraction, CuO oxidation) were conducted to analyze the extractable compounds and lignin-derived phenols respectively (Hedges and Mann 1979; Otto et al. 2005; Otto and Simpson 2007). Briefly, sediments (~20 g) were sequentially extracted by sonication for 10 min with 40 ml CH_2Cl_2, CH_2Cl_2:MeOH (1:1 v/v) and MeOH. The combined extracts were transferred to a flask by gravity filtration through pre-extracted cellulose filters (Fisher Scientific P8) and then filtered through glass fibre filters (Whatman GF/A), concentrated by rotary evaporation and completely dried in 2 ml glass vials under a N_2 stream. Yields were determined by weighing the dry residue. The remaining residue samples were air-dried and stored at −20°C. Total solvent-extracts were re-dissolved in 300 µl hexane and separated using silica column chromatography into alkane, aromatic and polar fractions by elution with 5 ml hexane, CH_2Cl_2, and MeOH respectively. The fractions were dried in 2 ml glass vials under N_2 and yields determined by weighing the dry residues.

The air-dried solvent-extracted sediment was then subjected to CuO oxidation to release lignin-derived phenols (Hedges and Mann 1979; Otto et al. 2005; Otto and Simpson 2007). Solvent-extracted sediment (~4 g) were extracted with 2 g CuO, 200 mg ammonium iron (II) sulfate hexahydrate [$Fe(NH_4)_2(SO_4)_2$ $6H_2O$] and 16 ml 2 M NaOH in Teflon-lined bombs at 170°C for 2.5 h. The extracts were acidified to pH = 1 with 6 M HCl, and kept for 1 h at room temperature in the dark to prevent polymerization of cinnamic acids. After centrifugation (2500 rpm, 30 min), the supernatants were liquid–liquid extracted (3×) with 50 ml of diethyl ether. The extracts were dried with anhydrous Na_2SO_4 to remove any remaining water, concentrated by rotary evaporation, transferred to 2 ml glass vials and dried under N_2.

A comprehensive selection of native plants from around Cape Bounty was collected and extracted using the previously described procedure to determine potential plant-derived sources for a series of *iso*- and *anteiso*-alkanes observed in the solvent-extracts. A total of 30 species (whole plant tissues, excluding roots) comprising the majority of the High Arctic tundra biomes present (Walker et al. 2005) were sampled and dried at 40°C. The plants were ground using a mortar and pestle, weighed into 125 ml amber glass bottles and stored until extraction at room temperature.

Derivatization and biomarker analysis by GC–MS

The solvent and CuO oxidation extracts were re-dissolved in 500 µl of CH_2Cl_2:MeOH (1:1 v/v). Aliquots of the extracts (50 µl) were transferred to 2 ml vials and dried in a stream of N_2 and then converted to trimethylsilyl (TMS) derivatives by reaction with 90 µl *N*,*O*-bis-(trimethylsilyl)trifluoracetamide (BSTFA) and 10 µl anhydrous pyridine for 3 h at 70°C. After cooling, 50 µl of hexane was added to dilute the extracts.

GC–MS analysis of derivatized extracts was performed with an Agilent model 6890N chromatograph coupled to an Agilent model 5973N quadrupole mass selective detector. Separation was achieved with a HP-5MS fused silica column (30 m × 0.25 mm i.d., 0.25 µm film thickness) with He as the carrier gas. GC operating conditions were: 65°C (2 min), to 300°C (held 20 min); the sample (2 µl) was injected in splitless mode with an injector port temperature of 280°C using an Agilent 7683 autosampler. The spectrometer was operated in the electron ionization mode (EI) at 70 eV and scanned from *m*/*z* 50 to 650. Data were acquired and processed with Agilent Chemstation G1701DA software. Compounds were identified by comparisons of the mass spectra to a MS library (Wiley275 MS library), comparison with authentic standards and with published data. The trimethylsilyl (TMS) derivatives of behenyl alcohol

(1-docosanol) and vanillic acid (as TMS ester) were used as external quantification standards for solvent-extracts and CuO oxidation products respectively (Otto et al. 2005; Otto and Simpson 2006).

Results

Composition of solvent extractable biomarkers

The extracts were dominated by similar compound distributions (Figs. 2 and 3; note only one sample is shown for brevity) that varied in concentration (Figs. 4 and 5). The dominant compounds included: aliphatic lipids (*n*-alkanols, *n*-alkanoic acids, *n*-alkanes, α-hydroxyalkanoic acids, *ω*-hydroxyalkanoic acids, hopanes, *iso*-alkanes, *anteiso*-alkanes), with lesser contributions from steroids, terpenoids, monoacylglycerols, carbohydrates, and wax esters. The OC content was observed to be: 4.1% for sample NW, 3.8% for sample S, 0.6% for sample N, and 0.5% for sample NE, however the biomarker extraction yields were highest at the sample locations in close proximity to the East River (N and NE; Fig. 4a). Flow into the East Lake is dominated by the East River that transports large sediment plumes of inorganic material that is deposited closer to the river inlet, diluting the overall OC% at these locations (Cockburn and Lamoureux 2008). Normalizing all biomarker concentrations to OC% corrects for any dilution and shows the relative contribution of identified biomarkers with respect to the total OC. *n*-Alkanols from C_{10} to C_{32} with an even preference and C_{max} at C_{26} are the predominant lipids in all sediment extracts (262–1380 μg/g OC). The concentration of *n*-alkanols is highest along the north shore of the East Lake at site N (Fig. 4b). The *n*-alkanoic acids were present at concentrations of 55.9–1,350 μg/g OC, ranging from C_{11} to C_{28} and with an even preference and C_{max} at C_{16} and C_{24}. Like the *n*-alkanols, the highest contents of alkanoic acids were along the north shore of the East Lake (sample N; Fig. 4b). α-Hydroxyalkanoic acids (C_{22}–C_{25}) with an

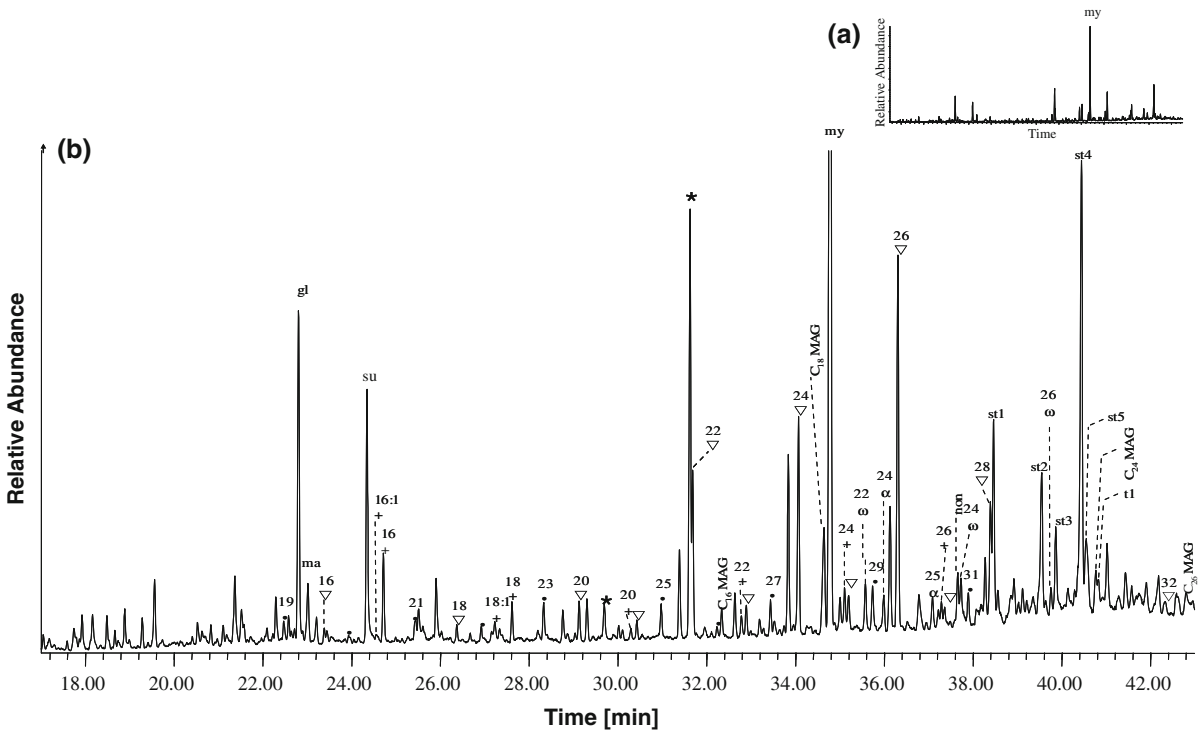

Fig. 2 GC-MS chromatograms (total ion current, TIC) of TMS solvent-extract of the Arctic littoral sediment S showing: **a** dominance of mycose (my) and **b** all identified compounds (*plus*, n-alkanoic acids; *inverted triangle*, n-alkanols; st1, cholesterol; st2, campesterol; st3, stigmasterol; st4, *β*-sitosterol; st5, stigmastanol; t1, α-amyrin; MAG, monoacylglycerols; gl, glucose; ma, mannose; su, sucrose; α, α-hydroxyalkanoic acids; *ω*, *ω*-hydroxyalkanoic acids *, contaminants). Numbers refer to total carbon numbers in aliphatic lipid series

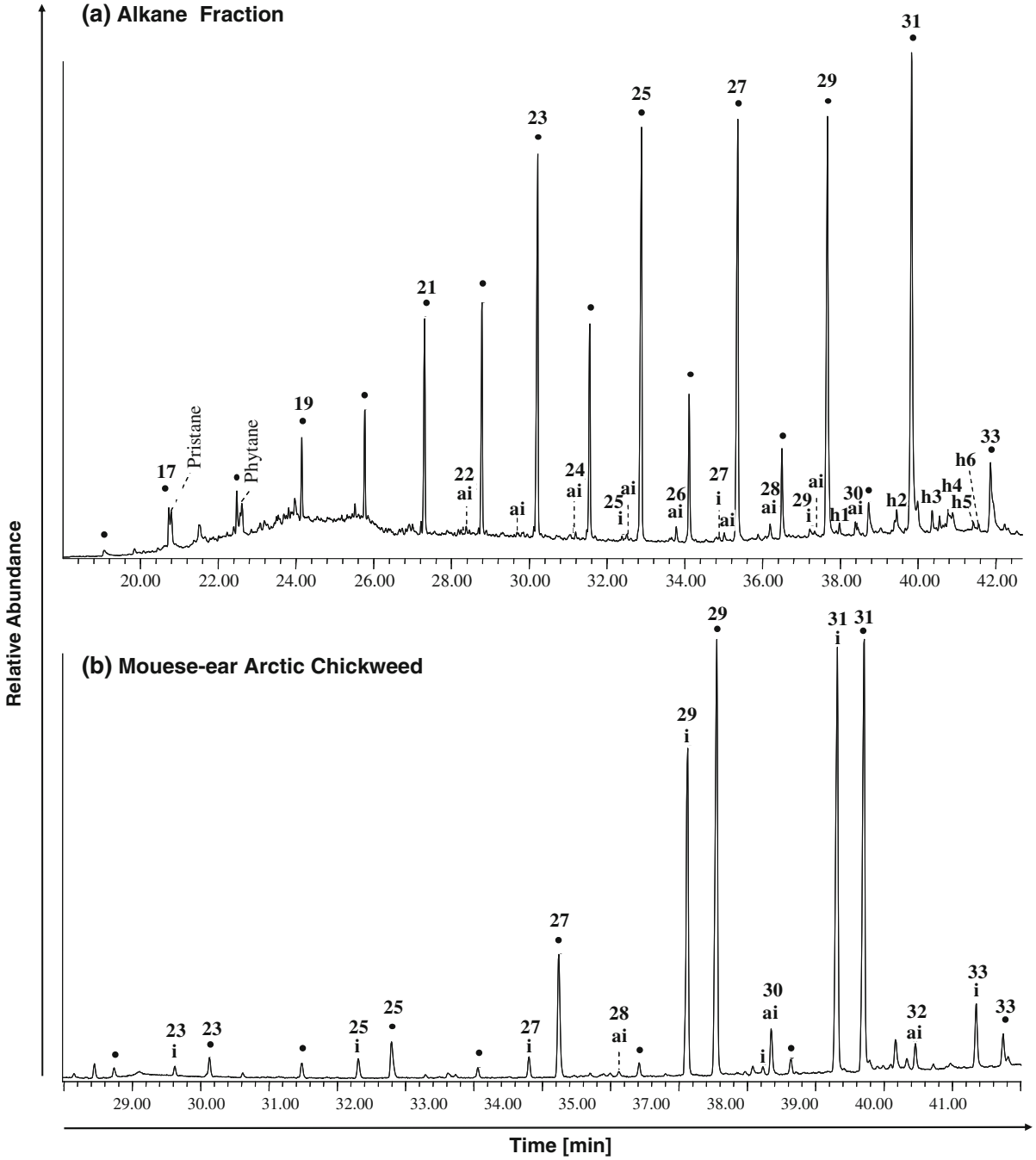

Fig. 3 GC–MS chromatogram (TIC) of **a** alkane fraction of solvent extract of S Arctic littoral sediment (*circle*, *n*-alkane; i, *iso*-alkane; ai, *anteiso*-alkane; h, hopane); **b** solvent extract of *Cerastium arcticum* (Arctic mouse-ear chickweed angiosperm *circle*, *n*-alkane; i, *iso*-alkane, ai, *anteiso*-alkane. Numbers refer to total carbon numbers in aliphatic lipid series

even preference and C_{max} at C_{24} and ω-hydroxyalkanoic acids (C_{22}, C_{24}, C_{26}) were found only in the west and south banks of the East Lake (NW and S) with yields ranging from 10.2–27.7 μg/g OC and 26.3–48.4 μg/g OC respectively. A series of wax esters derived from short-chain alkanoic acids and alkanols with total chain length C_{27} to C_{33} were detected in NW, with a total concentration of 66.0 μg/g OC.

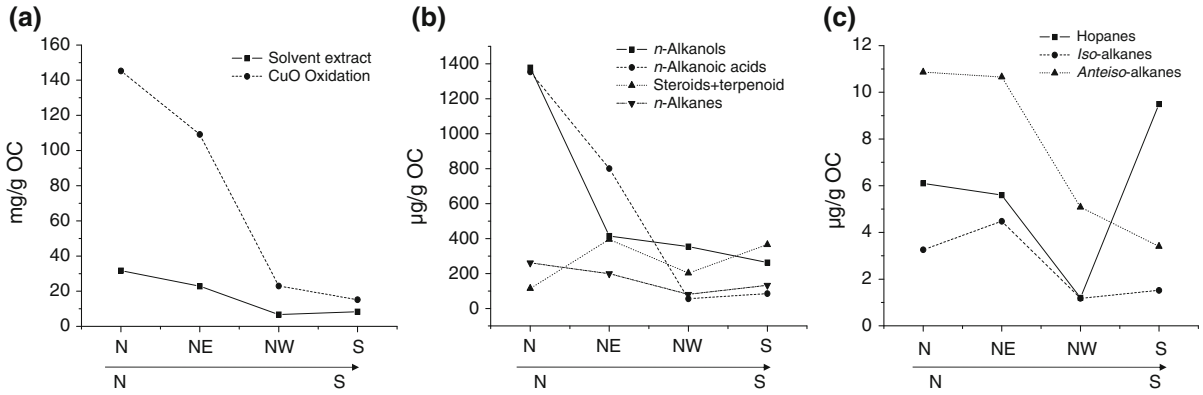

Fig. 4 Carbon-normalized extract yields and concentrations of major biomarker classes in Arctic littoral sediment samples from Cape Bounty, Melville Island, Nunavut, Canada: **a** Total yield of extractable compounds and CuO oxidation products; **b** aliphatic and cyclic lipids; **c** alkane fraction of hopanes, *iso*-alkanes and *anteiso*-alkanes (sample locations plotted from N to S)

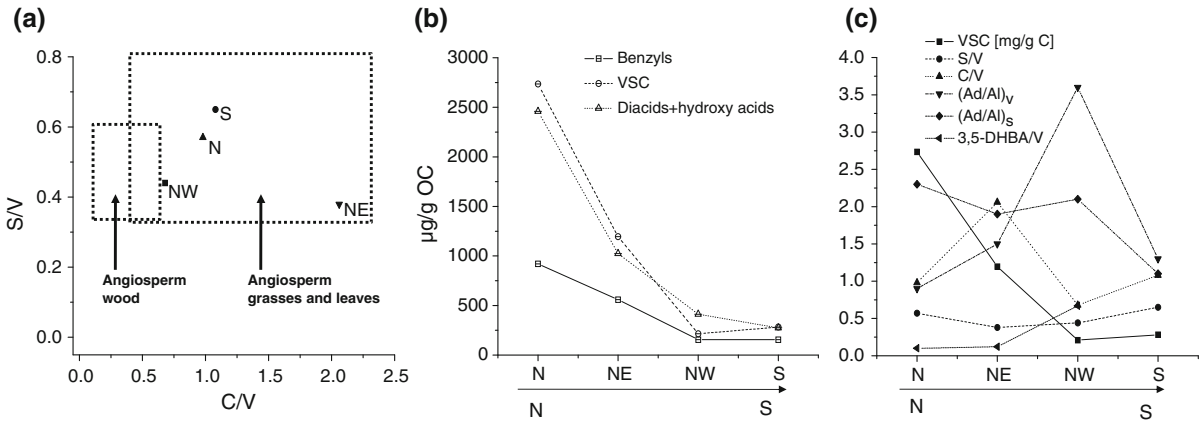

Fig. 5 Lignin-derived OM sources and degradation parameters: **a** Lignin source parameters for sediment samples (C/V, cinnamyl/vanillyl phenols; S/V, syringyl/vanillyl phenols); **b** carbon normalized extraction yields of benzene compounds, lignin-derived phenols (VSC), short-chain acids; **c** degradation parameters for CuO products: VSC, lignin-derived phenols; 3,5-DHBA, 3,5-dihydrobenzoic acids (sample locations plotted from N to S)

Silica column chromatography was performed to further separate the solvent extractable compounds into non-polar alkane, aromatic, and polar compounds. The alkane fraction contained *n*-alkanes, methyl branched alkanes and a series of hopanes (Fig. 3a). *n*-Alkanes ranged from C_{17} to C_{33} with an odd preference and highest abundance between C_{25} and C_{31}. Higher concentrations were found closer to the river inlet (N and NE) decreasing with increasing distance from the East River (NW and S; Fig. 4b). The methyl branched hydrocarbons include *iso*-alkanes (C_{23}–C_{30}, 1.2–4.5 μg/g OC) and *anteiso*-alkanes (C_{22}–C_{31}, 3.4–10.9 μg/g OC; Fig. 3). Hopanes (C_{27}–C_{31}) were in low abundance in all the East Lake littoral sediments (1.2–9.5 μg/g OC; Fig. 4c).

Five steroids and one triterpenoid were detected (203–1140 μg/g OC; Fig. 2). The sterols include cholesterol (st1), campesterol (st2), stigmasterol (st3), β-sitosterol (st4), and stigmastanol (st5) with β-sitosterol as the most abundant in all the sediments. α-Amyrin (olean-12-en-3α-ol; t1) was the only triterpenoid detected. C_{14} to C_{26} (even, absence of C_{20}) monoacylglycerols (MAGs) were also detected in East Lake sediments (51.4–389 μg/g OC). The

carbohydrates detected were glucose (gl), mannose (ma), sucrose (su), and mycose (my) with mycose as the dominant compound (Fig. 2).

Lignin-derived phenols

Major products after CuO oxidation included: benzenes, phenols and short-chain *n*-alkanedioic acids and hydroxy acids. All but one of the sediment samples (NE) contained the characteristic eight major lignin-derived biomarker compounds (vanillin, acetovanillone, vanillic acid, syringaldehyde, acetosyringone, syringic acid, *p*-coumaric acid and ferulic acid; Hedges and Mann 1979; Otto and Simpson 2006). The total concentrations of benzene compounds and phenols from the East Lake sediments ranged from 439–3,770 μg/g OC (Fig. 5b). Similarly, the concentrations of diacids and hydroxyl acids ranged from 274.7–2,460 μg/g OC (Fig. 5b). In addition to the eight major lignin-derived phenols, the observed benzene and phenol compounds were: benzoic acid, *p*-hydroxybenzaldehyde, *m*-hydroxybenzoic acid (3-OH), *p*-hydroxybenzoic acid (4-OH), and 3,5-dihydroxybenzoic acid. The short-chain acids include the *n*-alkane dioic acids: fumaric acid ($C_{4:1}$), suberic acid (C_8), azelaic acid (C_9) and the hydroxy acids malic acid (2-hydroxybutanedioic acid) and 2-hydroxypentanedioic acid. Additionally, pyrrole-carboxylic acid was identified in all the sediments. Ratios of the vanillyl (vanillin, acetovanillone, vanillic acid), syringyl (syringaldehyde, acetosyringone, syringic acid) and cinnamyl units (*p*-coumaric acid, ferulic acid) were about 1:1:1.

Discussion

Sources of solvent-extractable OM biomarkers

Long-chain ($>C_{20}$) *n*-alkanols, *n*-alkanoic acids and *n*-alkanes are typical constituents of epicuticular and associated waxes of higher plants (Tulloch 1976; Baker 1982; Kolattukudy and Espelie 1989; Bianchi 1995) while short-chain ($<C_{20}$) homologues are derived from algae and microorganisms (Meyers and Takeuchi 1978). The predominance of long-chain *n*-alkanols, *n*-alkanoic acids, and *n*-alkanes in East Lake littoral sediments suggests major OM inputs from vascular plant waxes and the absence of algal activity. The occurrence of α-amyrin, a specific biomarker for angiosperms (Peters and Moldowan 1993; Hernes and Hedges 2004) also denotes plant-derived inputs. Biomarkers from algae, bacteria and fungi were only minor contributors to the extractable portion of the littoral OM, reflected by a low abundance of short-chain *n*-alkanols, *n*-alkanoic acids and *n*-alkanes (Figs. 2 and 3). α-Hydroxyalkanoic acids and ωhydroxyalkanoic acids are only minor constituents of most plant waxes (Herbin and Robins 1968) and were present in the Arctic littoral sediments in low concentration. In addition, α-hydroxyalkanoic acids are generally found in phospholipid membranes of animals and plants (Otto et al. 2005); whereas ω-hydroxyalkanoic acids are found mainly in cyanobacteria and mosses (Matsumoto et al. 1988) and in the suberin biopolymer in plant roots (Otto et al. 2005). Higher concentrations of *n*-alkanes and *n*-alkanols were found in sample sites near river inlets (particularly N and NE) vs. the south edge site (S; Fig. 5b), suggesting that the East River may be an important pathway for delivering OM into littoral sediments.

Methyl branched hydrocarbons (*iso*-alkanes and *anteiso*-alkanes) are rarely reported in higher plants, although short-chain branched alkanes ($< C_{20}$) have been identified in cyanobacteria (Shiea et al. 1990). The branched alkanes in Arctic littoral sediments comprise predominantly homologues between C_{22} to C_{31} and are not derived from cyanobacteria. Rogge et al. (1994) reported the occurrence of these particular compounds in leaf surface waxes of tobacco plants and in much smaller concentration in typical urban herbaceous vegetation but their contribution to Canadian Arctic littoral sediments is very unlikely given the remote location and local plant distributions. Recently, Fukushima et al. (2005) detected long-chain *anteiso*-alkanes in some Japanese acidic freshwater lakes and assigned their source to planktonic microbes within lakes rather than external sources based on their presence in lake water and absence from particulate matter from inflowing river water. However, the occurrence of long-chain methyl-branched *iso*- and *anteiso*-alkanes in Canadian Arctic littoral sediments are distinctly different from those reported for Japanese sediments, although a contribution from planktonic microorganisms may contribute to some extent to the higher abundance of *anteiso*-alkanes in this case. The analysis of *Cerastium arcticum* plant

tissues (Arctic mouse-ear chickweed), a native angiosperm found sporadically throughout the watershed, shows that these methyl-branched alkanes constitute the majority of the extractable compounds (Fig. 3b) and strongly suggests that this plant is the source of the *iso*- and *anteiso*-alkanes observed in the littoral sedimentary OM. Spatial patterns show a decreasing trend in *iso*- and *anteiso*-alkanes with increasing distance from the East River inlet (Fig. 4c), further suggesting that these compounds result from fluvial transport and not synthesized in situ.

β-Sitosterol, stigmasterol and campesterol are common steroids in higher plants (Baker 1982; Bianchi 1995; Harwood and Russell 1984). Stigmasta-3,5-diene-7-one and sitosterone, degradation products of sitosterol and stigmasterol (Mackenzie et al. 1982), were not detected in any of the sediment samples. The absence of ergosterol, a common biomarker for fungi suggests a lack of recent fungal activity in the sediments (Weete 1976). Cholesterol is a major sterol in animals but is also found in fungi and algae (Weete 1976; Harwood and Russell 1984; Noda et al. 1988). As a result, the exact source is unclear but can be considered to be related to microbial activity as well as from plant inputs. α-Amyrin is a triterpenoid reported to be present in leaf waxes of angiosperms (Baker 1982; Volkman et al. 2000; Hernes and Hedges 2004). A series of even MAGs ranging from C_{14} to C_{26} and a C_{16} monounsaturated MAG were detected in the sediments. MAGs are major constituents of cell membranes and fats, resulting in a contribution from all organisms (Tulloch 1976; Harwood and Russell 1984). The carbohydrates detected in the extracts are ubiquitous to all organisms and are not suitable as specific biomarkers (Otto et al. 2005), with the exception of mycose, which originates from fungi, microalgae, bacteria and some plants at very low abundance (Arnold et al. 2003). However, the absence of ergosterol, a fungal-specific biomarker, in the littoral sediments suggests that mycose is more likely derived from plants rather than fungi.

Sources of lignin-derived phenol OM biomarkers

The lignin-derived phenol composition is characteristic of non-woody tissues from vascular plants (Hedges and Mann 1979; Hedges and Ertel 1982; Iiyama et al. 1990; Lam et al. 2001). The plotted C/V vs. S/V ratios from East Lake littoral sediments indicates that the lignin-derived OM and source vegetation are similar (likely angiosperms; Fig. 5a; Hedges and Mann 1979; Otto and Simpson 2006). Similar to the long-chain *n*-alkanes, *n*-alkanols and *n*-alkanoic acids, lignin-derived phenols show higher abundance for N and NE than S and NW, again suggesting that the East River has an important role in delivery of lignin-derived OM to littoral sediments (Figs. 4a and 5b). Our results are consistent with those of Requejo et al. (1991) who found that the lignin-derived phenol concentrations were highest in North American continental shelf sediments at their most northern location, the Yukon River delta. The proposed high inputs of vascular plant material from rivers during spring and summer run-off and enhanced preservation of this material in sediments as a result of low temperatures and seasonal ice cover for much of the year may contribute to the high lignin concentration and is supported by the results of this study.

In addition to lignin-derived phenols, CuO oxidation yielded benzoic acid, hydroxybenzoic acids, hydroxybenzaldehyde and pyrrole-2-carboxylic acids which are believed to be oxidation products of cutin, polysaccharides or proteins (Goñi et al. 2000). 3,5-Dihydroxybenzoic acids are thought to originate from tannins and other flavonoids (Goñi and Hedges 1992; Louchouarn et al. 1999). Further evidence suggesting that some of the littoral OM components are in an advanced stage of oxidation was the detection of a number of dialkanoic acids.

Biomarker assessment of OM degradation

Lipids in soils have been described as highly resistant to biodegradation (Dinel et al. 1990; Kögel-Knabner 2000) whereas studies of settling particles in lakes intercepted by sediment traps indicate that lipids may undergo substantial degradation when sinking to the bottom (Meyers and Ishiwatari 1993). Some biodegradation may occur along the lake edge, depending on microbial activity and physico–chemical conditions (Otto et al. 2005) and the preservation and accumulation of lipids has been observed in environments with inhibited microbial activity (Dinel et al. 1990; Bull et al. 2000). Fatty acid decomposition rates show that n-C_{16} homologues typically degrade faster than n-C_{30} (Meyers and Eadie 1993) and a depletion of the

algal biomarker n-C_{17} alkane vs. long-chain hydrocarbons has been reported (Kawamura et al. 1987). Aquatic OM is known to degrade during sinking to the bottom due to the freshness of the material (Meyers and Ishiwatari 1993), however we postulate that the land-derived lipid Arctic OM components have remained unaltered and are preserved in the littoral sediments (Nierop and Jansen 2009).

The yields of extractable compounds ranged from 6690–31700 μg/g OC (Fig. 4a). Lower yields for NW and S were observed in comparison to N and NE (Fig. 4a–c), indicating either a larger input source and/or higher degree of preservation for the latter. The carbon preference index (CPI) is a proxy that is applied to provide insight into the degree of diagenetic OM alteration acting as a numerical representation of the degree of the original biological chain length preserved in the extractable lipids (Bray and Evans 1961; Meyers and Ishiwatari 1993). In fresh material, odd-numbered chains dominate the hydrocarbons whereas even homologues dominate in fatty acids and alkanols (Meyers and Ishiwatari 1993). Values that are greater than two are an indication of fresh inputs while values less than two are the indication of a high degree of preferential degradation (Tuo and Li 2005). In the East Lake littoral sediments, values were between 2.6–3.6, 1.2–19.2 and 4.0–14.9 for n-alkanes, n-alkanols and n-alkanoic acids respectively. In all cases (with the exception of alkanols detected at S), the values are indicative of "fresh" inputs in an early stage of decomposition (Meyers and Ishiwatari 1993; Tuo and Li 2005). This "fresh" OM may result from new plant biomass, transport of relatively fresh or preserved OM from up-stream, possibly from melted permafrost released as a result of climatic warming in the Arctic (Schuur et al. 2009), which is known to contain OM in early stages of decomposition (White et al. 2002; Sjögersten et al. 2003; Turner et al. 2004). The CPI values suggest that overall the lipid OM is currently preserved in a relatively fresh, unaltered state, which is consistent with other studies (White et al. 2002; Sjögersten et al. 2003; Nierop and Jansen 2009). These lipid biomarkers are the result of a recent deposition or deposition of OM which was only recently released into active surface processes through permafrost melting and fluvial delivery.

CuO oxidation of OM in sediments generates products from lignin, cutin, proteins and tannins (Goñi et al. 2000; Kögel-Knabner 2000). Phenolic compounds derived from lignin have been employed as a valuable parameter for the degradation of OM in soils and fluvial sediments based on the composition of phenols and benzenes (Otto and Simpson 2006). Lignin biodegradation is governed by white–rot and brown–rot fungi by oxidative cleavage (Tien and Kirk 1983; Hedges et al. 1988). The fungal degradation of lignin is greatest in subaerial terrestrial environments but reported to be inhibited in water–logged wood (Hedges et al. 1988). Increased levels of lignin degradation are reflected in elevated acid/aldehyde (Ad/Al) values for both vanillyl and syringyl units (Ertel and Hedges 1985; Hedges et al. 1988; Goñi et al. 1993; Opsahl and Benner 1995). Ad/Al values for both vanillyls and syringyls of 0.1-0.2 have been reported for woody plant material (Hedges et al. 1988), whereas non-woody tissues such as leaves and grasses have been reported to have higher values (Benner et al. 1990; da Cunha et al. 2001). Preferential degradation of syringyl monomers compared to vanillyl units leads to a net decrease in S/V (Hedges et al. 1988; Opsahl and Benner 1995).

The yields of VSC were much lower for NW and S (209 and 282 μg/g OC) compared to N and NE (2740 and 1200 μg/g OC) suggesting a higher lignin input at N and NE (Fig. 5b). High values of $[(Ad/Al)_v$, 0.9–3.6] and $[(Ad/Al)_s$, 1.1–2.3] also suggest that lignin-derived OM in the littoral sediments is in an advanced oxidized state, but no apparent trend was observed with respect to fluvial transport (Fig. 5c). Ad/Al values for littoral sediments in this study are two to three times higher than those reported for littoral sediments in both temperate and Arctic regions (Hedges et al. 1982; Ishiwatari and Uzaki 1986; Hu et al. 1999; Kulinski et al. 2007). The tannin-derived 3,5-dihydroxybenzoic acid (3,5-DHBA) in the CuO oxidation products has been reported to accumulate in decaying cells exhibiting higher ratios of 3,5-DHBA over vanillyls (3,5-DHBA/V) with increasing degradation (Prahl et al. 1994; Louchouarn et al. 1999). Furthermore, positive correlations between 3,5-DHBA/V and $(Ad/Al)_v$ in soil and sedimentary OM have been reported (Prahl et al. 1994; Louchouarn et al. 1999; Farella et al. 2001). The 3,5-DHBA/V values for our experiments increased in a similar fashion to $(Ad/Al)_v$ but the value was below detection limits for sample S (Fig. 5c).

According to the degradation parameters for CuO oxidation products, the OM in these Arctic littoral sediments is at a relatively high degradation stage. This is in contrast to the lipid component, which is considered to be fresh on the basis of the CPI values. The results agree with a recent study that showed extensive degradation of lignin and enhanced preservation of extractable lipids in cold, wet soils (Nierop and Jansen 2009). The trend of increasing Ad/Al values with decreasing mean annual temperature has been observed for grassland soils in different climatic zones because of the readily metabolizable carbohydrates in warmer climates (Amelung et al. 1999). The high Ad/Al values observed for littoral sediments and the absence of ergosterol (fungal biomarker) from the solvent extracts suggests that the lignin-derived OM may not be the result of active biodegradation but may be "old" lignin recently released from permafrost due to Arctic warming or old lignin transported through the watershed and to the littoral sediments. Another driving force for lignin degradation in the Arctic could be abiotic processes including photochemical alteration or cross-linking (Opsahl and Benner 1998; Bertilsson et al. 1999). The role of abiotic mechanisms in lignin alteration needs to be investigated further as it may play an increasingly important role in lignin transformation in cooler climates (Otto and Simpson 2006).

The solvent-extractable and CuO oxidation biomarkers from Arctic sediments from the East Lake littoral zone on Melville Island, Nunavut was used as a case study for OM sources and degradation in this unique and previously unstudied ecosystem. The extractable compounds exhibited high CPI values indicative of "fresh" plant inputs and/or lipid preservation in littoral sediments with a spatial distribution pattern suggestive of inputs from newly deposited plant derived material or from melted permafrost soil via fluvial transport. Comparison of sediment biomarkers with those of a native Arctic plant shows that the observed series of C_{24} to C_{34} *iso*- and *anteiso*-alkanes are likely from a previously undocumented source for these biomarkers (*Cerastium arctium*; Arctic mouse-ear chickweed), which may now be used to monitor terrestrial OM input in this Arctic ecosystem. The littoral sedimentary OM is a mixture of fresh recently deposited and/or preserved lipids and oxidized lignin-derived OM that may originate from accumulated permafrost that has recently become bioavailable via melting and fluvial transport to littoral sediments. Interpretation of potential OM degradation in response to climate change based on bulk measurements is very complex due to the mixture of OM constituents, ages, and the different reaction rates (Davidson and Janssens 2006). Analysis of Arctic OM by this molecular-level biomarker methodology helps alleviate some of the complexity because not only does it provide insight into the sources, but may facilitate the prediction of the potential vulnerability of this carbon pool to environmental disturbances. For example, this Arctic OM may become more susceptible to degradation and release of carbon induced by climate change due to the lower metabolic activation energies of the large accumulation of preserved lipids (Mikan et al. 2002). This hypothesis will be the basis of future research involving the potential sensitivity and vulnerability of Arctic OM in the changing environment.

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