Biogeochemistry (2012) 111:569–581
DOI 10.1007/s10533-011-9688-6

Effects of pH and calcium on soil organic matter dynamics in Alaskan tundra

Kyle A. Whittinghill · Sarah E. Hobbie

Received: 14 November 2010 / Accepted: 29 November 2011 / Published online: 25 December 2011

Abstract In Northern Alaska (AK), large variation in biogeochemical cycling exists among landscapes underlain by different aged geologic substrates deposited throughout the Pleistocene. Younger, less weathered landscapes have higher pH (6.5 vs. 4.5), ten-fold higher exchangeable cation concentrations, and slower rates of microbial activity than older, more weathered landscapes. To tease apart the effects of polyvalent cations vs. pH on microbial activity and organic matter solubility and stabilization, we conducted a soil incubation experiment. We collected soils near Toolik Lake, Alaska from replicated sites along a chronosequence of landscape ages ranging from 11,000 to 4.8 million years since glaciation and manipulated soil pH and calcium (Ca, the dominant polyvalent cation across all landscape ages) using a factorial experimental design. As expected, microbial respiration was inhibited by high Ca concentrations at both pH 6.5 and 4.5. In contrast, soils with circumneutral pH (but similar Ca concentrations) exhibited higher rates of microbial respiration than soils with acidic pH, opposite of in situ patterns. Manipulated soils with acidic (4.5) pH (but similar Ca concentrations) exhibited higher cumulative dissolved organic nitrogen (DON) in leachates than soils with circumneutral (6.5) pH, similar to in situ patterns of leaching among landscape ages, but there was no consistent effect of pH on dissolved organic carbon (DOC) in leachates across landscape ages. Increasing Ca concentration inhibited cumulative DOC in leachates at circumneutral pH as expected, but had no effect on DOC or DON in leachates at acidic pH. Our results indicate that both polyvalent cation concentration and pH likely influence microbial activity in tundra soils, suggesting that heterogeneity in geochemical factors associated with landscape age should be considered in models of tundra biogeochemistry.

Keywords Dissolved organic carbon · Dissolved organic nitrogen · Polyvalent cations · Calcium · pH · Tundra

Introduction

In arctic ecosystems, climate, vegetation, permafrost cover, and geochemistry are important sources of variation in terrestrial organic matter cycling. Previous research on arctic soil carbon and nitrogen cycling has characterized the influence of climate (van Wijk et al. 2003; Epstein et al. 2004; Malmer et al. 2005), vegetation (Shaver and Chapin 1991; Callaghan and

K. A. Whittinghill · S. E. Hobbie
Department of Ecology, Evolution, and Behavior,
University of Minnesota, 100 Ecology,
1987 Upper Buford Circle, Saint Paul, MN 55108, USA

K. A. Whittinghill (✉)
Earth Systems Research Center, Department of Natural
Resources and the Environment, University of New
Hampshire, 208 Morse Hall, Durham, NH 03824, USA
e-mail: kyle.whittinghill@unh.edu

Jonasson 1995; Hobbie 1996), nutrient availability (Shaver and Jonasson 1999; Mack et al. 2004; Shaver et al. 2006), and permafrost cover (Kawahigashi et al. 2004; Frey and Smith 2005; Frey et al. 2007). Recent research has shown that geochemical differences among landscape ages also lead to significant variation in terrestrial organic matter cycling (Hobbie and Gough 2002; Hobbie et al. 2002, 2004; Whittinghill and Hobbie 2011). However, the mechanisms underlying relationships between landscape age and microbial activity in arctic organic soils remain unknown. As variation in watershed geochemistry exist throughout the circumpolar region, variation in organic matter processing among differing watersheds could have significant implications for understanding the arctic carbon budget.

Geologic controls on soil organic matter processing and watershed carbon and nutrient fluxes are well documented in temperate and tropical ecosystems where water has large contact with mineral soil layers (Yu et al. 2003; Lilienfein et al. 2004; Selmants and Hart 2008). In these ecosystems, dissolved organic matter (DOM) is retained by chemical stabilization of DOM as water moves through mineral soil horizons, decreasing the concentration of DOM in soil water with depth in the soil column (Michalzik et al. 2001; Kaiser et al. 2002; Qualls et al. 2002; Lilienfein et al. 2004; Worrall et al. 2006). Chemical stabilization of DOM and inorganic nutrients in mineral soils is controlled by water flow paths (contact with mineral soil components) (Kalbitz et al. 2000; Kaiser and Guggenberger 2005), the type of mineral soil (Kaiser and Guggenberger 2003), and the type of DOM (Meier et al. 2004). Although geologic variation in mineral soils has been well documented as a control on dissolved carbon and nutrient export, whether geologic variation among arctic organic soils can also lead to differences in DOM concentrations is less well studied. Yet, there is large variation in the pH and exchangeable base cation status of organic soils in the Arctic due to deposition of unweathered materials by fluvial, aeolian, cryoturbation, and glacial processes.

Two major mechanisms for control of soil organic matter processing on weathering gradients include pH-related changes in the solubility of DOM and stabilization of DOM by exchangeable base cations. A better understanding of both of these processes is necessary to elucidate geochemical controls on soil carbon stability in arctic organic soils. Generally, organic matter solubility increases with increasing pH due to the increasing number of negative charges on both organic matter and other soil components (Shen 1999; You et al. 1999; Andersson et al. 2000; Kalbitz et al. 2000; Oste et al. 2002). More soluble organic matter will result in higher DOM losses from the system so DOM efflux from soils is usually positively correlated with pH (Shen 1999; Michalzik et al. 2001; Oste et al. 2002). If more soluble organic matter results in easier access to substrates for microbial activity, microbial activity also should increase with increasing pH. Variation in exchangeable cation concentrations can affect fluxes of DOM by stabilizing negatively charged organic matter through sorption to positively charged cations. Polyvalent (with at least two positive charges) cation "bridges" can form between negatively charged particles, essentially binding organic molecules together or to minerals (Oades 1988; Tipping et al. 1995; Kaiser 1998; Shen 1999; Lofts et al. 2001; Moore and Turunen 2004). The bond between polyvalent cations and negatively charged organic matter functional groups is not easily reversible, preventing biological, chemical, or physical breakdown (Oades 1988; Shen 1999; Kaiser and Guggenberger 2000; Kalbitz et al. 2000; Oste et al. 2002). Because DOM is an important substrate for microbial activity, microbial activity and decomposition of soil organic matter should be lower in soils where higher exchangeable polyvalent cation concentrations result in less accessible DOM and soil organic matter. If polyvalent cation bridging is an important influence on organic matter stabilization in arctic organic soils, watershed differences in exchangeable polyvalent cations could explain observed variation in soil organic matter processing (Hobbie et al. 2002; Hobbie and Gough 2004; Whittinghill and Hobbie 2011).

The concentration of polyvalent cations and pH of soils also interact to affect stabilization of organic matter in soils and therefore microbial activity. Maximum DOM sorption in soils is generally around pH 4–5 (Shen 1999; Andersson et al. 2000), while organic matter is most soluble at pH 6–8 (Shen 1999; You et al. 1999; Andersson et al. 2000). At acidic pH (4–5), negative binding sites on organic and mineral soil components are occupied by hydrogen ions rather than polyvalent cations (Kipton et al. 1992; You et al. 1999; Andersson et al. 2000; Oste et al. 2002). Therefore, at acidic pH, hydrogen bonding among protonated DOM molecules reduces solubility, but the importance of stabilizing polyvalent cation bridges is also diminished. At pH 6–8, all functional groups on organic matter are deprotonated, increasing charge dispersion among organic matter but also increasing the availability of binding sites for stabilizing polyvalent cations. Therefore the net effect of changes in pH and non-proton cation concentrations on microbial respiration and DOM production is unclear. To tease apart the importance of pH and exchangeable cations on arctic soil biogeochemistry, we conducted a soil incubation experiment, manipulating pH and exchangeable calcium concentrations in organic soils from four landscape ages in Northern Alaska using a factorial experimental design. We focused on Ca because it represents the majority of polyvalent cations across all landscape ages in the study region (Whittinghill and Hobbie 2011). We expected less microbial activity in soils manipulated to a more acidic pH because organic matter is less soluble than at circumneutral pH, potentially reducing substrate for microbial activity. We also expected less microbial activity in soils manipulated to higher Ca concentrations due to stabilization of organic matter by polyvalent cation bridging, reducing access to organic matter for microbes. Due to the interaction between the changes in charge of organic matter with changes in pH and increased polyvalent cation bridging at high Ca concentrations, we expected the lowest rates of soil organic matter processing from soils manipulated to high Ca concentrations and circumneutral pH. Results from our study will help determine the net effect of changes in pH and non-proton cation concentrations on soil organic matter cycling in arctic soils, leading to a better understanding of regional variation in the arctic terrestrial carbon balance.

Methods

During July 2004, we collected soil samples of the entire organic soil layer (depth of 10–20 cm) from two to four sites on each of four landscape ages in the Upper Kuparuk River Region, AK that ranged in age between 11,000 and 4.8 million years since glaciation. Detailed descriptions of soil physical and chemical characteristics from our study sites can be found in Whittinghill and Hobbie (2011). To minimize the influence of Ca-rich road dust we selected sites located at least 0.5 km from roads. All sites were located in areas of mesic upland tundra with similar slope (1–15%) and aspect (20°W of N to 10°E of N) to minimize variation in vegetation and topography. Soils in the area are underlain entirely by permafrost and classified as Gelisols, either Turbels or Orthels depending on presence of cryoturbation (Monroe and Bockheim 2001). Older, more weathered soils (>50,000 years since glaciation) have significantly lower concentrations of exchangeable base cations and more acidic pH (<5.5) than younger, poorly weathered soils (<50,000 years since glaciation) with more circumneutral pH (>6.5) (Bockheim et al. 1998; Ping et al. 1998; Whittinghill and Hobbie 2011). Landscape age differences in soil organic matter processing are also apparent, with higher rates of microbial respiration, DOM leaching, nitrogen mineralization, and nitrification in soils from older, more weathered sites than in soils from younger, less weathered sites (Hobbie et al. 2002; Hobbie and Gough 2004; Whittinghill and Hobbie 2011). Detailed descriptions of area vegetation and soil chemical and physical characteristics can be found in Bockheim et al. (1998); Monroe and Bockheim (2001); Hobbie et al. (2002) and Hobbie and Gough (2004). All soil samples were homogenized in the field, frozen, and transported to Minnesota where they remained frozen until we began our experiment.

To examine the relative importance of pH and exchangeable Ca on organic matter cycling in arctic organic soils, we manipulated exchangeable Ca content and pH (within the natural range occurring among sites) in three replicate soil samples from each site using a factorial experimental design. Exchangeable Ca was first removed from the soils using repeated rinsing with solutions of potassium chloride (KCl) in a method adapted from Chorover et al. (2004). We shook 250 g (wet weight) of organic soil for 15 min at 180 oscillations per minute in each of three solutions in turn: 0.1, 0.05, and 0.01 M KCl. Between each extraction, we separated the soil from the solution by gravity filtration through pre-leached Whatman 42 filter paper. Samples of extracts were saved at each step for cation analysis (inductively coupled argon plasma optical emission spectrophotometry; ICAP-OES Optima 3000, Perkin Elmer, Waltham, MA) to evaluate the effectiveness of the Ca removal treatment. Calcium removal treatments removed approximately 15% of exchangeable Ca (measured by $BaCl_2$ extraction, Whittinghill and Hobbie 2011) from soil (Fig. 1a). Significantly more total Ca was removed from soils on the youngest, least weathered landscape than from soils on the three older landscapes (one-way analysis of variance (ANOVA): $F_{3,9} = 10.66$, $P = 0.002$; Tukey's HSD; $\alpha = 0.05$; data not shown), mirroring soil concentrations of exchangeable Ca (Whittinghill and Hobbie 2011). We then divided the resulting soil into five sub-samples of 50 g each, one for each of five treatments: (1) Ca removal without pH manipulation (CaR), (2) Ca removal with Ca added back at a higher concentration adjusted to pH 4.5 (HCa4.5), (3) Ca removal with Ca added back at a higher concentration adjusted to pH 6.5 (HCa6.5), (4) Ca removal with Ca added back at a lower concentration adjusted to pH 4.5 (LCa4.5), and (5) Ca removal with Ca added back at a lower concentration adjusted to pH 6.5 (LCa6.5).

For Ca addition we shook 50 g (wet weight) of soil (with exchangeable Ca removed) in 150 ml of Ca addition solution three times for 30 min at 180 oscillations per minute. To ensure Ca^{2+} ions in Ca addition solutions would replace exchangeable K^+ ions in soils we used solutions of CaOH (0.1 M for high Ca treatment, 0.01 M for low Ca treatment). We adjusted the pH of the Ca addition solutions to the desired pH (4.5 or 6.5) using concentrated NaOH or HCl (chosen to avoid the addition of carbon or nutrients) before adding solutions to soils. After each rinse we separated soil from solution by gravity filtration through pre-leached Whatman 42 filter paper. After the third rinse, before filtration, we measured the pH of soil and solution to determine how well adjusted soil pH matched the desired pH for our treatments. Because soil pH in solution remained variable within treatments and was still related to the underlying landscape age from which soils were collected (Fig. 1b), we adjusted pH of soils in solution to either 4.5 or 6.5 using NaOH or HCl. As a result all manipulated soils had a pH of either 4.5 or 6.5 at the start of our experiment. To quantify Ca added back to soil samples during treatments, we saved sub-samples of the solution resulting from each rinse for cation analysis (ICAP-OES Optima 3000, Perkin Elmer, Waltham, MA).

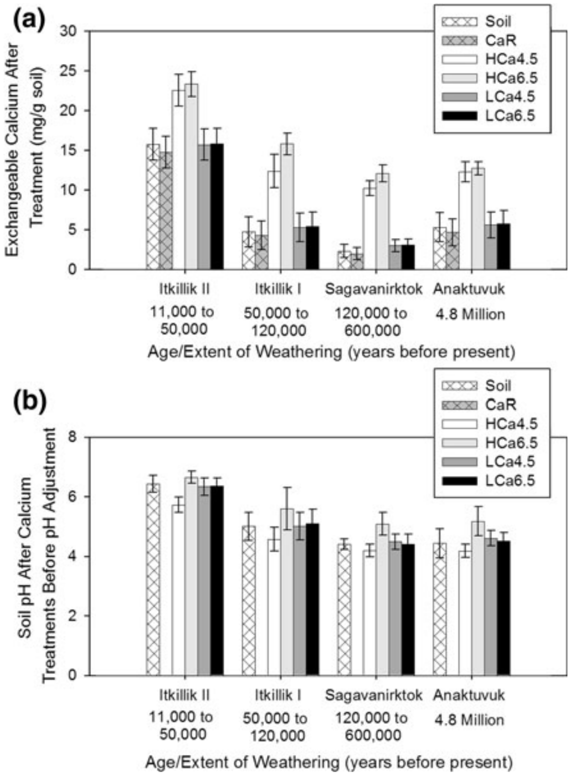

Fig. 1 Soil **a** exchangeable calcium and **b** pH after calcium removal and calcium addition soil manipulations but prior to final pH adjustment to pH 4.5 or 6.5. *Error bars* standard errors of the mean. Treatments are as follows: unmanipulated soil (data from Whittinghill and Hobbie (2011)), calcium removal (CaR), high calcium pH 4.5 (HCa4.5), high calcium pH 6.5 (HCa6.5), low calcium pH 4.5 (LCa4.5), and low calcium pH 6.5 (LCa6.5)

Before beginning the incubation experiment, we measured microbial biomass carbon and nitrogen in manipulated soils from all five treatments as well as in samples of unmanipulated organic soil to assess the effect of the Ca removal process and pH adjustment on microbial communities. Because some of the soil organic matter pool likely was lost as DOC during pre-treatment, we measured total soil carbon and nitrogen in treated soils to determine whether losses were consistent among treatments. We measured total soil carbon and nitrogen in a dried, ground, and homogenized subsample of all treated soils using a Universal CHNOS Elemental Analyzer (Vario III, Elementar, Hanau, Germany). We collected two 10 g subsamples of all treated soils to analyze microbial biomass carbon and nitrogen using a chloroform fumigation extraction (Brookes et al. 1985; Beck et al. 1997). We shook one subsample for 1 h at 180 oscillations per minute in 50 ml of 0.5 M potassium sulfate and collected the resulting extracts by filtering through pre-leached Whatman 42 filter paper. The other subsample was fumigated for 72 h in a vacuum cabinet with 20 ml ethanol-free boiling chloroform before extracting following the same procedure as for non-fumigated samples. We calculated chloroform-labile carbon and nitrogen, which are proportional to microbial biomass carbon and nitrogen, respectively, as the difference between concentrations of dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) in extracts from fumigated and non-fumigated samples. We measured concentrations of DOC and TDN using a total organic carbon and total nitrogen analyzer (TOC-V CSH and TNM-1, Shimadzu, Columbia, MD).

To examine the effect of pH and Ca treatments on organic matter processing, we conducted a 5 month incubation of manipulated soils. Soils were incubated at field capacity and 4°C (mean growing season soil temperature) in the dark and sampled monthly (five total sampling dates). For each of the five treatments (CaR, HCa4.5, HCa6.5, LCa4.5, and LCa6.5) we placed three replicate 25 g (wet weight) treated soil samples from each site in a Pall MicroFunnel® 100 ml filter funnel on an ashed Whatman GF/F filter. At the start of the incubation and each measurement date thereafter we added 90 ml of a micronutrient solution (Nadelhoffer et al. 1991) of 4.0 mM $CaCl_2$, 2.0 mM KH_2PO_4, 1.0 mM K_2SO_4, 1.0 mM $MgSO_4$, 25 µM H_3BO_3, 2.0 µM $MnSO_4$, 2.0 µM $ZnSO_4$, 0.5 µM $CuSO_4$, and 0.5 µM Na_2MoO_4 to each sample for 1 h before extracting the soil water solution with a vacuum pump. We analyzed leachate samples for ammonium (phenol hypochlorite, Solórzano 1969) and nitrate (cadmium reduction, Wood et al. 1967)) on an auto analyzer (Alpkem, O.I. Analytical, College Station, TX) and analyzed leachates for DOC and TDN on a total organic carbon and total nitrogen analyzer (TOC-V CSH and TNM-1, Shimadzu, Columbia, MD). We calculated DON as TDN less the sum of nitrate and ammonium in leachates. After leaching, we measured soil respiration by placing samples in sealed mason jars with septa and determining the change in headspace carbon dioxide concentration over a 24 h period. We analyzed headspace carbon dioxide concentrations using a gas chromatograph with a thermal conductivity detector and poropak N column (GC-14A, Shimadzu, Columbia, MD). We compared results of our manipulation to results from unmanipulated peat soils in a concurrent experiment described in Whittinghill and Hobbie (2011).

For all measured variables (carbon and nitrogen in leachates and microbial respiration), rates were highest at the first sampling date (Day 1) and then remained relatively constant throughout the rest of the experiment (Figs. 2, 3). Therefore, to avoid including the disturbance effects of our treatments we present cumulative data from day 40–137. Cumulative dissolved organic and inorganic carbon and nitrogen leaching were calculated as the sum measured in leachates on days 40, 70, 100, and 137. We calculated cumulative respiration rates by multiplying the number of days between sampling dates (~30) by the average of daily respiration rates for those sampling dates and summing over all samplings between day 40 and 137.

We present all data as treatment means with standard errors of the mean. Statistical analyses were completed using JMP software (JMP 7, SAS, Cary, NY). We used results of a two-way ANOVA with site number nested within landscape age and replicate nested within site as random variables and Tukey's HSD values ($\alpha = 0.05$) to evaluate significant differences among treatments and landscape ages in total soil carbon and nitrogen, microbial biomass carbon and nitrogen, and incubation data (cumulative respiration, DOC and DON leaching, and nitrate and ammonium leaching). The relative effects of Ca and pH on total soil carbon and nitrogen, microbial biomass carbon and nitrogen, cumulative rates of microbial respiration, and cumulative DOC, DON, and dissolved inorganic nitrogen leaching were analyzed using a two-way ANOVA on data from the four factorial Ca and pH manipulated treatments (HCa4.5, HCa6.5, LCa4.5, and LCa6.5).

Results

Efficacy of treatments

High Ca treatments had significantly higher exchangeable calcium across all landscape ages (one-way ANOVA: $F_{3,48} = 139.32$, $P < 0.001$, Tukey's HSD, $\alpha = 0.05$; Fig. 1a) with no landscape age differences in exchangeable Ca added to soils (one-way ANOVA: $F_{3,48} = 1.33$, $P = 0.28$, data not shown). While pH had no significant effect on Ca added back to into soils at high concentrations (two-way ANOVA: $P = 0.082$, $F_{1,21} = 3.85$, Fig. 1a), pH did significantly affect the quantity of Ca added back to soils at low concentrations (two-way ANOVA: $P = 0.001$, $F_{1,21} = 21.76$, Fig. 1a).

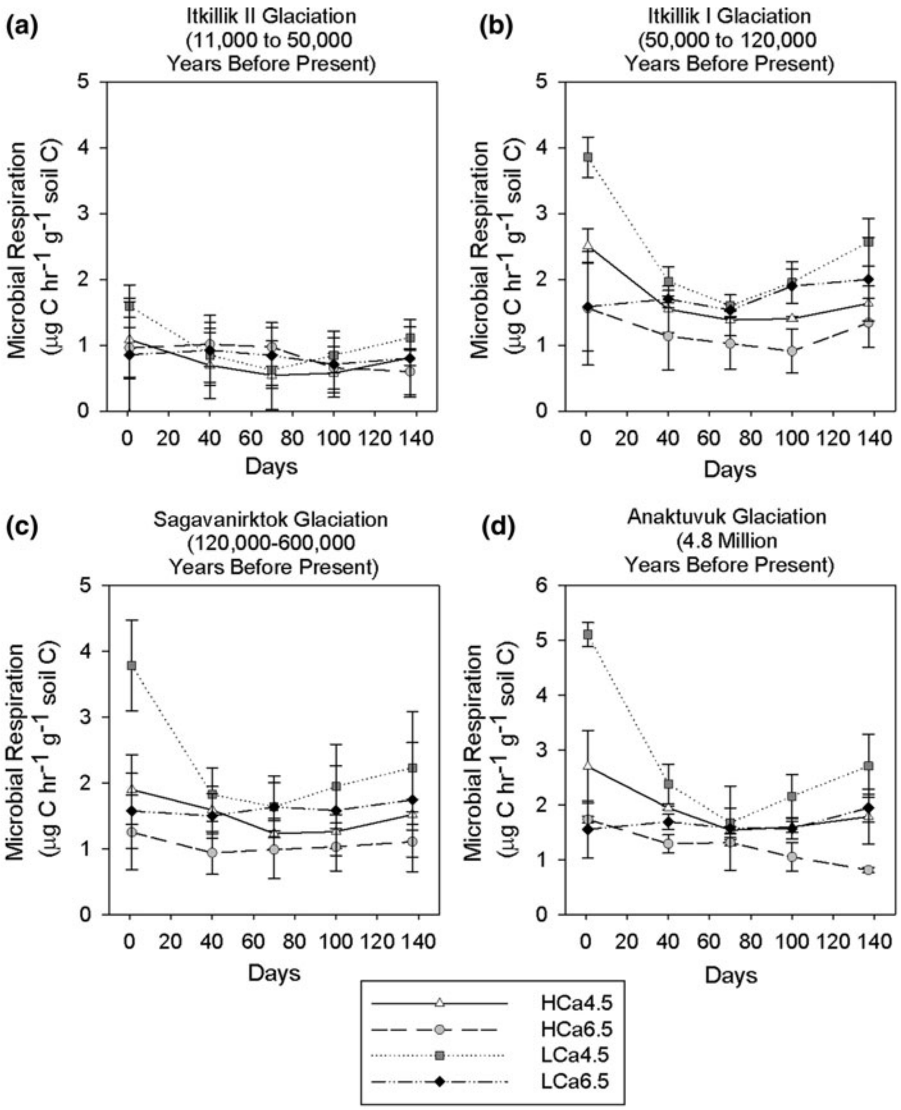

Fig. 2 Microbial respiration from soils from all six treatments from **a** the Itkillik II glaciation, **b** the Itkilik I glaciation, **c** the Sagavanirktok glaciation, and **d** the Anaktuvuk glaciation. *Error bars* standard errors of the mean. Treatments are as follows: unmanipulated soil (data from Whittinghill and Hobbie (2011)), calcium removal (CaR), high calcium pH 4.5 (HCa4.5), high calcium pH 6.5 (HCa6.5), low calcium pH 4.5 (LCa4.5), and low calcium pH 6.5 (LCa6.5)

Soil characteristics

Patterns among landscape ages in total soil carbon and nitrogen concentrations observed among untreated soils (Whittinghill and Hobbie 2011) remained apparent after applying our experimental treatments. As in untreated soils, among all treatments, total soil nitrogen concentrations were significantly higher in soils from the youngest landscape age (one-way ANOVA: $P = 0.021$, $F_{3,204} = 5.45$; Tukey's HSD; $\alpha = 0.05$; Table 1) with no significant differences among landscape ages in total soil carbon concentrations (one-way ANOVA: $P = 0.14$, $F_{3,204} = 2.33$; Table 1). As a result, soil C:N ratios in treated soils increased with landscape age (two-way ANOVA: $P = 0.023$, $F_{3,120} = 5.22$; Tukey's HSD; $\alpha = 0.05$; Table 1). Within all soils, microbial biomass carbon differed significantly among landscape ages, generally increasing with increasing landscape age (two-way ANOVA: $P = 0.035$, $F_{3,120} = 4.45$; Table 1) with no corresponding differences in microbial biomass nitrogen (two-way ANOVA: $P = 0.13$, $F_{3,120} = 3.76$; Table 1). Therefore, the C:N ratio of the microbial biomass increased significantly with increasing landscape age across all treatments (one-way ANOVA: landscape age: $P = 0.030$, $F_{3,183} = 4.79$; Table 1).

There were significant treatment effects when comparing among the five manipulated soils and

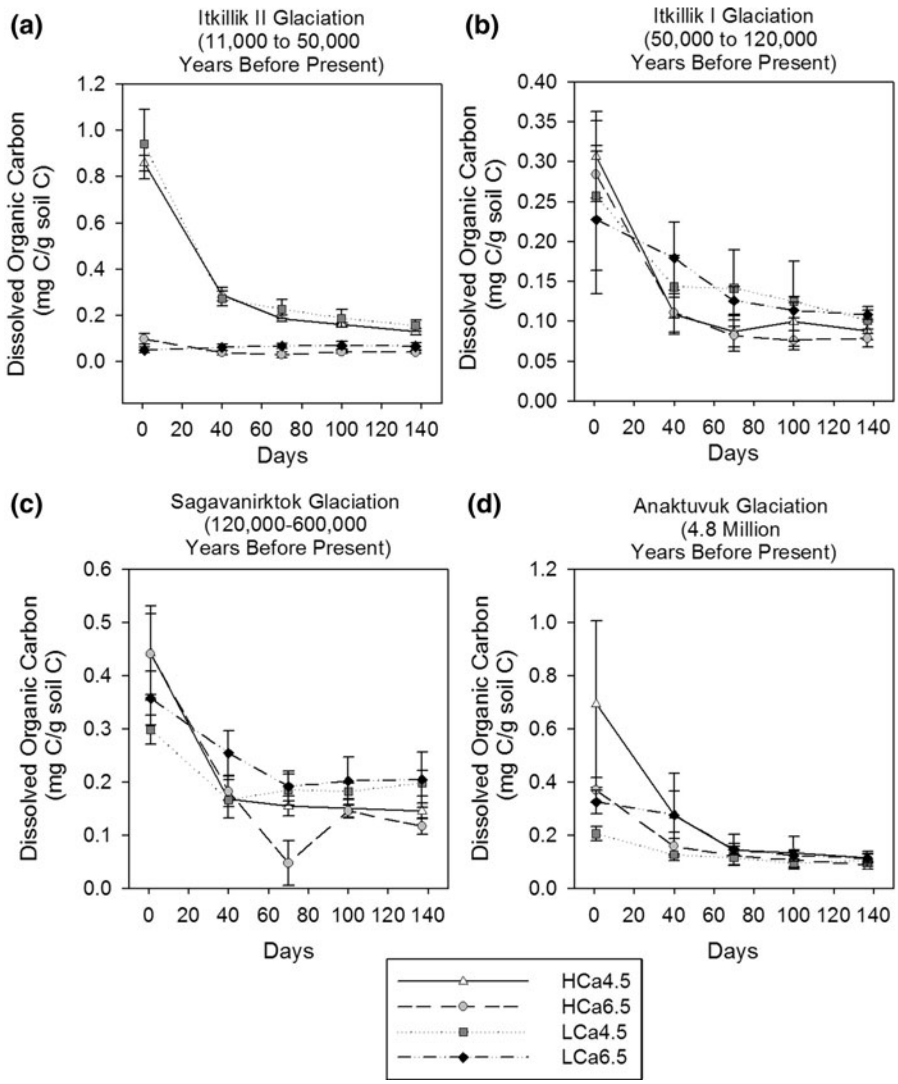

Fig. 3 Dissolved organic carbon in leachates from soils from all six treatments from **a** the Itkillik II glaciation, **b** the Itkilik I glaciation, **c** the Sagavanirktok glaciation, and **d** the Anaktuvuk glaciation. *Error bars* standard errors of the mean. Treatments are as follows: unmanipulated soil (data from Whittinghill and Hobbie (2011)), calcium removal (CaR), high calcium pH 4.5 (HCa4.5), high calcium pH 6.5 (HCa6.5), low calcium pH 4.5 (LCa4.5), and low calcium pH 6.5 (LCa6.5)

unmanipulated organic soil for both total soil carbon (one-way ANOVA: $P < 0.001$, $F_{5,204} = 46.24$; Table 1) and total soil nitrogen (one-way ANOVA: $P < 0.001$, $F_{5,204} = 5.89$; Table 1) concentrations. Soils from the high Ca treatments had significantly lower carbon and nitrogen concentrations than unmanipulated soils, Ca removal soils, and soils from low Ca treatments, regardless of pH (Tukey's HSD; $\alpha = 0.05$; Table 1). However, soil C:N ratios did not significantly differ among treatments (one-way ANOVA: $P = 0.94$, $F_{5,204} = 0.24$; Table 1). Total soil carbon and nitrogen concentrations in organic soils were significantly affected by Ca treatment (two-way ANOVA: carbon: $P < 0.001$, $F_{1,120} = 213.51$; nitrogen: $P < 0.001$, $F_{1,120} = 21.76$; Table 1) but not by pH treatment (two-way ANOVA: carbon: $P = 0.058$, $F_{1,120} = 3.67$; nitrogen: $P = 0.28$, $F_{1,120} = 1.16$; Table 1). To account for differences in soil carbon among treatments, we present our results normalized per gram soil carbon.

Although there were significant differences in microbial biomass carbon and nitrogen among treatments (one-way ANOVA: C: $P = 0.026$, $F_{5,178} = 2.62$; N: $P = 0.021$, $F_{5,178} = 2.72$; Tukey's HSD; $\alpha = 0.05$; Table 1), microbial biomass carbon and nitrogen were not significantly different between the Ca removal treatment and unmanipulated soils (Tukey's HSD; $\alpha = 0.05$; Table 1). Significant treatment differences in microbial biomass were caused by differences among the four factorial Ca and pH manipulation treatments with a significant Ca by pH interaction for microbial

Table 1 Soil total C and N content, soil C:N ratio, microbial biomass C, N, and C:N ratio of soils, and C:N ratio of DOM in leachates used in the experiment from all treatment and landscape age combinations

Landscape age and treatment	Soil			Microbial biomass			DOM
	mg C/g soil	μg N/g soil	C:N ratio	mg C/g soil	mg N/g soil	C:N ratio	C:N ratio
Itkillik II							
Soil	0.39 (0.01)	18.5 (0.6)	22.1 (1.6)	5.61 (0.66)	0.91 (0.11)	6.3 (0.37)	15.31 (2.23)
CaR	0.38 (0.01)	17.6 (0.6)	22.5 (1.6)	6.80 (0.85)	1.07 (0.14)	6.4 (0.47)	15.61 (2.34)
HCa4.5	0.36 (0.01)	17.3 (0.6)	21.5 (1.6)	4.89 (0.63)	0.79 (0.10)	6.2 (0.35)	17.2 (7.64)
HCa6.5	0.35 (0.01)	16.8 (0.6)	21.6 (1.6)	4.21 (0.63)	0.73 (0.10)	5.8 (0.35)	27.25 (2.47)
LCa4.5	0.39 (0.01)	18.3 (0.6)	22.1 (1.6)	4.08 (0.66)	0.70 (0.11)	5.9 (0.37)	17.87 (5.57)
LCa6.5	0.39 (0.01)	18.6 (0.6)	21.6 (1.6)	5.00 (0.63)	0.97 (0.11)	5.0 (0.37)	23.25 (2.13)
Itkillik I							
Soil	0.44 (0.01)	13.9 (0.7)	34.6 (1.9)	7.84 (0.73)	1.17 (0.12)	6.6 (0.41)	16.75 (2.80)
CaR	0.43 (0.01)	12.5 (0.7)	36.3 (1.9)	7.14 (0.83)	0.96 (0.13)	7.3 (0.47)	16.90 (2.62)
HCa4.5	0.35 (0.01)	11.5 (0.7)	33.0 (1.9)	6.68 (0.78)	1.06 (0.12)	6.3 (0.44)	20.70 (3.78)
HCa6.5	0.36 (0.01)	11.4 (0.7)	34.1 (1.9)	6.26 (0.73)	1.05 (0.12)	6.1 (0.41)	38.26 (2.46)
LCa4.5	0.43 (0.01)	13.1 (0.7)	35.5 (1.9)	4.94 (0.78)	0.75 (0.12)	6.8 (0.44)	22.51 (3.01)
LCa6.5	0.42 (0.01)	12.6 (0.7)	35.7 (1.9)	6.92 (0.78)	1.27 (0.12)	6.3 (0.44)	31.33 (2.62)
Sagavanirktok							
Soil	0.42 (0.01)	11.5 (0.6)	40.2 (1.6)	5.41 (0.80)	0.84 (0.13)	7.0 (0.45)	20.92 (2.61)
CaR	0.42 (0.01)	12.0 (0.6)	38.6 (1.6)	6.73 (0.70)	0.91 (0.11)	7.7 (0.39)	20.54 (2.23)
HCa4.5	0.37 (0.01)	10.3 (0.6)	39.2 (1.6)	6.55 (0.66)	0.94 (0.11)	7.2 (0.37)	25.19 (2.36)
HCa6.5	0.35 (0.01)	10.1 (0.6)	37.2 (1.6)	6.06 (0.63)	0.85 (0.10)	7.2 (0.35)	35.33 (2.69)
LCa4.5	0.42 (0.01)	11.9 (0.6)	37.5 (1.7)	5.41 (0.80)	0.79 (0.12)	5.9 (0.42)	18.85 (2.47)
LCa6.5	0.41 (0.01)	11.0 (0.6)	39.9 (1.6)	5.97 (0.70)	0.98 (0.11)	6.2 (0.39)	38.70 (2.83)
Anatuvuk							
Soil	0.43 (0.01)	10.1 (0.8)	43.7 (2.3)	7.79 (0.89)	1.10 (0.14)	8.1 (0.50)	27.81 (3.01)
CaR	0.44 (0.01)	11.0 (0.8)	41.3 (2.3)	8.12 (1.12)	1.08 (0.16)	7.9 (0.63)	20.42 (3.01)
HCa4.5	0.38 (0.01)	8.9 (0.8)	44.4 (2.3)	9.64 (0.99)	1.40 (0.16)	6.8 (0.55)	21.95 (4.49)
HCa6.5	0.35 (0.01)	8.4 (0.8)	43.9 (2.3)	9.25 (0.89)	1.35 (0.14)	6.8 (0.50)	41.99 (3.31)
LCa4.5	0.44 (0.01)	10.2 (0.8)	44.4 (2.3)	7.32 (0.89)	1.06 (0.14)	6.9 (0.50)	26.32 (3.31)
LCa6.5	0.42 (0.01)	10.0 (0.9)	42.6 (2.5)	8.78 (0.99)	1.32 (0.16)	6.4 (0.50)	38.49 (3.31)

Standard errors of the mean presented in parentheses. Treatments are as follows: unmanipulated soil (data from Whittinghill and Hobbie (2011)), *CaR* calcium removal, *HCa4.5* high calcium pH 4.5, *HCa6.5* high calcium pH 6.5, *LCa4.5* low calcium pH 4.5, and *LCa6.5* low calcium pH 6.5

nitrogen (two-way ANOVA: $P = 0.004, F_{1,120} = 8.45$; Table 1) and for microbial carbon (two-way ANOVA: $P = 0.025, F_{1,120} = 5.19$; Table 1). As a result, the C:N ratio of the microbial biomass was significantly different among treatments (one-way ANOVA: $P < 0.001$, $F_{5,178} = 4.83$; Tukey's HSD; $\alpha = 0.05$; Table 1).

Incubation experiment

Landscape age, Ca, and pH significantly affected cumulative respiration rates per gram soil carbon (two-way ANOVA: landscape age: $P = 0.013$, $F_{3,130} = 6.44$; Ca: $P = 0.005$, $F_{1,130} = 8.38$; pH: $P < 0.001$, $F_{1,130} = 22.74$; Figs. 2, 4a). As expected, soils from acidic pH treatments exhibited significantly lower respiration rates than soils from circumneutral pH treatments (Tukey's HSD; $\alpha = 0.05$; Figs. 2, 4a). Increasing Ca concentrations significantly decreased cumulative respiration rates as expected (Tukey's HSD; $\alpha = 0.05$; Figs. 2, 4a). Although rates of cumulative microbial respiration were significantly different among treatments (one-way ANOVA:

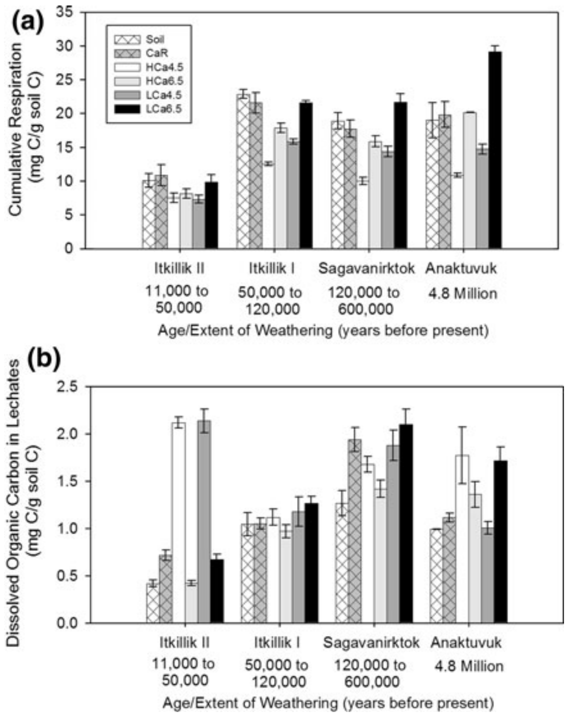

Fig. 4 **a** Cumulative soil respiration per gram soil carbon in soils from all four landscape ages and all six treatments. **b** Cumulative dissolved organic carbon leaching per gram of soil carbon from all four landscape ages and all six treatments. *Error bars* standard errors of the mean. Treatments are as follows: unmanipulated soil (data from Whittinghill and Hobbie (2011)), calcium removal (CaR), high calcium pH 4.5 (HCa4.5), high calcium pH 6.5 (HCa6.5), low calcium pH 4.5 (LCa4.5), and low calcium pH 6.5 (LCa6.5)

$P < 0.001$, $F_{5,204} = 11.14$; Figs. 2, 4a), they were not significantly different between the Ca removal treatment and the unmanipulated soil (Tukey's HSD; $\alpha = 0.05$; Figs. 2, 4a). Similar to results from previous studies (Hobbie et al. 2002; Whittinghill and Hobbie 2011), soils from the youngest landscape exhibited significantly lower rates of cumulative microbial respiration across all pH and Ca treatments (Tukey's HSD; $\alpha = 0.05$; Figs. 2, 4a). However, neither decreasing pH nor reducing Ca alone or in combination with reduced pH increased respiration rates of soil from the youngest landscape to rates of unmanipulated soils from the three older landscapes.

Cumulative DOC leaching per gram of soil carbon exhibited a pH by Ca interaction (two-way ANOVA: $P = 0.044$, $F_{1,130} = 4.13$; Figs. 3, 4b). In contrast to expectations, cumulative DOC leaching was similar between high and low Ca concentrations in soils with acidic pH, but in soils with circumneutral pH, increasing Ca concentrations significantly decreased DOC leaching as expected (Tukey's HSD; $\alpha = 0.05$; Figs. 3, 4b). As predicted, cumulative DOC leaching in soils from the circumneutral pH, high Ca treatment was significantly lower than in all other treatments (Tukey's HSD; $\alpha = 0.05$; Figs. 3, 4b). There was also a significant landscape age by pH interaction in cumulative DOC leaching (two-way ANOVA: $P < 0.001$, $F_{1,130} = 26.13$; Figs. 3, 4b). Contrary to expectations, pH did not significantly affect cumulative DOC leaching in treated soils from the three older landscape ages (Tukey's HSD; $\alpha = 0.05$; Figs. 3, 4b). However, in soils from the youngest landscape age reducing soil pH resulted in significantly higher DOC leaching compared to circumneutral pH treatments (Tukey's HSD; $\alpha = 0.05$; Figs. 3, 4b). Lowering the pH alone (and not lowering Ca concentrations) increased DOC leaching in soils from the youngest site to levels found in soils from the three older sites. Although there were significant effects of treatments on DOC leaching (one-way ANOVA: $P < 0.001$, $F_{5,204} = 11.21$; Figs. 3, 4b), there were no significant differences between DOC leaching in untreated soil and in soils from the Ca removal treatment (Tukey's HSD; $\alpha = 0.05$; Figs. 3, 4b).

Organic nitrogen in leachates averaged between 70 and 90% of TDN leaching during the experiment (Fig. 5). Among treated soils, the percent of TDN leaching that was organic nitrogen was not significantly affected by landscape age (two-way ANOVA: $P = 0.11$, $F_{3,111} = 2.66$), Ca (two-way ANOVA: $P = 0.19$, $F_{1,111} = 1.74$), or pH (two-way ANOVA: $P = 0.39$, $F_{1,111} = 0.76$). Cumulative ammonium and nitrate leaching were at or near detection limit for most samples (Fig. 5a, b).

There were significant pH and landscape age effects on cumulative DON leaching per gram of soil carbon during our incubations (two-way ANOVA: landscape age: $P = 0.003$, $F_{3,111} = 9.92$; pH: $P < 0.001$, $F_{1,111} = 24.47$; Fig. 5c), but no significant effects of Ca (two-way ANOVA: $P = 0.81$, $F_{1,111} = 0.056$; Fig. 5c). Contrary to expectations, we observed significantly lower cumulative DON leaching at circumneutral pH than at acidic pH (Tukey's HSD; $\alpha = 0.05$; Fig. 5c). As with DOC, lowering the pH alone (and not lowering Ca concentrations) increased cumulative DON leaching in soils from the youngest site to levels found in soils from the three older sites. Soils from the

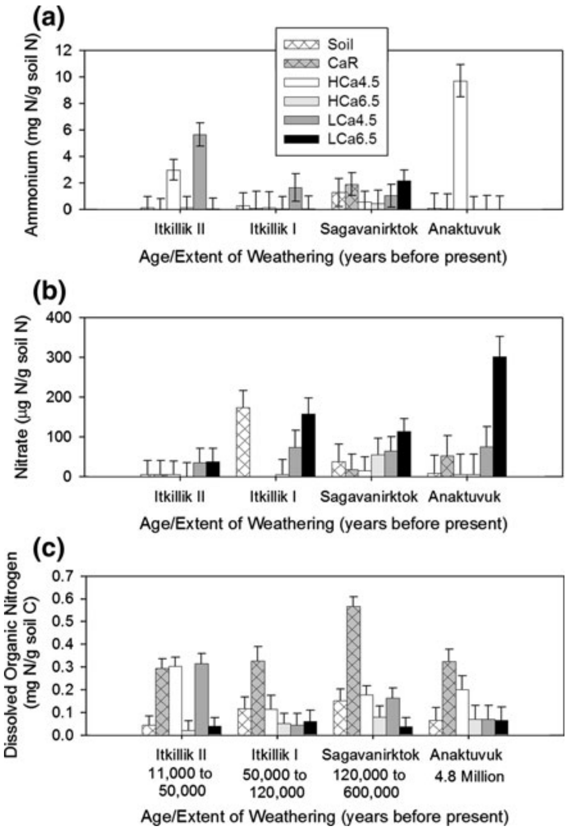

Fig. 5 Cumulative leaching of **a** ammonium, **b** nitrate, and **c** dissolved organic nitrogen from all four landscape ages and all six treatments throughout the experiment. *Error bars* standard errors of the mean. Treatments are as follows: unmanipulated soil (data from Whittinghill and Hobbie (2011)), calcium removal (CaR), high calcium pH 4.5 (HCa4.5), high calcium pH 6.5 (HCa6.5), low calcium pH 4.5 (LCa4.5), and low calcium pH 6.5 (LCa6.5)

Ca removal treatment and high pH treatments exhibited significantly higher cumulative DON leaching than soils from low pH treatments (one-way ANOVA: $P < 0.001$, $F_{5,170} = 6.19$; Tukey's HSD; $\alpha = 0.05$; Fig. 5c).

Discussion

Results from our study indicate that both exchangeable Ca concentrations and pH appear to influence arctic soil biogeochemistry. However, variation in exchangeable Ca among landscape ages can better explain in situ patterns of microbial activity than variation in pH. We hypothesized that microbial activity would be lower in soils with acidic pH than in soils at circumneutral pH due to less soluble DOM and therefore potentially less substrate for microbial activity at more acidic pH. Indeed, rates of microbial activity were lower at acidic pH than circumneutral pH. However, this is the opposite of patterns of in situ rates of microbial activity which show higher rates on older, more acidic landscapes (Hobbie et al. 2002; Hobbie and Gough 2004; Whittinghill and Hobbie 2011). We expected lower rates of microbial activity in soils manipulated to higher Ca concentrations due to stabilization of organic matter by cation bridging with Ca ions reducing availability of substrate for microbial activity. Indeed, Ca removal increased respiration rates and respiration rates were higher in soils manipulated to low Ca concentrations than high Ca concentrations. These patterns do correspond to in situ patterns of microbial activity, with higher microbial respiration in soils from younger landscapes with higher exchangeable Ca concentrations (Hobbie et al. 2002; Whittinghill and Hobbie 2011).

The net effect of variation in exchangeable Ca and variation in pH on microbial activity in arctic organic soils appears to depend on the microbial process in question. The combined effect of exchangeable cation concentration and pH on rates of microbial activity in natural soils leads to lower rates in soils with high exchangeable Ca concentrations and circumneutral pH than in soils with low exchangeable Ca concentrations and acidic pH (Hobbie et al. 2002; Hobbie and Gough 2004; Whittinghill and Hobbie 2011). Lower rates of microbial respiration in more acidic soils found in this study are consistent with previous research showing that soil organic matter is least soluble at pH 4–5 (Shen 1999; Andersson et al. 2000), which may reduce substrate availability for microbial decomposition at acidic compared to circumneutral pH. However, DOC and DON concentrations in leachates tended to decrease with increasing pH. In our experiment, the depressing effect of increased Ca on microbial activity and DOM in leachates at high pH is consistent with results from previous laboratory experiments where less weathered soils showed depressed rates of microbial activity (Hobbie et al. 2002; Hobbie and Gough 2004; Whittinghill and Hobbie 2011) and increased sorption of DOC to soil surfaces (Kaiser 1998; Shen 1999; Kalbitz et al. 2000; Nilsson et al. 2001).

Although pH effects on DOM leaching in our experiment contrast expectations based on known pH effects on solubility of soil organic matter, they are consistent with landscape patterns of DOM leaching (Hobbie et al. 2002; Hobbie and Gough 2004; Whittinghill and Hobbie 2011). In addition, high DOC, DON, and NH_4^+ leaching in soils from the youngest landscape age at low pH may be an artifact of treating soils with HCl. If treatment with HCl increased exchangeable C and N (rather than altering the production of DOM or NH_4^+), that may have promoted C and N leaching. Among soils not treated with HCl, pH did not significantly affect DOC leaching. Therefore, another factor correlated with pH across landscape ages, such as Ca, is likely a more important control on DOM efflux in these soils than pH effects on organic matter solubility.

As our experimental pH and Ca treatments did not increase respiration rates in soils from young landscapes (that naturally had higher Ca concentrations and circumneutral pH) to levels of soils from older landscapes (that naturally had lower Ca concentrations and acidic pH), it appears that there are other landscape age-related controls on microbial activity in addition to geochemical differences among landscape ages in pH and exchangeable cations. Other such controls likely include variation in the quality of soil organic matter or in the microbial community among landscape ages. Lower rates of microbial activity on soils from younger landscape ages despite higher concentrations of total soil nitrogen (Whittinghill and Hobbie 2011) suggest there may be differences in the recalcitrance of soil organic matter among landscape ages. Extractable N was higher in soils from older landscape ages (Hobbie and Gough 2002; Hobbie et al. 2002), so differences in available N rather than total N among landscape ages may also contribute to differences in microbial activity. In addition to differences in soil organic matter quality, differences in DOM quality among landscape ages would also lead to differences in microbial activity. However, previous research showed that DOM quality does not vary among landscape ages in the region (Whittinghill et al. "in review").

Microbial biomass and community composition both have the potential to influence soil biogeochemistry through altered rates of microbial activity. Lower microbial biomass in soils from sites on the youngest glacial drift across all experimental treatments may contribute to lower rates of microbial activity in soils from the youngest landscape age, although these results further beg the question of why such landscape differences in microbial biomass exist. Significant differences in microbial communities among landscape ages were found in a study by Schmidt and Bååth ("unpublished data") who found a greater proportion of fungi in soils from one older, acidic pH site than in soils from one younger, circumneutral pH site. Microbial community composition differences among landscape ages could lead to changes in the types of enzymes produced for breakdown of organic matter, altering microbial activity. In addition, variation in microbial community composition among landscape ages could lead to and variation in the chemistry of microbial metabolic products among landscape ages, which might influence the quality of substrates available for microbial decomposition.

Implications

Our results indicate that geochemical differences among arctic organic soils can control both microbial activity and concentrations of DOM in soil water. Therefore, geochemical variation among soils influences arctic soil carbon balance through both soil organic matter decomposition rates and export to aquatic ecosystems. However, other differences among landscape ages, such as potential differences in microbial communities, also appear to affect soil organic matter cycling. The importance of geochemical variation in both mineral and organic soils throughout the arctic as a control on soil organic matter dynamics and DOM export is likely to increase as permafrost melts and contact between soil water and mineral soils increases with future climate warming. This would further amplify differences in DOM transport to aquatic ecosystems among landscape ages. Therefore, large variation in pH and soil cation concentrations found throughout the arctic due to fluvial, aeolian, and glacial processes should be included in models of arctic carbon and nitrogen cycling.

Acknowledgments We thank Jim Cotner, Edward Rastetter, Gus Shaver, Joe McFadden, Paul Bloom, and Sandy Weisberg for their help and advice on this project and the Toolik Lake Field Station and Arctic Long Term Ecological Research program staff for logistical support. We would especially like to thank Megan Ogdahl and Jeff Eickhoff for their help with laboratory work. This material is based upon work supported by the Dayton-Wilkie Natural History Fund, the National Science

Foundation Long-Term Ecological Research Program, and the National Science Foundation under the following grants: NSF DEB-008958, NSF OPP-0352897, and NSF-DEB 0423385.

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