Effect of Topography and Glaciation History on the Movement of Carbon and Nitrogen within Arctic Hillsides

A DISSERTATION
SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL
OF THE UNIVERSITY OF MINNESOTA
BY

Kyle A. Whittinghill

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

Dr. Sarah E. Hobbie, Dr. Jacques C. Finlay

April 2010

Acknowledgements

We would like to 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, Henry Kemp, Jenna Cook, and Jeff Eickhoff for their help with field and laboratory work.

This material is based upon work supported by the Dayton-Wilkie Natural History Fund, the NSF Long-Term Ecological Research Program, and the National Science Foundation under Doctoral Dissertation Improvement Grant No. 080278 and under the following grants: NSF DEB-008958, NSF OPP-0352897, and NSF-DEB 0423385.

Abstract

The transport of dissolved organic matter (DOM) down hillslopes to aquatic ecosystems has important implications for both terrestrial and aquatic primary productivity. DOM is an important energy and nutrient source for both terrestrial and aquatic microbes. Within watersheds, physical, chemical, and biological processes transform DOM, but it not well known how landscape heterogeneity may affect these processes in arctic watersheds.

In the northern foothills of the Brooks Range, expansion and contraction of mountain glaciers over the last several ice ages have created a mosaic of landscape ages with similar climate and vegetation. My research indicates that younger landscapes (<50,000yrs) have significantly lower pH, 10x higher exchangeable base cation concentrations, and significantly lower rates of DOM production and microbial respiration than older landscapes, which could significantly affect fluxes of carbon and nutrients across the landscape. At the watershed scale, I examined patterns in soil and stream water concentrations of DOM within hillslopes across the chronosequence. I found that while concentrations of dissolved organic carbon decreased significantly moving downslope from the hilltop to the stream; dissolved organic nitrogen concentrations remain similar within the hillslope, but are significantly different among landscape ages. I also used a variety of indices to examine spatial patterns in the biodegradability of DOM within hillslopes and among landscape ages in northern Alaska. My results suggest the low biodegradability of DOM found in streams and rivers in the

region is not due to microbial processing of labile DOM in terrestrial ecosystems, but rather to production of recalcitrant DOM throughout the landscape.

Table of Contents

List of Tables

List of Figures

Introduction

Accurately modeling the response of terrestrial and aquatic systems to climate change requires improved understanding of controls on ecosystem processes and how these processes scale up to landscapes and regions. This is especially important in the Arctic where feedbacks from changes in carbon storage could potentially affect global climate. Carbon stored in arctic tundra may be particularly vulnerable to climate warming because these soils currently are either very cold or frozen during the growing season. Future climate warming is predicted to be most intense at high latitudes (Shaver et al. 1992, McGuire et al. 2000, Mack et al. 2004, Shaver et al. 2006) and significant warming trends have already been observed at several arctic sites (Overpeck et al. 1997, Chapin et al. 2005, Hinzman et al. 2005, Malmer et al. 2005). However, heterogeneity in arctic ecosystems which can lead to large variation in organic matter cycling across the landscape is not always included in models of arctic carbon and nitrogen cycling. In addition, terrestrially derived dissolved organic matter (DOM) represents a substantial source of energy and nutrients to arctic aquatic ecosystems so understanding variation in terrestrial organic matter cycling is important for understanding aquatic ecosystem functioning, as well.

Previous research has characterized the influence of climate (Chapin et al. 1995, Hartley et al. 1999, van Wijk et al. 2003, Epstein et al. 2004, Malmer et al. 2005, Sjogersten and Wookey 2005, Shaver et al. 2006), vegetation (Chapin and Shaver 1989, Shaver and Chapin 1991, Callaghan and Jonasson 1995, Hobbie 1996, Shaver et al. 2001, Weintraub and Schimel 2005a, Zak and Kling 2006), nutrient availability (Shaver and Jonasson 1999, Mack et al. 2004, Shaver et al. 2006), permafrost cover (Kawahigashi et

al. 2004, Frey and Smith 2005, Frey et al. 2007a, Frey et al. 2007b), and topography (Giblin et al. 1991, Nadelhoffer et al. 1991, Shaver et al. 1996, Stieglitz et al. 2003) on arctic biogeochemical cycles. Relatively few studies of limited scope have focused on how differences in geologic parent material or glacial history affect arctic soil biogeochemistry (Bockheim et al. 1998, Ping et al. 1998, Walker et al. 1998, Gough et al. 2000, Walker 2000, Hobbie and Gough 2002, Hobbie et al. 2002, Hobbie and Gough 2004). Nor are topographic and geologic controls on fluxes of DOM from terrestrial to aquatic ecosystems well understood in tundra. This dissertation aims to help elucidate controls on arctic organic matter cycling by determining how a) landscape age influences arctic soil biogeochemistry (Chapter 1), b) glacial age affects arctic soil organic matter cycling and fluxes of DOM between arctic terrestrial and aquatic ecosystems (Chapters 2 and 3, c) hillslope topography affects fluxes of DOM in tundra ecosystems (Chapter 3), and d) variation in topography and glacial age affect the biodegradability of DOM (Chapter 4).

Dissolved organic matter is an important source of both energy and nutrients in arctic terrestrial and aquatic ecosystems. In soil, sources of DOM include plant and microbial exudates and the products of biotic and abiotic breakdown of complex and simple organic molecules (Nilsson et al. 2001, Swift 2001). Although individual molecules of DOM have a wide range of structural complexity, for the purposes of this research I consider DOM as a single pool of soluble organic compounds. Since DOM from terrestrial ecosystems can be mineralized to CH4 or CO2 in aquatic ecosystems, measurements of arctic tundra C cycling without consideration of DOM fluxes underestimate regional CO2 flux (Kling 1991, Cole and Caraco 2001, Walter et al. 2006,

Cole et al. 2007). DOM is particularly important in arctic terrestrial and aquatic systems because the majority of nutrients in these systems are in the organic form (Peterson et al. 1992, Wollheim et al. 1999, Nordin et al. 2004, Weintraub and Schimel 2005b, Hobbie and Hobbie 2006). When physical or chemical factors reduce DOM availability to plants or microbes in nitrogen-limited terrestrial ecosystems, dissolved organic nitrogen (DON) can also be lost from ecosystems via leaching, contributing to nitrogen limitation over long time scales (Perakis 2002, Perakis and Hedin 2002, Neff et al. 2003).

Despite its relative importance in ecosystem element cycling and productivity, little is known about if and how controls of DOM fluxes known to be important in temperate (Qualls et al. 1991, Swift 2001, Yu et al. 2003, Lilienfein et al. 2004, Richardson et al. 2004, Selmants and Hart 2008) and tropical systems (Crews et al. 1995, Hedin et al. 2003, Cleveland et al. 2004) operate in arctic systems. The amount of DOM transported from terrestrial to aquatic ecosystems depends on the balance of DOM production, stabilization, and mineralization in soils. Geologic factors can affect DOM stabilization and production directly, through influences on soil mineralogy and structure, and indirectly via their effect on vegetation type which in turn affects DOM production. In temperate and tropical ecosystems, geologic factors are an important control on the magnitude of vertical DOM transport through sorption reactions of DOM with mineral soil components (Qualls and Haines 1992, Qualls 2000, Qualls et al. 2002, Lilienfein et al. 2004). However, it is not know if geochemical variation among organic soils affects stabilization of DOM in arctic environments where the organic horizon may dominate the thawed soil layer in large portions of watersheds.

Some of the most apparent differences in soils related to geologic variation that could influence DOM dynamics in arctic systems include variation in pH and base cation concentrations of organic soils present throughout the circumpolar region. Landscapes of northern Alaska are a mosaic of different aged geologic substrates because limestone soil parent material from the Brooks Range was deposited by glacial, fluvial, and aeolian processes at various times and places (Bockheim et al. 1998, Walker et al. 1998, Hamilton 2002). Previous work in this region has shown 10-fold variation in exchangeable Ca^{2+} concentrations and two pH-unit differences between soils of two distinct glacial drifts, related to variation in the extent of weathering (Walker 1994, Hobbie and Gough 2002, Hobbie et al. 2002). Studies that were unreplicated for landscape age showed correspondingly higher rates of microbial activity, DOM production, nitrogen mineralization, and nitrification on the older (low Ca and pH) landscape relative to the younger (high Ca and pH) glacial landscape (Bockheim et al. 1998, Hobbie et al. 2002). However, the mechanism(s) behind differences among landscape ages in DOM production is not well understood, nor is it known whether this pattern extends regionally across a longer chronosequence. In addition, it is not known how well variation in DOM production among landscape ages determined in laboratory studies translate into differences in DOM fluxes at the hillslope or watershed scale in the Arctic.

At smaller spatial scales, hillslopes are an important landscape feature in arctic ecosystems with significant variation in vegetation type (Giblin et al. 1991, Shaver et al. 1996), rates of soil respiration and nutrient cycling (Giblin et al. 1991, Nadelhoffer et al. 1991, Zak and Kling 2006), inorganic nutrient availability (Giblin et al. 1991,

Nadelhoffer et al. 1991), plant productivity (Shaver et al. 1996), and microbial community structure (Zak and Kling 2006). These differences in biogeochemical cycling within hillslopes potentially are significant for larger scale tundra carbon balance and export of carbon and nutrients to streams and eventually the Arctic Ocean, so have been included in some landscape scale biogeochemical models (Stieglitz et al. 1999, Stieglitz et al. 2003, Rastetter et al. 2004). However previous research has focused primarily on plant processes, respiration, and fluxes of inorganic nutrients within hillslopes, rather than on fluxes of DOM and associated organic nutrients. Since organic nutrients support the majority of arctic primary productivity (either through direct plant uptake of amino acids or indirect uptake through mychorrizae) fluxes of organic nutrients are important for understanding variation in plant productivity within hillslopes.

In the future, changes in climate will likely interact with geologic factors to influence arctic terrestrial organic matter cycling. Climate affects DOM production and mineralization (e.g., DOM production and mineralization are positively related to temperature) and transport (e.g., DOM transport is positively related to runoff). As arctic climate warms in the future, permafrost soils will thaw, increasing contact of soil water with mineral soil and accentuating differences among landscape ages. Therefore, with higher temperatures, DOC production may increase, but arctic soils may also transition from low to high DOC stabilization, depending on the reactivity of thawing mineral soils. By examining geologic controls on microbial activity as well as DOM production, availability, and degradation, this research should allow for more accurate predictions of the effects of changing climate on biogeochemical cycling in diverse arctic ecosystems.

Chapter 1: Effects of landscape age on soil organic matter processing in the Kuparuk River region, Alaska

Summary

Previous research on arctic soil biogeochemistry has focused largely on the effects of climate, organisms, and relief rather on effects of geologic factors such as parent material and time since geologic disturbance. However, a few studies suggest that biogeochemical cycling of carbon and nitrogen in tundra may be significantly affected by variation in glacial history, although the scope of these studies is limited. To determine if variation in landscape age-related differences in geochemistry are an important control of decomposition of organic matter in tundra soils, we conducted field measurements, soil analyses, and a soil incubation study across a chronosequence of landscape ages in the Upper Kuparuk River region, Alaska. We collected organic soil from two to four sites on each of four glacial surfaces ranging in age from 11,000 to 4.8 million years since glaciations, keeping climate, relief, parent material and vegetation relatively constant. We analyzed organic soil samples for pH, microbial biomass, exchangeable cations, and total carbon and nitrogen stocks and concentrations and measured respiration and production of dissolved organic carbon and nitrogen from homogenized organic soil over a five-month incubation.

Our results indicate that there are landscape-age related controls on microbial activity, with a distinct boundary between sites older than 50,000 years and sites younger than 50,000 years throughout the region. As expected, microbial biomass, respiration, and production of dissolved organic carbon and nitrogen were higher in soils from the three older landscape ages than in soils from younger, less weathered landscape ages. This

biological boundary corresponds to a chemical boundary that is consistent with effects of mineral soil weathering processes, with increased landscape age. Older soils had lower pH (4.5-5 vs. 6.5) and exchangeable cations (primarily Ca) than the youngest soils, but changes with weathering did not appear to further reduce soil pH and exchangeable cations after 50,000 years. There were no differences among landscapes in total carbon stocks in organic soils; however, total nitrogen stocks in the organic soil decreased with increasing landscape age. Differences among landscape ages in microbial activity and nitrogen availability due to geochemical variation may have important consequences for tundra carbon budgets because differences in soil pH and cation content exist throughout the circumpolar region. Therefore, differences in geochemistry due to landscape age or loess deposition, which also creates variation in soil pH and cation content, must be considered in models of arctic soil carbon and nitrogen cycling.

Introduction

Throughout the circumpolar region variation in climate, vegetation, topography, geologic parent material, and glacial history all potentially lead to significant variation in tundra biogeochemistry across the landscape. These five soil state factors (climate, organisms, relief, parent material, and time) were proposed by Hans Jenny (1941) to control soil formation. However, not all of these potential sources of variation are accounted for in regional models of arctic carbon balance, nor are their effects on arctic soil organic matter (SOM) processing fully understood. Previous research on arctic soil biogeochemistry has focused largely on the effects of climate (Chapin et al. 1995, Hartley et al. 1999, Dutta et al. 2006, Shaver et al. 2006, Sjogersten and Wookey 2009), organisms (vegetation) (Chapin and Shaver 1989, Shaver et al. 2001, Weintraub and Schimel 2005a, Zak and Kling 2006), and relief (topography) (Giblin et al. 1991, Nadelhoffer et al. 1991, Shaver et al. 1996, Stieglitz et al. 2003) rather than on differences in parent material (Bockheim et al. 1998, Ping et al. 1998, Walker et al. 1998, Walker 2000) or time (e.g. since glaciation) (Gough et al. 2000, Hobbie and Gough 2002, Hobbie et al. 2002, Hobbie and Gough 2004). Therefore, little is known about whether geologic controls on terrestrial soil biogeochemistry, known to be important in tropical (Crews et al. 1995, Hedin et al. 2003, Cleveland et al. 2004) and temperate (Qualls et al. 1991, Swift 2001, Yu et al. 2003, Lilienfein et al. 2004, Richardson et al. 2004, Selmants and Hart 2008) ecosystems, influence tundra biogeochemistry. A few studies of limited scope (i.e., that were unreplicated at the landscape scale) suggest biogeochemical cycling of carbon and nitrogen may be significantly affected by differences in landscape age

(Gough et al. 2000, Hobbie and Gough 2002, Hobbie et al. 2002, Hobbie and Gough 2004).

In temperate terrestrial ecosystems, geologic factors are an important control on biogeochemical cycling in soils (Swift 2001, Yu et al. 2003, Lilienfein et al. 2004, Richardson et al. 2004, Selmants and Hart 2008). Similarly, differences in geology throughout the circumpolar region may lead to variation in carbon dioxide fluxes and export of dissolved nutrients and organic matter to the Arctic Ocean. One mechanism by which geologic variation in temperate systems influences organic matter cycling is through effects on the chemical stabilization of dissolved organic matter that occurs via sorption reactions of dissolved molecules with mineral soil components (Shen 1999a, Qualls 2000, Qualls et al. 2002, Lilienfein et al. 2004). The magnitude of nutrient and organic matter removal from the soil solution within the vertical soil column is affected by the mineral composition of the soil, including soil pH and cation status (Kalbitz et al. 2000, Oste et al. 2002, Lilienfein et al. 2004). Soil pH affects the degree to which functional groups on organic matter are protonated, which in turn influences the solubility of dissolved organic matter in soils. Reduced pH increases protonation which in turn reduces solubility (You et al. 1999, Kalbitz et al. 2000, Oste et al. 2002). Therefore dissolved organic matter and associated respiration may be expected to be higher in arctic soils with circumneutral pH. Polyvalent exchangeable cations (those with at least two positive charges) may also reduce dissolved organic matter and respiration in soils through the formation of cation bridges that bind organic molecules together or to minerals (Kalbitz et al. 2000, Oste et al. 2002, Lilienfein et al. 2004). This reduces dissolved organic matter solubility and removes dissolved organic matter from the soil

solution as it moves vertically through mineral soil layers (Kalbitz et al. 2000, Oste et al. 2002, Lilienfein et al. 2004). Therefore dissolved organic matter and associated respiration may be expected to be higher in arctic soils with lower concentrations of exchangeable polyvalent cations.

Whether sorption of dissolved nutrients and organic matter to soil components is also an important control on biogeochemistry in arctic ecosystems is unknown. The majority of organic matter cycling in arctic soils occurs in organic horizons as permafrost restricts soil solution contact with mineral soil layers. However, large differences in soil pH and cation status exist throughout the circumpolar region in both mineral and organic horizons (Bockheim et al. 1998, Ping et al. 1998, Walker 2000, Walker et al. 2002). Throughout arctic landscapes, glacial deposition and loess transport add unweathered parent material to the surface increasing soil concentrations of base cations and pH (Bockheim et al. 1998, Ping et al. 1998, Walker et al. 1998, Walker 2000). Over time, soil weathering reduces the pH and alters soil cation composition and concentration through acidification and the leaching of base cations. Therefore, variation in glaciation history leads to differences in the degree of weathering and in the mineral composition of arctic soils, potentially leading to variation in organic matter cycling across the landscape.

The Upper Kuparuk River region in northern Alaska is an ideal location to examine how differences in landscape age affect arctic biogeochemistry. The landscape in this region is a mosaic of different aged geologic substrates because limestone material from the Brooks Range was deposited by glacial, fluvial, and aeolian processes at various times and in various places (Bockheim et al. 1998, Ping et al. 1998, Walker et al. 1998,

Walker 2000, Monroe and Bockheim 2001, Hamilton 2002). Previous work in this area on two sites of different ages (11,000-50,000 years and 50,000-120,000 years since deglaciation) showed greater *in situ* decomposition rates on the older relative to the younger glacial landscape (Hobbie and Gough 2004). In laboratory incubations of soils from these two sites, soils from older landscape ages exhibited higher rates of respiration, dissolved organic carbon (DOC) production, and net nitrogen mineralization than soils from the younger landscape age (Hobbie et al. 2002). Because these studies were unreplicated with respect to landscape age, it is not known if these geochemical differences lead to significant differences in terrestrial organic matter processing among these two landscape ages throughout the region, nor how sites younger and older than these compare. The present study expands this research to replicated sites across a chronosequence of landscape ages to examine how variation in landscape age (time since glaciation) affects decomposition of organic matter in the Upper Kuparuk River region, Alaska.

To determine if landscape age-related differences in geochemistry are an important control on arctic biogeochemistry, we conducted field measurements of geochemical differences among landscapes of different ages and a soil incubation study to examine rates of microbial respiration and dissolved organic matter production across the chronosequence. Previous results (Hobbie and Gough 2002, Hobbie et al. 2002, Hobbie and Gough 2004) suggest increased rates of organic matter cycling on older, more weathered landscapes with lower pH that should directly reduce solubility of microbial substrates because of hydrogen bonding among organic molecules. However, older landscapes also have lower concentrations of exchangeable polyvalent cations

available for stabilizing organic matter through ionic bonding. Variation in pH and polyvalent cation concentrations could have synergistic effects on organic matter stabilization, as reduced protonation with increasing pH would increase the number of organic matter functional groups available to form cation bridges simultaneously with an increase in the availability of polyvalent cations. Therefore, we hypothesized that geochemical differences among hillslopes of varying landscape age would lead to lower rates of organic matter decomposition on younger, less weathered landscapes. Across the chronosequence, we expected higher rates of microbial respiration and higher rates of production of dissolved nutrients and organic matter with increasing landscape age, as pH and the concentrations of exchangeable polyvalent cations declined.

Methods

To investigate the effects of landscape age-related variation in geochemistry on arctic organic matter dynamics, we examined a chronosequence of replicated sites varying in time since glaciation in the Upper Kuparuk River region, Alaska near the Toolik Field Station. During July 2004, we collected soil from two to four sites on each of four glacial surfaces ranging in age from 11,000 to 4.8 million years since glaciations (Table 1.1, Figure 1.1). We located sites that varied in one of Jenny's state factors (time) but among which the other four state factors (climate, relief, parent material, and organisms) (Jenny 1941) were relatively constant because large differences in glacial age occur on scales of kilometers (Hamilton 2002). Parent material deposited from the Brooks Range during the last five glacial advances between 11,000 and 4.8 million years ago is of similar mineralogy among sites (Bockheim et al. 1998, Ping et al. 1998, Monroe and Bockheim 2001, Hamilton 2002). Sites were selected in areas of mesic upland tundra

at least 500km from the nearest road to reduce the influence of calcium-rich road dust. Although the plant growth form composition was similar among sites, less weathered sites were dominated by moist nonacidic tundra species while older sites were dominated by moist acidic tundra species (Gough et al. 2000, Hobbie and Gough 2002, 2004). To reduce differences among sites in hydrology, soil temperature, and soil thaw depth we chose sites with similar slope (1-15%) and aspect (20^{o} W of N to 10^{o} E of N) within 15 miles of each other.

At each site, we measured soil temperature (at 10cm depth) and depth of permafrost thaw (n=1 per site) using a metal thaw probe in mid July (approximately the middle of the growing season). We then collected a 10x10cm (length by width) sample (n=1 per site) of the entire thawed organic horizon (between the bottom of the living moss layer and the top of the permafrost or mineral soil layer, whichever was shallower). From this sample we calculated bulk density, depth of the thawed organic horizon, and gravimetric soil moisture (60^{o}C). Sub-samples of bulk density cores were also used to measure soil pH in water slurries. We then collected and homogenized three replicate soil samples of the entire thawed organic horizon at each site. Soil samples were collected along 12-m transects perpendicular to the slope of the hillside with 4m between each sample. From each of the three replicate samples we analyzed sub-samples of soil for microbial biomass, exchangeable cations, and total carbon and nitrogen before freezing the remaining soil for use in our incubation experiment. We dried and ground soil sub-samples to analyze for total carbon and nitrogen using a Universal CHNOS Elemental Analyzer (Vario EL III, Elementar, Hanau, Germany).

We analyzed microbial biomass carbon and nitrogen with a chloroform fumigation extraction (Brookes et al. 1985, Beck et al. 1997). We fumigated a 6g subsample of homogenized organic soil from each of the three replicate soil samples per site for 72hr in a vacuum cabinet with 20mL of ethanol-free chloroform. We extracted these fumigated subsamples along with three replicate 6g subsamples of homogenized unfumigated soil from each site by shaking them in 50mL of 0.5M potassium sulfate for 1hr at 180 oscillations per minute and gravity filtering the resulting solution through pre-leached (with 0.5M potassium sulfate) Whatman #42 filter paper. We analyzed the resulting extracts for DOC and total dissolved nitrogen (TDN) using a total organic carbon and total nitrogen analyzer (TOC-V CSH and TNM-1, Shimadzu, Columbia, MD) and calculated microbial biomass carbon and nitrogen as the difference between extract concentrations for fumigated and unfumigated samples from the same site. We report results uncorrected for extraction inefficiency, since efficiency is unknown for these soils.

We conducted a barium chloride extraction adapted from Chorover (2004) to measure exchangeable hydrolyzing (aluminum (Al) and iron (Fe)) and base (calcium (Ca), sodium (Na), potassium (K), and magnesium (Mg)) cations. We shook 1g of dry organic soil in 60mL of 0.1M barium chloride for 15 minutes at 180 oscillations per minute. The resulting extracts were filtered through Whatman #42 Filter paper and analyzed for concentrations of cations using inductively coupled argon plasma optical emission spectrophotometry (ICAP-OES Optima 3000, Perkin Elmer, Waltham, MA) by the University of Minnesota Research Analytical Laboratory.

We conducted soil incubations of homogenized peat samples to measure respiration and production of dissolved organic carbon and nutrients monthly for five months in 2005. We placed 25g (wet weight) sub-samples of peat collected during July 2004 (three replicates from each site) on top of ashed Whatman GF/F filters in Pall MicroFunnel^{TM} 100mL filter funnels. Throughout the course of the incubation we kept samples at field capacity in the dark at 4^{o}C. At each measurement date we added 90mL of a micronutrient solution (Nadelhoffer et al. 1991) of 4.0mM $CaCl_2$, 2.0mM KH_2PO_4, 1.0mM K_2SO_4, 1.0mM $MgSO_4$, 25µM H_3BO_3, 2.0µM $MnSO_4$, 2.0µM $ZnSO_4$, 0.5µM $CuSO_4$, and 0.5µM Na_2MoO_4 to each sample. After one hour, we extracted the soil water solution with a vacuum pump. We analyzed the resulting leachates for DOC and TDN as described for microbial biomass. We used an auto analyzer (Alpkem, O.I. Analytical, College Station, TX) to measure nitrate plus nitrite (NO_3^- and NO_2^-) (cadmium reduction, (Wood et al. 1967)) and ammonium (NH_4^+) (phenol hypochlorite, (Solórzano 1969)) in leachates. Dissolved organic nitrogen (DON) export was calculated as TDN less the sum of NO_3^--N and NH_4^+-N leached. To calculate cumulative rates of DOC, DON, NO_3^-, and NH_4^+ production, we summed monthly exports to obtain 5-month totals. After leaching, we measured soil respiration over a 24hr period by placing soil samples in sealed mason jars with septa and sampling headspace CO_2 concentrations. Respiration over the 24hr period was calculated as the difference between initial and final headspace CO_2 concentrations as measured on a gas chromatograph with a thermal conductivity detector and poropak N column (GC-14A, Shimadzu, Columbia, MD). Cumulative respiration rates were calculated by multiplying the average daily respiration rates for two

consecutive sampling dates by the number of dates between sampling (~28 days) and summing across the entire length of the incubation.

One-way analysis of variance (ANOVA) and Tukey's HSD values (α=0.05) were used to evaluate differences among the four landscape ages for soil temperature, gravimetric soil moisture, July thaw depth, organic horizon depth, bulk density, and exchangeable cations (n=1 per site). For soil pH, microbial biomass carbon and nitrogen, total soil carbon and nitrogen, and incubation data (cumulative respiration, and DOC, DON, NO_3^-, and NH_4^+ production) we used one-way ANOVA with sites nested within landscape age (n=3 per site) as a random effect in the model and Tukey's HSD values (α=0.05) to evaluate differences among the four landscape ages. To analyze relationships between DOC production, soil carbon to nitrogen (C:N) ratio, total soil nitrogen, or microbial biomass carbon and respiration, DOC production, or DON production across landscape ages we calculated correlations using Pearson's r. Results of analysis of covariance (ANCOVA) were used to evaluate combined effects of landscape age and predictor variables (DOC, microbial biomass carbon, total soil nitrogen, or soil C:N ratio) on respiration, DOC production and DON production accounting for site to site variability by including sampling site as a random effect within the model. All data are presented as treatment means with standard errors of the mean. All statistical analyses were completed using JMP software (JMP 7, SAS, Cary, NY).

Results

Site Characteristics

There were no significant physical differences between soils sampled among the four landscape ages (Table 1). Neither soil temperature (ANOVA: p=0.054, $F_{3,9}$=3.73)

nor soil moisture (ANOVA: p=0.33, $F_{3,9}$=1.31) was significantly different among landscape ages at the time of sampling. There were also no significant differences among the four landscape ages in bulk density (ANOVA: p=0.13, $F_{3,9}$=2.47), organic horizon depth (ANOVA: p=0.92, $F_{3,9}$=0.17), or thaw depth (ANOVA: p=0.48, $F_{3,7}$=0.82) (Table 1.1).

By contrast, there were significant geochemical differences in organic soil among the four landscape ages. As expected, the younger, less weathered sites had significantly higher soil pH than sites older than 50,000 years since glaciation (ANOVA: p=0.004, $F_{3,9}$=9.30) (Table 1.1). However, organic horizon pH did not differ among the three older landscape ages (Tukey's HSD: α=0.05, see Table 1.1). The total exchangeable cation concentration was higher in soils from sites on the youngest surface than in soils from the older surfaces as expected from weathering over time (Figure 1.2). Exchangeable calcium (Ca) concentrations were two to eight times higher than concentrations of other exchangeable cations in soils from all landscape ages (Figure 1.2). There was significantly more exchangeable Ca in soils from the youngest age than the older landscape ages; however, there were no significant differences among the older ages (ANOVA: p=0.001, $F_{3,9}$=14.48; Tukey's HSD: α=0.05; significant age effects in Figure 1.2). Concentrations of exchangeable magnesium (Mg) were significantly different among landscape ages, with highest concentrations in the youngest landscape age (ANOVA: p=0.011, $F_{3,9}$=6.80; Tukey's HSD: α=0.05; significant age effects in Figure 1.2). There were no significant differences among landscape ages in concentrations of exchangeable aluminum (Al), iron (Fe), or manganese (Mn) (ANOVA: Al: p=0.072,

$F_{2,2}$=3.30; Fe: p=0.17, $F_{3,9}$=2.11; Mn p=0.062, $F_{3,9}$=3.51; Figure 1.2); however, there was no detectable aluminum in soils from the youngest landscape age.

In addition to differences in inorganic chemistry, there was variation in both total and chloroform extractable carbon and nitrogen among landscape ages. Although there were no significant differences in either total soil carbon concentration or stocks in the organic horizon among landscape ages (ANOVA: carbon concentration: p=0.14, $F_{3,16}$=2.33; Figure 1.3; carbon stocks: p=0.309, $F_{3,16}$=1.513, Table 1.1), both total soil nitrogen concentration and stocks in the organic horizon were highest in soils from the youngest landscape age (nitrogen concentration: ANOVA: p=0.035, $F_{3,16}$=4.49; Tukey's HSD: α=0.05; significant age effects in Figure 1.3; nitrogen stocks: ANOVA: p=0.021, $F_{3,16}$=6.22; Tukey's HSD: α=0.05; significant age effects in Table 1.1). This led to increasing soil C:N ratios with increasing landscape age (ANOVA: p=0.053, $F_{3,16}$= 3.78). Microbial biomass (uncorrected chloroform-extractable) carbon and nitrogen were lower in sites on the youngest landscape age than on the three older landscape ages (Figures 1.3a and 1.3b) with significant differences among landscape ages for microbial biomass carbon and nitrogen when normalized per gram soil (ANOVA: C p<0.001, $F_{3,15}$=17.44, N: p=0.006, $F_{3,15}$=8.28; Tukey's HSD: α=0.05; data not shown) and per gram soil carbon (ANOVA: C: p=0.001, $F_{3,15}$=12.28; N: p=0.017, $F_{3,15}$=5.806; Tukey's HSD: α=0.05; significant age effects in Figure 1.4). There were no significant differences among landscape ages in microbial C:N ratios (ANOVA: p=0.77, $F_{3,15}$=0.38).

Soil Incubation

Similar to previous results (Hobbie et al. 2002), there was a trend towards both lower cumulative DOC in leachates and significantly lower microbial respiration in soils

from the youngest landscape age compared to soils from the three older landscape ages (Figure 1.5). Differences in cumulative DOC production among landscape ages were not significant when expressed per gram soil (ANOVA: $p=0.076$, $F_{3,16}=3.20$; data not shown) or per gram soil carbon (ANOVA: $p=0.078$, $F_{3,16}=3.17$; Figure 1.5). There were significant differences among landscape ages in microbial respiration when normalized per gram soil (ANOVA: $p=0.011$; $F_{3,16}=6.74$; Tukey's HSD: $\alpha=0.05$; data not shown) and per gram soil carbon (ANOVA: $p=0.007$; $F_{3,16}=7.98$; Tukey's HSD: $\alpha=0.05$; significant age effects in Figure 1.5). There were also significant differences among landscape ages in the cumulative metabolic quotient (cumulative respiration/microbial biomass carbon) among landscape ages, with the higher values on older landscape ages (ANOVA: $p=0.035$; $F_{3,15}=4.48$; Tukey's HSD: $\alpha=0.05$, significant age effects in Figure 1.4).

The primary form of dissolved nitrogen produced in soil incubations was DON, making up 70-96% of total dissolved nitrogen production with no significant differences in the percent contribution of organic nitrogen to total dissolved nitrogen among landscape ages (ANOVA: $p=0.35$, $F_{3,16}=1.25$, Figure 1.6). Cumulative DON leached was lower for soils from the youngest landscape age than from the three older ages (ANOVA: $p=0.045$, $F_{3,16}= 4.03$; Tukey's HSD: $\alpha=0.05$; significant age differences in Figure 1.6). DON was significantly correlated with DOC production across all landscape ages (Pearson's r, Table 2). However, when accounting differences among hillslopes within each landscape age, DOC production was not a significant predictor of DON production (ANCOVA, Table 1.3). Cumulative inorganic nitrogen production in leachates was extremely low (<50 μg N/g soil total) and was not significantly different among ages (ANOVA: NO_3^--N: $p=0.37$, $F_{3,16}=1.19$ and NH_4^+-N: $p=0.33$, $F_{3,16}=1.33$; Figure 1.5).

Overall, cumulative microbial respiration was significantly correlated with DOC production in leachates across all landscape ages (Pearson's r, Table 1.2). Together, effects of landscape age and DOC production explained 94% of variation in microbial respiration (ANCOVA, Table 1.3). By contrast, microbial biomass carbon was not significantly correlated with microbial respiration, DOC production, or DON production across all landscape ages (Pearson's r, Table 1.2). Nor was microbial biomass carbon a significant predictor of DOC production, DON production, or microbial respiration when accounting for site-to-site variation within a landscape age (ANCOVA, Table 1.3).

Microbial respiration, DOC production, and DON production were significantly negatively correlated with total soil nitrogen concentrations and significantly positively correlated with soil C:N ratios (Pearson's r, Table 1.2). The combined effect of landscape age and total soil nitrogen concentrations accounted for 86% of the variation in microbial respiration, 74% of the variation in DON production, and 86% of the variation in DOC production (ANCOVA, Table 1.3). When accounting for site to site variability among landscape ages, soil C:N ratios were a significant positive predictor of DOC production and microbial respiration, but not of DON production (ANCOVA, Table 1.3).

Discussion

Our results indicate that there is landscape-age related control on microbial activity in upland tundra of the Upper Kuparuk River region, with a distinct boundary between sites older than 50,000 years and sites younger than 50,000 years throughout the region. Soils from sites on landscape ages younger than 50,000 years since glaciation exhibited slower rates of microbial activity than did soils from older landscapes. However, rates did not continue to increase with increasing landscape age beyond 50,000

years. This pattern is consistent with results of Hobbie and others (2002, 2004) who found microbial activity was higher in samples from a single site older than 50,000 years than from a single site younger than 50,000 years. North of the Brooks Range, 17% of the landscape is moist non-acidic tundra (on surfaces younger than 50,000 years) and 40% of the landscape is moist acidic tundra (on surfaces older than 50,000 years) (Walker et al. 1998). Results from multiple sites across multiple landscape ages in our study demonstrate that differences in microbial activity resulting from landscape age can be generalized throughout the region using the 50,000 year age divide.

Physical environment is a significant control on microbial activity in organic soils, but does not appear to cause the difference we observed in microbial activity among landscape ages. Physical factors related to climate or topography, such as slope, aspect, soil moisture, soil temperature, or active layer depths, did not differ between landscape ages, so it is unlikely that they caused differences in SOM and contributed to patterns in microbial activity among landscape ages. Furthermore, physical factors such as soil moisture, temperature, and water flow were controlled in our laboratory incubations, so variation in microbial activity among soils from different landscape ages was not directly caused by variation in environmental conditions.

Differences in microbial activity among landscape ages are also unlikely to result from variation in the chemical quality of inputs to SOM in the organic horizon. Although the 50,000 year boundary in geochemical characteristics is consistent with changes in vegetation species composition between moist nonacidic (younger soils) and moist acidic (older soils) tussock tundra (Ping et al. 1998, Hamilton 2002), species differences

between moist acidic and non-acidic tundra do not lead to significant differences in the quality of litter inputs among landscape ages (Hobbie and Gough 2004).

Landscape age associated variation in geochemistry likely influences rates of microbial activity through its control on substrate availability. Geochemistry is an important control on availability of microbial substrates in temperate systems through its effects on chemical mechanisms of SOM stabilization (Qualls and Haines 1991, Qualls et al. 1991, Qualls 2000, Qualls et al. 2002, Yu et al. 2003, Lilienfein et al. 2004) and significant variation in soil pH and exchangeable cation concentrations exists throughout the study region (Ping et al. 1998, Monroe and Bockheim 2001, Hobbie and Gough 2002, Keller et al. 2007, this study). Soils in the foothills of the Brooks Range are undergoing intense cryoturbation and buried material is gradually brought up to the surface and weathered over time (Ping et al. 1998, Monroe and Bockheim 2001). Consistent with effects of mineral soil weathering processes, older soils had lower pH and polyvalent exchangeable cations than the youngest soils, but changes with weathering did not appear to further reduce soil pH and exchangeable cations after 50,000 years. Keller et al (2007) found a similar pattern in soil and stream calcium concentrations among landscape ages in the region, with highest concentrations on the surfaces younger than 50,000 years and low concentrations on all older surfaces. Our results expand for the entire region research done by Hobbie and Gough (2002) who found significantly higher pH and cation concentrations from one site older than 50,000 years than in soils from a single site younger than 50,000 years since glaciation. As glacial drift of varying landscape age occurs in adjacent valleys throughout the foothills of the Brooks Range, geochemical

differences among landscape ages could cause significant variability in substrate availability for microbial activity.

Differences in soil pH and exchangeable polyvalent cations can both lead to variation in substrate availability for microbial activity among landscape ages by controlling solubility of DOC. DOC is typically more soluble at circumneutral pH (found on the youngest landscape age) than at more acidic pH (found on the older landscape ages) (You et al. 1999, Kalbitz et al. 2000, Oste et al. 2002). Conversely, higher concentrations of exchangeable polyvalent cations in soils on the youngest landscape age may result in greater stabilization of DOC and other microbial substrates by binding negatively charged organic molecules to each other or to mineral soil components, reducing their accessibility to breakdown by microbial enzymes (Oades 1988, Kalbitz et al. 2000, Oste et al. 2002). The importance of polyvalent cation bridging should increase in soils with circumneutral pH relative to more acidic soils, as a greater portion of SOM functional groups are negatively charged (You et al. 1999, Oste et al. 2002). Stabilization of microbial substrates by sorption to mineral soil components in younger, less weathered soils because of decreased protonation of dissolved organic matter combined with higher calcium concentrations would explain lower observed levels of microbial activity in soils from younger landscape ages. Therefore polyvalent cation bridging may be an important control on microbial carbon cycling in arctic soils.

Landscape age also appears to be an important control on nitrogen cycling and availability in arctic soils, with higher rates of nitrogen cycling in soils on older landscape ages despite higher soil C:N ratios. These results contrast with previous results from grasslands and temperate forests where nitrogen mineralization is negatively

correlated with soil and litter C:N ratios (Finzi et al. 1998, Lovett et al. 2002, Lovett et al. 2004, Hobbie et al. 2007). Greater stabilization of organic nitrogen through polyvalent cation bridging in soils on younger landscape ages would also explain lower observed nitrogen mineralization and nitrification rates in soils from a site younger than 50,000 years old than in soils from a site older than 50,000 years old (Hobbie et al. 2002), despite higher concentrations of soil nitrogen on younger landscapes. Narrower soil C:N ratios might result from landscape-age related differences in microbial community composition. Indeed, a comparison between a sites younger and older than 50,000 years revealed distinct microbial communities, with greater fungi at the older site (I. K. Schmidt and E. Bååth, unpublished data). Microbial community differences among landscape ages could lead to variation in the contribution of microbial metabolites to SOM, resulting in different SOM chemistry across landscape ages. Higher rates of nitrogen mineralization on older landscape ages are also consistent with increases in ammonium availability in laboratory incubations with increasing landscape age. Increased rates of nitrogen mineralization combined with higher DON production on older landscape ages should lead to greater nitrogen availability for plant and microbial uptake, or transport to aquatic ecosystems.

Implications

Differences among landscape ages in microbial activity and nitrogen availability due to geochemical variation may have important consequences for tundra carbon budgets because differences in soil pH and cation content exist throughout the circumpolar region. Lower fluxes of carbon to the atmosphere from soils with relatively high base cation status and pH resulting from loess deposition have been observed in

some studies in Northern Alaska (Walker et al. 1998, Oechel et al. 2000). Landscape age related differences in nitrogen availability also affect regional carbon balance through their influence on both decomposition and plant productivity. Hobbie and Gough (2004) found faster rates of litter decomposition and higher aboveground net primary productivity at one site older than 50,000 years since glaciation than at one site younger than 50,000 years since glaciation. Likewise, Walker (1995, 1998) found higher plant biomass and gross photosynthesis on acidic landscapes in the Kuparuk River Region than on nonacidic landscapes. Because arctic plants use DON as a major nitrogen source (directly or through symbioses with mychorrizae) (Kielland 1994, Lipson and Nasholm 2001, Hobbie and Hobbie 2006), the higher DON production we observed in older landscapes is consistent with and likely contributes to the higher plant productivity on those landscapes observed in other studies (Walker et al. 1995, Walker et al. 1998, Gough et al. 2000, Hobbie and Gough 2002, 2004).

If patterns of dissolved organic matter leaching from our experiment correspond to patterns in dissolved organic matter production and export *in situ*, differences in terrestrial production and retention of DOC and DON due to glacial history could have consequences for the composition of runoff to lakes, rivers, and the Arctic Ocean. Within aquatic ecosystems worldwide, terrestrially derived dissolved organic carbon and nutrients are important resources for aquatic primary and microbial productivity (Kling 1991, Cole and Caraco 2001, Caraco and Cole 2002, Hessen et al. 2004, Cole et al. 2007). Further research is necessary to determine whether landscape age differences in soil DOC and DON leaching observed in laboratory incubations correspond to variation in *in situ* soil water or stream dissolved organic carbon and nutrient concentrations.

Significant differences in arctic biogeochemistry among landscapes of varying glacial history could influence of the response of the arctic regional carbon balance to global climate change. Future climate warming will be most intense at high latitudes (McGuire et al. 2000, IPCC 2007) and significant warming trends have already been observed at a number of arctic sites (Overpeck et al. 1997, Chapin et al. 2005, Hinzman et al. 2005, Malmer et al. 2005, IPCC 2007). Climate will likely interact with geologic factors to influence rates of microbial respiration, plant productivity, nutrient availability and fluxes of DOC (McGuire et al. 2000, Mack et al. 2004, Malmer et al. 2005, Shaver et al. 2006). In arctic environments, variation in permafrost cover and thaw depth causes variation in the degree of contact between soil water and mineral soil layers as well as variation in the depth of active soil layers. As permafrost soils thaw under warmer conditions (Hinzman et al. 2005, Lawrence and Slater 2005, Osterkamp et al. 2009), large amounts of presently very cold or frozen organic matter will become available for decomposition, potentially increasing rates of microbial respiration, nutrient availability, and DOC export (Frey and Smith 2005, Shaver et al. 2006, Frey et al. 2007a, Kimball et al. 2007, Walvoord and Striegl 2007). However, increasing soil thaw may also enhance drainage through soil, increasing contact between dissolved organic matter and thawed mineral soil layers (Finlay et al. 2006, Frey et al. 2007b) and thereby increasing the potential for chemical stabilization of organic matter. This could accentuate differences in geochemical effects on organic matter dynamics among sites that already exist because of variation in landscape age or other aspects of geology. Therefore, the importance of geologic controls on tundra biogeochemistry is likely to increase with future climate

warming, further highlighting the importance of considering differences between landscape ages in regional carbon models.

This study has shown that geologic factors, particularly landscape age and accompanying variation in exchangeable base cation concentrations and pH are important in determining arctic landscape patterns of SOM processing. This is especially important since mineral soils throughout the region exhibit similar geochemical differences to organic soil layers, with higher pH and exchangeable cation status on younger landscape ages (Bockheim et al. 1998, Hobbie and Gough 2002). As future climate in arctic ecosystems is predicted to continue current warming trends, sorption of DOC and associated nutrients to mineral soil components may alter predicted changes in soil carbon storage. Increased rates of nutrient mineralization and decomposition predicted with increased temperatures may be partially offset by increased stabilization of organic matter by mineral soil components as contact between them increases. Therefore, differences in geochemistry due to landscape age or loess deposition must be considered in models of arctic soil carbon and nitrogen cycling.

Chapter 2: Effects of pH and calcium on soil organic matter dynamics in Alaskan tundra

Summary

In Northern Alaska (AK), large variation in the biogeochemical cycling of carbon and nitrogen exists among landscapes underlain by different aged geologic substrates deposited by the expansion and contraction of glaciers throughout the Pleistocene. Younger, less weathered landscapes have circumneutral pH, ten-fold higher exchangeable cation concentrations, and slower rates of microbial activity than older, more weathered landscapes with more acidic pH (4.5). We aimed to determine the relative importance of variation in multivalent cation bridging versus pH for influencing solubility of organic matter and thus microbial activity. We collected soils near Toolik Lake, AK from replicated sites along a chronosequence of four landscape ages ranging from 11,000 to 4.8 million years since glaciation. We manipulated calcium concentration and pH within these soils to tease apart the effects of polyvalent cations and pH on dissolved organic matter production and microbial respiration in soil. We focused on calcium as a representative polyvalent cation because it represents the dominant polyvalent cation across all landscape ages. Microbial respiration and dissolved organic matter production were measured monthly during a five-month incubation of soils at 11^{o}C in the dark.

Manipulated soils with acidic (4.5) pH (but similar calcium concentrations) exhibited higher cumulative dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) in leachates than soils with circumneutral (6.5) pH, similar to *in situ* patterns of dissolved organic matter production among landscape ages of varying pH. In

contrast, soils with circumneutral pH (but similar calcium concentrations) exhibited higher rates of microbial respiration than soils with acidic pH, opposite of *in situ* patterns. At circumneutral pH (6.5), increasing calcium concentration inhibited cumulative DOC in leachates as expected. However, increasing calcium concentration had no effect on DOC or DON in leachates at acidic pH (4.5). Although microbial respiration was inhibited by high calcium concentrations at both pH 6.5 and 4.5, the effect was stronger at pH 6.5. The landscape age of soil origin also influenced rates of microbial respiration and concentrations of DOC and DON in leachates even after accounting for differences in pH and exchangeable calcium concentrations. Our results indicate that both polyvalent cation concentration and pH influence microbial activity in tundra soils, suggesting that heterogeneity in geochemical factors associated with landscape age should be considered in models of tundra soil organic matter dynamics.

Introduction

In arctic ecosystems, climate, vegetation, permafrost cover, and geologic characteristics of watersheds are important sources of variation in terrestrial organic matter cycling. Understanding this variation is important for understanding linkages between terrestrial and aquatic ecosystems as terrestrially derived dissolved organic matter (DOM) represents a substantial source of energy and nutrients to arctic aquatic ecosystems. Previous research on arctic soil carbon and nitrogen cycling characterized the influence of climate (van Wijk et al. 2003, Epstein et al. 2004, Malmer et al. 2005, Sjogersten and Wookey 2005), vegetation (Shaver and Chapin 1991, Callaghan and Jonasson 1995, Hobbie 1996), fertilization (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. 2007b). 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, Hobbie and Gough 2004, Chapter 1). However, the mechanisms underlying possible relationships between landscape age and microbial respiration or DOM production 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 (Swift 2001, Yu et al. 2003, Lilienfein et al. 2004, Richardson et al. 2004, Selmants and Hart 2008). In many temperate and tropical

ecosystems, greater than 90% of DOM entering forest soils may be retained by chemical stabilization of DOM in mineral soil horizons as water moves through mineral soils before entering streams (Qualls et al. 1991, Qualls et al. 2002, Lilienfein et al. 2003, 2004, Worrall et al. 2006). As a result, the concentration of DOM decreases in soil water with depth in the soil column (McDowell 1988, Dalva 1991, Michalzik et al. 2001, Kaiser et al. 2002, Marschner and Kalbitz 2003, Kaiser and Guggenberger 2005). Once DOM has been sorbed to mineral soil particles, it is much less susceptible to microbial decomposition (Oades 1988, Shen 1999a, Kaiser and Guggenberger 2000, Kalbitz et al. 2000, Elkins and Nelson 2001, Oste et al. 2002). Chemical stabilization of DOM and inorganic nutrients in mineral soils is controlled by water flow paths (contact with mineral soil components) (Aiken and Cotsaris 1995, Kaiser and Guggenberger 2005), the type of mineral soil (Shen 1999b, 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, even in tundra soils (Kawahigashi et al. 2006), whether geologic variation among organic soils can also lead to differences in DOM concentrations is less well studied.

In mineral soils, 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. In arctic ecosystems where the majority of thawed soil is organic the relative importance of differences in pH and exchangeable base cations for controlling variation in soil organic matter processing has not been 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, and glacial processes.

The relationship between pH and the solubility of DOM is complicated because different types of DOM have different solubility at varying pH (Kipton et al. 1992). Generally, DOM solubility increases with increasing pH as there are an increasing number of negative charges on both DOM and other soil components (Shen 1999a, You et al. 1999, Andersson et al. 2000, Kalbitz et al. 2000, Oste et al. 2002). At acidic pH proton concentration is high, causing DOM and soil particles to bind with protons and then form hydrogen bonds with other compounds and soil particles, stabilizing DOM (Shen 1999a, You et al. 1999, Andersson et al. 2000, Kalbitz et al. 2000, Oste et al. 2002). At higher pH, sites with pH dependent charge are primarily deprotonated causing charge dispersion among molecules leading to higher solubility (Kipton et al. 1992, You et al. 1999, Andersson et al. 2000, Oste et al. 2002). Maximum DOC sorption in soils is generally around pH 4-5 (Shen 1999a, Andersson et al. 2000), while all DOM is deprotonated at pH 6-8 (Shen 1999a, You et al. 1999, Andersson et al. 2000). More soluble DOM will result in higher DOM losses from the system so DOM efflux from soils is usually correlated with pH (Shen 1999a, Elkins and Nelson 2001, Michalzik et al. 2001, Oste et al. 2002).

Variation in exchangeable cation concentrations can affect fluxes of DOM through stabilization of negatively charged DOM by sorption to positively charged cations. Polyvalent (with at least two positive charges) cation “bridges” can form between two negatively charged particles, essentially binding organic molecules together or to minerals. The bond between polyvalent cations in mineral soils and negatively

charged functional groups in DOM is not easily reversible, preventing biological, chemical, or physical breakdown (Oades 1988, Shen 1999a, Kaiser and Guggenberger 2000, Kalbitz et al. 2000, Elkins and Nelson 2001, Oste et al. 2002). Therefore, DOM efflux and decomposition of soil organic matter should be lower in soils with higher exchangeable polyvalent cations. Polyvalent cation bridging is strongest with hydrolyzing cations (aluminum and iron), while calcium is important for forming bonds with organic matter in alkaline soils and rivers (Oades 1988, Aiken and Cotsaris 1995, Kaiser 1998, Shen 1999a, Moore and Turunen 2004). Although cation bridging has been shown to be an important control of DOM retention in mineral soils, its importance is unknown for DOM stabilization in organic soils. However, previous research indicates that variation in organic soil geochemistry may cause differences in rates of microbial activity among arctic ecosystems (Hobbie et al. 2002, Hobbie and Gough 2004, Chapter 1). If polyvalent cation bridging is an important influence in arctic organic soils, large differences in exchangeable polyvalent cations among watersheds throughout the circumpolar region would lead to significant variation in soil organic matter processing.

The concentration of polyvalent cations and pH of soils also interact to affect stabilization of DOM in soils. At acidic pH (4-5), negative binding sites on organic and mineral soil components are occupied by hydrogen ions rather than polyvalent cations (Kaiser 1998, Elkins and Nelson 2001). Therefore, at acidic pH, hydrogen bonding among protonated DOM reduces solubility, but the importance of stabilizing polyvalent cation bridges is also diminished. At pH 6-8, all functional groups on DOM are deprotonated, increasing charge dispersion among DOM 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.

This study aims to determine the relative effects of landscape age-associated differences in pH and exchangeable cation concentrations on microbial activity in arctic soils. In the northern foothills of the Brooks Range, AK, variation in glaciation history causes large differences in aquatic and terrestrial geochemistry throughout the region. 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, Monroe and Bockheim 2001, Hobbie and Gough 2002, Hobbie et al. 2002, Hobbie and Gough 2004, Keller et al. 2007, Chapter 1). Similarly, lakes and streams on the younger glacial drifts have higher conductivity, higher concentrations of base cations and bicarbonate, and higher pH compared to those on older surfaces (Keller et al. 2007). Landscape age differences in soil organic matter processing are also apparent, with higher rates of microbial respiration, DOC production, 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, Chapter 1).

To examine the importance of both pH and exchangeable cations on arctic soil biogeochemistry, we conducted a soil incubation experiment, factorially manipulating pH and exchangeable calcium concentrations in organic soils from four landscape ages in the northern foothills of the Brooks Range, AK. We focused on calcium because calcium represents the majority of polyvalent cations across all landscape ages and exhibits the

greatest differences in concentrations among landscape ages in the study region. We expected less DOM in leachates and less microbial respiration in soils manipulated to a more acidic pH because DOM is less soluble than at circumneutral pH. We also expected less microbial respiration and less DOM in leachates in soils manipulated to higher calcium concentrations due to stabilization of DOM by polyvalent cation bridging. Due to the interaction between the changes in charge of DOM with changes in pH and increased polyvalent cation bridging at high calcium concentrations, we expected the lowest rates of soil organic matter processing from soils manipulated to high calcium 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.

Methods

During July 2004, we collected soil samples from two to four sites on each of four landscapes in the Upper Kuparuk River Region, AK that ranged in age between 11,000 and 4.8 million years since glaciations (Table 1). To minimize the influence of calcium-rich road dust we selected sites located at least 0.5km from roads. All sites were located in areas of mesic upland tundra with similar slope (1-15%) and aspect (20^{o} W of N to 10^{o} E of N) to minimize variation in vegetation and topography. A detailed description of site physical and geochemical characteristics can be found in Chapter 1. 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 calcium on organic matter cycling in arctic organic soils, we factorially manipulated exchangeable calcium

content and pH (within the natural range occurring among sites) in three replicate soil samples from each site. Exchangeable calcium 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 250g (wet weight) of organic soil for 15 minutes at 180 oscillations per minute in each of three solutions in turn: 0.1M KCl, 0.05M KCl, and 0.01M 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 calcium removal treatment. We then divided the resulting soil into five sub-samples of 50g each, one for each of our five treatments. Treatments consisted of:

1) calcium removal without pH manipulation (CaR),
2) calcium removal with calcium added back at a higher concentration with 0.1M CaOH adjusted to pH 4 (HCa4),
3) calcium removal with calcium added back at a higher concentration with 0.1M CaOH adjusted to pH 6.5 (HCa6.5),
4) calcium removal with calcium added back at a lower concentration with high 0.01M CaOH adjusted to pH 4 (LCa4), and
5) calcium removal with calcium added back at a lower concentration with 0.01M CaOH adjusted to pH 6.5 (LCa6.5).

For calcium addition we shook 50g (wet weight) of soil (with exchangeable calcium removed) in 150mL of calcium addition solution three times for 30 minutes at

180 oscillations per minute. After each rinse the pH of soil and solution were adjusted to the desired pH using concentrated NaOH or HCl (chosen to minimize the addition of carbon or nutrients). After pH adjustment, we separated soil from solution by gravity filtration through pre-leached Whatman 42 filter paper. To quantify the amount of calcium added back soil samples during treatments, we saved sub-samples of the solution resulting from each rinse for cation analysis (inductively coupled argon plasma optical emission spectrophotometry; ICAP-OES Optima 3000, Perkin Elmer, Waltham, MA).

Before beginning the incubation experiment, we measured total soil carbon and nitrogen and 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 calcium removal process and pH adjustment on soil organic matter and microbial communities. 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 10g 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) at both the beginning and end of our experiment. We shook one subsample for one hour at 180 oscillations per minute in 50mL of 0.5M potassium sulfate and collected the resulting extracts by filtering through pre-leached Whatman 42 filter paper. The other subsample was fumigated for 72 hours in a vacuum cabinet with 20mL 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 in extracts from fumigated and non-fumigated samples. We measured concentrations of DOC and total dissolved nitrogen 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 calcium treatments on organic matter processing, we conducted a 5 month incubation of manipulated soils at field capacity and 4^{o}C (mean growing season soil temperature) in the dark. For each of the five treatments (CaR; HCa4; HCa6.5; LCa4; and LCa6.5) we placed three replicate 25g (wet weight) treated soil samples from each site in a Pall MicroFunnel^{TM} 100mL filter funnel on an ashed Whatman GF/F filter. We measured microbial respiration and of DOC and dissolved organic nitrogen (DON) in leachates monthly. At the start of our incubation and each measurement date thereafter we added 90mL of a micronutrient solution (Nadelhoffer et al. 1991) of 4.0mM $CaCl_2$, 2.0mM KH_2PO_4, 1.0mM K_2SO_4, 1.0mM $MgSO_4$, 25µM H_3BO_3, 2.0µM $MnSO_4$, 2.0µM $ZnSO_4$, 0.5µM $CuSO_4$, and 0.5µM Na_2MoO_4 to each sample for one hour 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 total dissolved nitrogen (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 hour 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 Chapter 1.

We calculated cumulative rates of microbial respiration and cumulative rates DOC, DON, nitrate, and ammonium in leachates over the experiment. For all measured variables (rates of carbon and nitrogen production in leachates and microbial respiration rates), rates were highest at the first sampling date (Day 1) and then remained relatively constant throughout the rest of the experiment. 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 production were calculated as the sum of production in leachates on days 40, 70, 100, and 137. We calculated cumulative respiration rates by multiplying the number of days between sampling dates (~28) by the average of daily respiration rates for those sampling dates and summing over all samplings between day 40 and day 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 one-way analysis of variance (ANOVA) with site number nested with landscape age and replicate nested within site as random variables and Tukey's HSD values (α=0.05) to evaluate significant differences among treatments and landscape ages in soil total soil carbon and nitrogen, microbial biomass carbon and nitrogen, and incubation data (cumulative respiration, DOC and DON production, and nitrate and ammonium production). The relative effects of calcium and pH on total soil carbon and

nitrogen and microbial biomass carbon and nitrogen were analyzed using a two-way ANOVA on data from the four factorial calcium and pH manipulated treatments (HCa4, HCa6.5, LCa4, and LCa6.5). Cumulative rates of microbial respiration, and DOC, DON, and dissolved inorganic nitrogen production were analyzed using a two-way ANOVA on data from the four calcium and pH manipulated treatments (HCa4, HCa6.5, LCa4, and LCa6.5) to determine the effects of calcium and pH treatments.

To analyze relationships between DOC production and respiration or DON production across landscape ages we used simple linear regression with DOC as a predictor. Results of analysis of covariance (ANCOVA) were used to evaluate the combined effects of landscape age and DOC production on respiration and DON production accounting for site-to-site variability by including sampling site as a random effect within the model.

Results

Soil characteristics

There were significant treatment effects when comparing among the five manipulated soils and unmanipulated organic soil for both total soil carbon (one-way ANOVA: $p<0.001$, $F_{5,204}=46.24$; Figure 2.1a) and total soil nitrogen (one-way ANOVA: $p<0.001$, $F_{5,204}=5.89$; Figure 2.1b) concentrations. Soils from the high calcium treatments had significantly lower carbon concentrations than unmanipulated soils, calcium removal soils, and soils from low calcium treatments, regardless of pH (Tukey's HSD; $\alpha=0.05$; Figure 2.1a). High calcium soils also had the lowest concentrations of total soil nitrogen (Tukey's HSD; $\alpha=0.05$; Figure 2.1b). Total soil carbon and nitrogen concentrations in organic soils were significantly affected by calcium concentration (two-way ANOVA:

carbon: $p<0.001$, $F_{1,120}=213.51$; nitrogen: $p<0.001$, $F_{1,120}=21.76$; Figure 2.1) but not by pH (two-way ANOVA: carbon: $p=0.058$, $F_{1,120}=3.67$; nitrogen: $p=0.28$, $F_{1,120}=1.16$; Figure 2.1). Low calcium treatments had significantly higher soil carbon and nitrogen than high calcium treatments (Tukey's HSD; $\alpha=0.05$; Figure 2.1). As a result, there were no significant treatment effects on soil carbon to nitrogen (C:N) ratios when comparing among the five manipulated soils and unmanipulated organic soil (one-way ANOVA: $p=0.94$, $F_{5,204}=0.24$; Figure 2.1c). Carbon to nitrogen ratios in treated organic soils were not significantly affected by calcium (two-way ANOVA: $p=0.37$, $F_{1,120}=0.80$; Figure 2.1c) or pH (two-way ANOVA: $p=0.97$, $F_{1,120}=0.002$; Figure 2.1c).

Significant differences among landscape ages in total soil nitrogen concentrations remained after applying our experimental treatments, with the highest nitrogen concentrations in soils from the youngest landscape age (one-way ANOVA: $p=0.021$, $F_{3,204}=5.45$; Tukey's HSD; $\alpha=0.05$; Figure 2.1b). Similar to previous results, there were no significant differences among landscape ages in the total soil carbon concentration of treated soils (one-way ANOVA: $p=0.14$, $F_{3,204}=2.33$; Figure 2.1a). As a result, significant differences among landscape ages existed in carbon to nitrogen ratios of treated soils (two-way ANOVA: $p=0.023$, $F_{3,120}=5.22$; Figure 2.1c). Treated soils from the youngest site had the lowest C:N ratio among landscape ages and C:N ratios in treated soils increased with landscape age (Tukey's HSD; $\alpha=0.05$; Figure 2.1c). In order to account for differences in soil carbon among treatments, we present our experimental results as rates normalized per gram soil carbon.

Although there were significant differences in microbial biomass carbon and nitrogen per gram soil carbon and in microbial C:N ratios 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; $\alpha=0.05$; Figure 2.2), microbial biomass carbon, nitrogen, and C:N ratios were not significantly different between the calcium removal treatment and unmanipulated soils at the beginning of the experiment (Tukey's HSD; $\alpha=0.05$; Figure 2.2). Significant treatment differences in microbial biomass were caused by differences among the four factorial calcium and pH manipulation treatments. There was a significant calcium by pH interaction for microbial nitrogen (two-way ANOVA: $p=0.004$, $F_{1,120}=8.45$; Figure 2.2b) and for microbial carbon (two-way ANOVA: $p=0.025$, $F_{1,120}=5.19$; Figure 2.2a). In the low calcium treatments, circumneutral pH soils had greater microbial carbon and nitrogen than acidic pH soils (Figure 2.2). However, in the high calcium treatments, soils had higher concentrations of microbial carbon in acidic pH soils than circumneutral pH soils but similar concentrations of microbial nitrogen in high and acidic pH soils (Figure 2.2). Increasing calcium concentrations decreased microbial biomass carbon and nitrogen at acidic pH, but had little effect on microbial biomass carbon and nitrogen at circumneutral pH (Figure 2.2). As a result, the C:N ratio of the microbial biomass was significantly different among treatments (one-way ANOVA: $p<0.001$, $F_{5,178}=4.83$; Figure 2.2) with significantly higher microbial C:N ratios in the calcium removal treatment than in the low calcium treatments and significantly lower microbial C:N ratios in the low calcium, circumneutral pH treatment than in unmanipulated soils (Tukey's HSD; $\alpha=0.05$; Figure 2.2).

Microbial biomass nitrogen was not significantly different among landscape ages at the beginning of the experiment (two-way ANOVA: $p=0.13$, $F_{3,120}=3.76$; Figure 2.2b). However, microbial biomass carbon did differ significantly among landscape ages at the

beginning of the experiment, generally increasing with increasing landscape age (two-way ANOVA: $p=0.035$, $F_{3,120}=4.45$; Figure 2.2a). The C:N ratio of the microbial biomass at the beginning of the experiment showed a significant effect of landscape age (one-way ANOVA: landscape age: $p=0.030$, $F_{3,183}=4.79$; Figure 2.2c). At the beginning of the experiment, microbial biomass carbon was significantly higher in treated soils from the Anaktuvuk glaciation than in treated soils from the Itkillik II glaciation while microbial biomass C:N ratios were significantly higher in treated soils from the Sagavanirktok glaciation than in treated soils from the Itkillik II glaciation (Tukey's HSD; $\alpha=0.05$; Figure 2.2). Results for microbial biomass carbon and nitrogen were generally similar when expressed per gram soil (analyses not shown).

Incubation Experiment

Landscape age, calcium, and pH significantly affected cumulative respiration rates per gram soil carbon (two-way ANOVA: landscape age: $p=0.013$, $F_{3,130}=6.44$; calcium: $p=0.005$, $F_{1,130}=8.38$; pH: $p<0.001$, $F_{1,130}=22.74$; Figure 2.3). As expected, soils from acidic pH treatments exhibited significantly lower respiration rates than soils from circumneutral pH treatments (Tukey's HSD; $\alpha=0.05$; Figure 2.3). Increasing calcium concentrations significantly decreased cumulative respiration rates as expected (Tukey's HSD; $\alpha=0.05$; Figure 2.3). Although rates of cumulative microbial respiration were significantly different among treatments (one-way ANOVA: $p<0.001$, $F_{5,204}=11.14$; Figure 2.3), they were not significantly different between the calcium removal treatment and the unmanipulated soil (Tukey's HSD; $\alpha=0.05$; Figure 2.3). Similar to results from previous studies (Hobbie et al. 2002, Chapter 1), soils from the youngest landscape exhibited significantly lower rates of cumulative microbial respiration across all pH and

calcium treatments (Tukey's HSD; α=0.05; Figure 2.3). However, neither decreasing pH nor reducing calcium alone or in combination increased respiration rates of soil from the youngest landscape to rates of unmanipulated soils from the three older landscapes.

Cumulative DOC production per gram of soil carbon exhibited a pH by calcium interaction (two-way ANOVA: $p=0.044$, $F_{1,130}=4.13$; Figure 2.4). In contrast to expectations, cumulative DOC production was similar between high and low calcium concentrations in soils with acidic pH, but in soils with circumneutral pH, increasing calcium concentrations significantly decreased DOC production as expected (Tukey's HSD; α=0.05; Figure 2.4). As predicted, cumulative DOC production in soils from the circumneutral pH, high calcium treatment was significantly lower than in all other treatments (Tukey's HSD; α=0.05; Figure 2.4). There was also a significant landscape age by pH interaction in cumulative DOC production (two-way ANOVA: $p<0.001$, $F_{1,130}=26.13$; Figure 2.4). Contrary to expectations, pH did not significantly affect cumulative DOC production per gram soil carbon in treated soils from the three older landscape ages (Tukey's HSD; α=0.05; Figure 2.4). However, in soils from the youngest landscape age where soil pH was adjusted using HCl there was significantly higher DOC production in acidic pH treatments than in circumneutral pH treatments (Tukey's HSD; α=0.05; Figure 2.4). Lowering the pH alone (and not lowering calcium concentrations) increased DOC production 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 production (one-way ANOVA: $p<0.001$, $F_{5,204}=11.21$; Figure 2.4), there were no significant differences between DOC production in untreated soil and in soils from the calcium removal treatment (Tukey's HSD; α=0.05; Figure 2.4).

Organic nitrogen in leachates averaged between 70% and 90% of total dissolved nitrogen production during the experiment (Figure 2.5). Ammonium and nitrate production rates were at or near detection limit for most samples. Among treated soils, the percent of total dissolved nitrogen production that was organic nitrogen was not significantly affected by landscape age (two-way ANOVA: $p=0.11$, $F_{3,111}=2.66$), calcium (two-way ANOVA: $p=0.19$, $F_{1,111}=1.74$), or pH (two-way ANOVA: $p=0.39$, $F_{1,111}=0.76$). However, there was a significantly greater proportion of organic nitrogen in calcium removal soils than in soils manipulated to low calcium and acidic pH (one-way ANOVA: $p=0.012$, $F_{5,172}=3.03$; Tukey's HSD: $\alpha=0.05$; Figure 2.5)

There were significant pH and landscape age effects on cumulative DON production per gram of soil carbon during our incubations (two-way ANOVA: landscape age: $p=0.019$, $F_{3,111}=5.28$; pH: $p<0.001$, $F_{1,111}=38.10$; Figure 2.5c), but no significant effects of calcium (two-way ANOVA: $p=0.28$, $F_{1,111}=1.20$; Figure 2.5c). Contrary to expectations, we observed significantly lower DON production at circumneutral pH than at acidic pH, but the magnitude of this change was affected by landscape age and was highest in soils from the youngest landscape age (ANOVA: $p<0.001$, $F_{3,111}=7.02$; Tukey's HSD; $\alpha=0.05$; Figure 2.5c). As with DOC, lowering the pH alone (and not lowering calcium concentrations) increased DON production in soils from the youngest site to levels found in soils from the three older sites. In contrast to DOC, soils from the calcium removal treatment exhibited significantly higher DON production than soils from any other treatment (one-way ANOVA: $p<0.001$, $F_{5,170}=24.62$; Tukey's HSD; $\alpha=0.05$; Figure 2.5c).

Overall DOC concentration in leachates was significantly positively correlated to microbial respiration, but explained only 9.4% of the variation in respiration (Table 2.2). Averaging across all treatments, concentration of DOC in leachates was only significantly correlated with respiration in the two intermediate landscape ages (Itkillik I and Sagavanirktok) and concentration of DOC in leachates explained at most 20% of the variation in respiration (Table 2.2). However, averaging across all landscape ages, but examining treatments separately, concentration of DOC in leachates was significantly positively correlated with respiration in unmanipulated soils and soils at circumneutral pH, regardless of calcium concentration, with DOC explaining 48-50% of the variation in microbial respiration (Table 2.2). In calcium removal treatments, soils respiration was also significantly correlated with concentration of DOC, explaining only 13% of variation in respiration Concentration of DOC and microbial respiration were not significantly correlated in soils at pH 4, however, regardless of calcium concentration (Table 2.2).

The concentration of DOC in leachates was significantly positively correlated to DON concentration overall, but explained only 15% of the variation in DON (Table 2.2). DON in leachates was only significantly correlated to concentration of DOC in leachates in soils from the youngest landscape age, but not the three older landscape ages when averaging across all treatments (Table 2.2). Variation in DOC explained 30% of the variation in DON in soils from the youngest landscape age. Averaging across all landscape ages, DON and DOC concentrations in leachates were not significantly correlated in unmanipulated soils or in soils with low calcium concentrations at circumneutral pH (Table 2.2). However, DOC and DON concentrations were

significantly positively correlated in calcium removal soils, low calcium soils with acidic pH and high calcium soils regardless of pH (Table 2.2).

Discussion

Soils from younger, less weathered sites had consistently lower rates of respiration across all treatments in our experiment, suggesting 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 potential landscape-age related influences on microbial respiration include variation in the quality of SOM or in the microbial community among landscape ages. Other research indicates that biodegradability of DOM is similar among landscape ages, at least during the growing season (when soils used in these incubations were collected) (Chapter 1). Microbial biomass nitrogen was significantly lower and microbial biomass carbon was lowest (although not significantly so) in soils from sites on the youngest, least weathered glacial drift across all treatments at the beginning of the experiment. Lower microbial biomass 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. Differences in microbial community composition among landscape ages could also lead to both differences in microbial activity among landscape ages and variation in the chemistry of microbial metabolic products among landscape ages, which might influence the quality of substrates available for microbial decomposition. Significant differences in microbial communities among landscape ages were found in a study by I.K. Schmidt and E. 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. Lower rates of microbial activity on soils from younger landscape ages despite higher concentrations of soil nitrogen (Chapter 1) also suggest there may be differences in the recalcitrance of soil organic matter among landscape ages.

Nevertheless, results from our study indicate that both polyvalent cation concentrations and pH appear to influence arctic soil biogeochemistry. Variation in exchangeable polyvalent cations among landscape ages can better explain lower rates of DOM production from younger, less weathered soils with a high potential for stabilizing DOM 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 at more acidic pH and did find lower rates of microbial activity 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, Chapter 1). While we also expected lower rates of microbial activity in soils manipulated to higher calcium concentrations due to stabilization of DOM by polyvalent cation bridging with calcium ions; we saw that calcium removal increased DOM production and respiration rates were higher in soils manipulated to high calcium concentrations than those manipulated to low calcium concentrations. This pattern corresponds to *in situ* patterns of microbial activity, with higher DOM production and microbial respiration in soils from younger landscapes with higher exchangeable polyvalent cation concentrations (Hobbie et al 2002, Chapter 1).

Our results indicate both changes in pH and changes in exchangeable calcium concentrations exert a direct control on respiration rates in arctic soils. However, we were not able to increase respiration rates in soils that naturally had higher calcium

concentrations and circumneutral pH to levels of soils that naturally had lower calcium concentrations and acidic pH by manipulating either calcium or pH. Similar to previous results with higher rates of respiration from older, more weathered soils (Hobbie et al 2002, Chapter 1), soils in our experiment showed lower rates of respiration in high calcium treatments than in low calcium treatments. Unlike previous studies showing higher rates of microbial respiration in more weathered soils with acidic pH (Oades 1988, Hobbie et al. 2002, Hobbie and Gough 2004, Chapter 1), we found lower rates of microbial respiration at acidic pH than at circumneutral pH. Lower rates of microbial respiration are consistent with our expectations based on previous research showing that SOM is least soluble at pH 4-5 (Shen 1999a, Andersson et al. 2000). At acidic pH higher concentrations of protons cause hydrogen bonding between SOM molecules, reducing its solubility (Shen 1999a, Andersson et al. 2000). If SOM is less soluble at acidic pH, there may be less substrate available for microbial decomposition at acidic pH than at circumneutral pH.

In our experiment, the depressing effect of increased calcium on concentrations DOC in leachates at high pH is consistent with results from previous laboratory experiments, with younger, less weathered soils showing depressed rates of microbial activity (Hobbie et al. 2002, Hobbie and Gough 2004, Chapter 1) and increased sorption of DOC to soil surfaces (Kaiser 1998, Shen 1999a, Kalbitz et al. 2000, Nilsson et al. 2001). Although we did not see a significant difference in DON concentrations in leachates between high and low calcium treatments, we did see a significant increase in DON production with calcium removal, which also suggests reducing cation concentrations influences DON solubility. Unlike Oste et al (2002), who found that

variations in concentrations of calcium were more important than variation in pH for controlling leaching of DOC, we found that exchangeable calcium concentrations did not directly control DOC concentration in leachates, but did influence the response of DOC concentration in leachates to changes in pH. At acidic pH many of the charged sites on DOM are protonated and cannot bind with polyvalent cations such as calcium; however, at acidic pH the charged sites on DOM molecules are negatively charged and can thus be removed from solution by polyvalent cation bridges.

DOC and DON concentrations in leachates tended to decrease with increasing pH, similar to previous results from homogenized peat which showed decreased DOC and DON fluxes at circumneutral pH than at acidic pH (Hobbie et al. 2002, Hobbie and Gough 2004, Chapter 1). Although these pH effects are consistent with landscape patterns of DOM production, they contrast expectations based on known pH effects on solubility of SOM, whereby increased pH should have increased SOM solubility, presumably leading to greater DOM availability. It is possible that despite higher rates of DOM production in acidic soils (Hobbie et al 2002, Chapter 1) higher DOM availability and higher rates of microbial respiration in soils with circumneutral pH than in soils with acidic pH lead to lower net DOM in leachates due to faster DOM decomposition.

The net effect of variation in exchangeable polyvalent cations and variation in pH on microbial activity in arctic organic soils appears to depend on the microbial process in question. Among the four manipulation treatments, soils from the high calcium, circumneutral pH treatment showed significantly lower DOC concentrations in leachates, than all other treatments. These results are similar to those of Andersson et al (2000), who found lower rates of microbial respiration and DOC and DON production in unlimed

soils (lower pH and calcium) than in limed soils (higher pH and calcium). However, in our experiment, the treatment exhibiting the lowest microbial respiration was the high calcium, low pH treatment. It appears that landscape age influences the production of DON through pH and other landscape age effects (such as total soil N pools) not included in this factorial manipulation, rather than by increased calcium concentrations in younger, less weathered sites. However the combined effect of exchangeable cation concentration and pH on rates of microbial respiration, DOC, and DON in leachates in natural soils leads to lower rates in soils with high exchangeable calcium concentrations and circumneutral pH than in soils with low exchangeable concentrations calcium and acidic pH (Hobbie et al. 2002, Hobbie and Gough 2004, Chapter 1).

Implications

Our results indicate that geochemical differences among arctic organic soils can control both soil organic matter cycling and concentrations of DOM in soil water. 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 soils increase 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.

Chapter 3: Effects of landscape age on small watershed carbon and nutrient fluxes in arctic Alaska

Summary

Dissolved organic matter (DOM) represents an important component of carbon and nutrient cycling in arctic ecosystems, so differences in availability and fluxes of DOM among or within hillslopes could affect microbial and plant productivity. Previous research in arctic Alaska has shown that geochemical differences associated with landscape age (time since glaciation) significantly affect terrestrial organic matter cycling with higher rates of DOM production, soil respiration and soil N mineralization on older, more weathered landscapes. However, it is unknown if these differences in terrestrial biogeochemical cycling translate into variation in concentrations of DOM in soils and streams. To investigate whether higher rates of laboratory DOM production in soils from older landscapes translate into differences in *in situ* concentrations of DOM among hillslopes we collected soil and stream water samples from a chronosequence of landscape ages near Toolik Lake, Alaska. To study topographic variation in soil water DOM concentrations within hillslopes, we sampled saturated (with perforated needles) and unsaturated (with microlysimeters) soil water across hillslope toposequences that included upslope, vegetation boundary (boundary between mesic upland tundra and the riparian vegetation within the watershed) and streamside locations in each watershed.

In all sites soil water dissolved organic carbon (DOC), dissolved organic nitrogen (DON), and phosphate concentrations were significantly higher in upslope samples while concentrations of bicarbonate in soil water were significantly higher in riparian samples, indicating significant transformations of C and N within the hillslope. High pH sites on

younger glacial drift had significantly higher soil water bicarbonate concentrations and significantly lower concentrations of DON in soil water than older, more weathered soils. Unlike previous laboratory results, there was no consistent pattern of DOC concentrations in soil water with landscape age. Despite differences in rates of soil organic matter processing and in soil water DON and bicarbonate concentrations among landscapes, watershed concentrations of inorganic and organic carbon and nutrients did not differ among landscape ages during summer conditions. Our results suggest that under current permafrost and soil conditions DOM availability is highly variable within the hillslope, but within-stream processing masks landscape ages effects at the watershed scale.

Introduction

Although fluxes of inorganic nutrients (Giblin et al. 1991, Nadelhoffer et al. 1991) and gaseous emissions of carbon from soils have been well studied (Shaver et al. 1992, Waelbroeck et al. 1997, Wagner et al. 2005, Shaver et al. 2006), the controls on the transport of carbon and nutrients from terrestrial arctic ecosystems as dissolved organic matter (DOM) are less well understood (Benner et al. 2004, Streigl et al. 2005, Frey and McClelland 2009). Because the organic horizon dominates the thawed soil layer in large portions of arctic watersheds, water is in contact almost exclusively with organic, rather than mineral, soil in arctic hillslopes, generating relatively large DOM fluxes from terrestrial to aquatic ecosystems. As permafrost soils thaw with climate warming (Shaver et al. 1992, McGuire et al. 2000, Hinzman et al. 2005, Lawrence and Slater 2005, Malmer et al. 2005, Shaver et al. 2006, Osterkamp et al. 2009), large amounts of cold or frozen organic matter will become available for nutrient mineralization and denitrification, decomposition to methane or carbon dioxide, or transport as DOM (Waelbroeck et al. 1997, McGuire et al. 2000, Streigl et al. 2005, Shaver et al. 2006, Frey and McClelland 2009).

Previous research has shown that geochemical differences associated with landscape age (time since glaciation) are an important control on soil organic matter cycling in arctic Alaska (Hobbie and Gough 2002, Hobbie et al. 2002, Hobbie and Gough 2004, Hobbie et al. 2005, Chapter 1, Chapter 2). However, it is unknown if these differences in soil organic matter processing translate into variation in transport of DOM from terrestrial to aquatic ecosystems. To determine if observed regional differences in soil DOM production (observed in laboratory studies) among landscape ages are apparent

at the hillslope and watershed scale we conducted a survey of soil and stream water in small watersheds in northern Alaska across a chronosequence of landscape ages.

Hillslopes are an important landscape unit in arctic ecosystems because they exhibit significant variation in water and nutrient availability, vegetation type, microbial community composition, and organic matter cycling (Giblin et al. 1991, Nadelhoffer et al. 1991, Shaver et al. 1996, Stieglitz et al. 2003, Rastetter et al. 2004, Zak and Kling 2006). As water moves down a hillslope, physical, chemical, and biological processes act on dissolved materials within the water altering nutrient availability to plants at different positions along the slope. Because plant growth in arctic tundra systems is highly nutrient-limited (Nordin et al. 2004, Weintraub and Schimel 2005a, b), within-hillslope differences in nutrient and water availability likely lead to important differences in plant community structure and plant productivity along hillslopes (Chapin et al.1988). Until recently, research on arctic hillslopes focused primarily on within-hillslope variation in plant species composition, plant productivity, and inorganic nutrient cycling. However, understanding controls on cycling of dissolved organic carbon and nutrients in arctic systems is critical to understanding hillslope variation in productivity, as the majority of dissolved nutrients in arctic soils are present in organic form. To study how the availability of dissolved organic carbon and nutrients change within tundra hillslopes we examined soil water concentrations at three different hillslope elevations within each watershed.

An important control on fluxes of DOM within terrestrial ecosystems is the stabilization of DOM by mineral soil components (Aiken and Cotsaris 1995, Kalbitz et al. 2000, Kaplan and Newbold 2000). In upland temperate ecosystems, the majority of

DOM is removed from the soil solution by adsorption to mineral soils before entering aquatic ecosystems (Qualls and Haines 1992, Kaplan and Newbold 2000, Qualls 2000, Qualls et al. 2000, 2002, Marschner and Kalbitz 2003, Kaiser and Guggenberger 2005, Worrall et al. 2006). Geochemical differences among soils due to factors such as landscape age can affect soil organic matter processing and DOM fluxes because of increased solubility of DOM on older, more weathered soils with more acidic pH and lower concentrations of exchangeable base cations (Shen 1999a, Shen 1999b, You et al. 1999, Andersson et al. 2000, Oste et al. 2002, Chapter 2). In arctic ecosystems, geochemical differences between soils due to variation in landscape age also have significant effects on terrestrial organic matter processing and DOM production (Hobbie and Gough 2002, Hobbie et al. 2002, Hobbie and Gough 2004, Hobbie et al. 2005, Chapter 1, Chapter 2) as well as stream and lake chemistry (Kling et al. 1992, Kawahigashi et al. 2006, Keller et al. 2007). It is not known if differences in production and stabilization of DOM and nutrients among landscape ages in soils translate into lower DOM availability and transport within watersheds on younger glacial drifts.

Differences in availability and fluxes of DOM between landscape ages or within hillslopes potentially affect microbial productivity of terrestrial and downslope aquatic ecosystems. DOM is used by aquatic and terrestrial microbes for cell growth and terrestrial DOM represents up to 75% of energy inputs to streams (Kling 1995, Harvey et al. 1997, Kaplan and Newbold 2000, Marschner and Kalbitz 2003, Hessen et al. 2004). Fluxes of terrestrial DOM also represent an important source of nutrients to downslope aquatic ecosystems (Berman and Bronk 2003, Dittmar 2003, Brookshire et al. 2005, Kaushal and Lewis 2005). The availability and composition of terrestrial DOM can also

alter bacterial community composition in soils, lakes, and streams (Crump et al. 2003, Judd et al. 2006, Crump et al. 2007, Judd et al. 2007). As terrestrial DOM can be mineralized in downstream aquatic ecosystems, it should be included in overall flux of carbon from terrestrial ecosystems (Kling 1991, 1992, Cole and Caraco 2001, Walter et al. 2006, Cole et al. 2007). In addition, approximately 25% of the DOM in the Arctic Ocean is from river inputs (Opsahl et al. 1999, Hansell et al. 2004, Benner et al. 2005) and is primarily from terrestrial sources (Peterson et al. 1986, Waelbroeck et al. 1997, Lara et al. 1998, Dittmar 2003, Gueguen et al. 2006, Guo and Macdonald 2006).

Fluxes of terrestrial DOM also represent a pathway for loss of nutrients in plant unavailable forms from highly nutrient limited terrestrial ecosystems (Perakis and Hedin 2002, Neff et al. 2003, Jones et al. 2005, Perakis and Hedin 2007). Arctic ecosystems are highly nutrient limited and the majority of nutrients in arctic soils, streams, and lakes are in the organic form (Kling 1995, Lara et al. 1998, Dittmar and Kattner 2003, Kawahigashi et al. 2004, Nordin et al. 2004, Weintraub and Schimel 2005a, b, Hobbie and Hobbie 2006). The uptake of organic nutrients either as direct uptake of amino acids by plant roots or through associations with mychorrizae make up 60-80% of total plant nutrient uptake in the arctic (Chapin III et al. 1993, Kielland 1994, Lipson and Nasholm 2001, Weintraub and Schimel 2005a, b, Hobbie and Hobbie 2006). However, the controls on organic nutrient availability in arctic terrestrial ecosystems are not well characterized.

To examine hillslope and geologic controls on terrestrial transport and availability of dissolved organic carbon and nutrients in arctic watersheds, we conducted a survey of stream and soil water concentrations of DOM. For this research we had two main research questions:

1) Are geologic controls on DOM at the plot scale (i.e. chemical stabilization of DOM) important for regulating the transport of DOM in arctic watersheds?
2) How does the availability of dissolved organic carbon and nutrients change within tundra hillslopes?

We selected watersheds across a chronosequence of landscape ages in the Kuparuk River region to determine if chemical stabilization of DOM is an important control on transport of DOM in arctic watersheds. We expected hillslopes on younger, less weathered glacial drifts to have lower concentrations of dissolved organic carbon and nutrients than hillslopes on older glacial drifts, consistent with previous laboratory studies showing greater production of DOM on older surfaces and greater stabilization of DOM on younger surfaces. Within hillslopes DOM may be decomposed and/or transformed by microbes, mineralized to inorganic carbon and nutrients, taken up by plants, or adsorbed to mineral soil components (Aiken and Cotsaris 1995, Kalbitz et al. 2000, McDowell 2003). Therefore, we expected DOM to decrease moving downslope and landscape age differences in DOM production and stabilization would be amplified within hillslopes.

Materials and Methods

Study Sites

To determine whether higher rates of laboratory DOM production on older landscapes translate into differences in *in situ* concentrations of DOM among hillslopes

of varying landscape we collected soil water samples from small watersheds along a chronosequence of landscape ages in the foothills of the Brooks Range, AK during the summer of 2005 (Table 3.1; Figure 3.1). We chose one to three watersheds from four distinct landscape ages such that each watershed was contained entirely by within a single age of glacial drift (Table 3.1). Potential watersheds for study were identified using ArcView GIS (ESRI, Redlands, CA) and datasets from Toolik Field Station GIS (http://www.uaf.edu/toolik/gis/). In the field we then selected sampling sites within each watershed adjacent to streams with running water and with no upstream lakes or thermokarst.

To study topographic variation in soil water DOM concentrations within hillslopes, we measured soil water DOM concentrations in three transects along each hillslope (Figure 3.1). Transects were located in three hillslope positions: a) the "upslope" transect in mesic upland tundra, b) the "vegetation boundary" transect at the boundary between mesic upland tundra and the riparian vegetation within the watershed, and c) the "streamside" transect at the edge of each stream. We sampled soil water at 10cm depth using both perforated needles and microlysimeters (Eijkelkamp Rhizon soil moisture sampler, 0.1 μm pore size, Soil Moisture, Santa Barbara, CA). In four watersheds (one in each landscape age) we sampled soil water from both microlysimeters and with perforated needles during the weeks of June 20th, July 4th, July 11th, July 18th, August 1st, and August 8th, for a total of 7 sampling dates. In these four watersheds we sampled 4 tension lysimeters and 4 needle sampling points (2m apart) at each of the three hillslope positions for a total of 12 lysimeter and 12 needle sampling points within each watershed. In between sampling dates, we used a vacuum pump to create a vacuum in plastic side-

arm flasks attached to each microlysimeter. In four additional watersheds (two older and two younger than 50,000 years since glaciation) we sampled during the weeks of July 11th, July 18th, and August 8th from 4 needle sampling points (4m apart) at each hillslope position for a total of 12 sampling points in each watershed. In all 8 watersheds we also examined stream water concentrations of DOM on the soil water sampling dates. We collected three replicate stream water samples along a 100m reach at the bottom of each hillslope and measured stream pH and concentrations of organic and inorganic carbon and nutrients in all three samples.

Soil and Vegetation Characteristics

On each sampling date throughout the summer, we measured both soil thaw depth and soil temperatures (at 10cm depth) in three locations along each hillslope position transect (Figure 3.1). We collected a 10x10cm (length by width) sample of the entire thawed organic horizon to calculate depth of the thawed organic horizon and bulk density during the week of July 25th in two locations in each watershed. The two locations were: a) at the center of the upslope transect and b) 5m upslope from that point, both in tussock tundra. We sampled the thawed organic horizon as everything between the bottom of the living moss layer and the top of the permafrost or mineral soil layer, whichever was shallower. From each bulk density core we also used a sub-sample of soil to measure soil pH in water slurries. At the end of July 2005 we also examined absolute percent cover of plant species in four 1mx1m quadrates five meters uphill from the upslope hillslope position to characterize vegetation as either moist acidic tundra or moist non-acidic tundra (see Appendix).

Chemical and Statistical Analyses

Soil and stream water samples were analyzed for concentrations of dissolved organic carbon (DOC), total dissolved nitrogen (TDN), bicarbonate, nitrate (NO_3^-) plus nitrite (NO_2^-), total dissolved phosphorus (TDP), and phosphate (PO_4^-). To analyze water samples for concentrations of bicarbonate, DOC, and TDN we used a total organic carbon and total nitrogen analyzer (TOC-V CSH and TNM-1, Shimadzu, Columbia, MD). We used an autoanalyzer (Alpkem, O.I. Analytical, College Station, TX) to analyze concentrations of PO_4^- (molybdenum blue method (Eaton et al. 1995)) and NO_3^- and NO_2^- (cadmium reduction, (Wood et al. 1967)) in water samples. We analyzed TDP in water samples with potassium persulfate digestion (Valderrama 1981) followed by phosphate analysis using the method described above. We calculated dissolved organic nitrogen (DON) as TDN less NO_3^- and dissolved organic phosphorus (DOP) as TDP less PO_4^-.

We analyzed differences in soil thaw depth, soil temperature, and soil water chemistry (both needle- and lysimeter-sampled) using split-plot repeated-measures one-way analysis of variance (ANOVA) with age as the whole plot factor, transect as a sub-plot factor, and sampling date as a sub-sub plot factor. We used stream name nested within landscape age as a random variable in the model. We used repeated measures ANOVA to analyze differences in stream temperature, pH, and chemistry among landscape ages and among sampling dates with landscape age as a whole plot factor, stream name nested within landscape age as a random variable, and sampling date as a sub-plot factor. We performed all statistical analyses using JMP software (JMP 7, SAS, Cary, NY).

Results

Site Characteristics

As expected, there were significant increases in both soil temperature and thaw depth throughout the summer from late June until early August (ANOVA: temperature: $F_{5,160}$=20.05, p<0.001; thaw depth: $F_{5,160}$=15.19, p<0.001; Tukey's HSD: α=0.05; Table 1). There were no significant differences among landscape ages in either soil temperature or thaw depth when averaged across hillslope positions and sampling dates (ANOVA: temperature: $F_{3,172}$=1.05, p=0.46; thaw depth: $F_{3,172}$=0.96, p=0.51; Table 1). When averaged across landscape ages and sampling dates, soil temperatures were significantly higher in streamside than in the two higher hillslope positions (ANOVA: $F_{2,170}$=17.45, p<0.001; Tukey's HSD: α=0.05; Table 1) and soil thaw depth increased significantly downslope (ANOVA: $F_{2,170}$=165.60, p<0.001; Tukey's HSD: α=0.05; Table 1). As expected, soil pH decreased with increasing landscape age and was significantly higher for soils from the youngest landscape age than for soils from the oldest landscape age (ANOVA: $F_{3,50}$=14.22, p=0.013; Tukey's HSD: α=0.05; Table 1).

Soil Water

There were no significant differences in needle-sampled soil water DOC concentrations among sampling dates (ANOVA: $F_{4,158}$=0.91, p=0.46). However, DOC concentrations in lysimeter-sampled soil water decreased significantly as the summer progressed (ANOVA: $F_{4,123}$=9.68, p<0.001). Concentrations of DOC were significantly higher during the first week than during the last three weeks and were significantly higher during the second week than the last two weeks (Tukey's HSD: α=0.05). As expected, concentrations of DOC in needle-sampled soil water decreased significantly downslope,

when averaged across landscape ages, with significantly higher concentrations at the upslope position than at either of the lower hillslope positions, and significantly higher concentrations of DOC at the vegetation boundary than at the streamside hillslope position (ANOVA: $F_{2,168}$=41.47, p<0.001; Tukey's HSD: α=0.05). In addition, concentrations of DOC in lysimeters were significantly higher at the upslope hillslope position than in streamside lysimeters when averaged across all landscape ages (ANOVA: $F_{2,133}$=6.06, p=0.003; Tukey's HSD: α=0.05). Contrary to expectations, there were no significant differences in concentrations of DOC in needle-sampled or lysimeter-sampled soil water among landscape ages when averaged across hillslope positions and sampling dates (ANOVA: needle-sampled: $F_{3,170}$=1.16, p=0.43; lysimeter-sampled: $F_{3,135}$=2.12, p=0.10; Figure 3.2). However, there was a significant age by hillslope position interaction with concentrations of DOC in needle-sampled soil water decreasing more rapidly moving down the hillslope in some landscape ages than in others (ANOVA: $F_{6,162}$=4.10, p<0.001; Tukey's HSD: α=0.05; Figure 3.2a). There was also a significant age by transect interaction in lysimeter-sampled soil water with DOC concentrations decreasing downslope on some landscape ages, while in other landscape ages DOC concentrations in lysimeters remained relatively constant across all hillslope positions (ANOVA: $F_{6,127}$=5.43, p<0.001; Tukey's HSD: α=0.05; Figure 3.2b).

Concentrations of DON within hillslopes mirrored patterns of DOC concentrations within hillslopes; however, unlike for concentrations of DOC, concentrations of DON varied among hillslopes of different landscape age. As expected, DON concentrations in needle-sampled soil water decreased downslope with significantly higher concentrations of DON in soil water at the upslope hillslope position

than in soil water at the two lower hillslope positions (ANOVA: $F_{2,146}$=24.07, p<0.001; Tukey's HSD: α=0.05). However, DON concentrations in lysimeters did not exhibit significant differences among hillslope positions when averaged across landscape ages (ANOVA: $F_{2,93}$=0.24, p=0.78; Figure 3.3b). Needle- and lysimeter-samples DON concentrations were both significantly different among landscape ages with higher concentrations of DON in soils from older landscape ages than in soils from younger landscape ages, consistent with expectations (ANOVA: needle-sampled: $F_{3,148}$=5.22, p<0.001; lysimeter-sampled: $F_{3,95}$=3.55, p=0.016; Tukey's HSD: α=0.05; Figure 3.3). Similar to DOC, concentrations of DON in needle-sampled soil water exhibited an age by transect interaction as the magnitude of the decrease in DON concentration moving down hillslopes depended on landscape age (ANOVA: $F_{6,140}$=2.54, p=0.022; Tukey's HSD: α=0.05; Figure 3.3a), but lysimeter DON concentrations did not exhibit an age by transect interaction (ANOVA: $F_{6,88}$=0.97, p=0.45; Figure 3.3b). DON concentrations from lysimeters were significantly higher at the first collection date than any other collection date (ANOVA: $F_{4,84}$=7.55, p<0.001; Tukey's HSD: α=0.05).

As a result of differences in concentrations of DOC and DON in needle-sampled soil water among transects there was a significantly higher DOC:DON ratio in needle-sampled soil water at the upslope than at the two lower hillslope positions (ANOVA: $F_{2,146}$=6.25, p=0.002; Tukey's HSD: α=0.05; Figure 3.4). However, there were no significant differences among landscape ages in DOC:DON ratios (ANOVA: $F_{3,148}$=2.17, p=0.25), nor were there significant age by hillslope position interactions in DOC:DON ratios in needle-sampled soil water (ANOVA: needle-sampled: $F_{6,149}$=1.09, p=0.37). For lysimeter-sampled soil water there were no significant landscape age, sampling date, or

hillslope effects on DOC:DON ratios (ANOVA: age: $F_{3,95}$=1.47, p=0.23; sampling date: $F_{4,84}$=1.61, p=0.18; hillslope: $F_{2,93}$=0.065, p=0.94).

There were no significant differences in needle-sampled soil water concentrations of DOP among landscape ages, hillslope positions, or sampling dates (ANOVA: age: $F_{3,148}$=0.82, p=0.57; hillslope position: $F_{2,146}$=0.95, p=0.39; sampling date: $F_{4,136}$=0.35, p=0.85; Figure 3.5a). Similarly, lysimeter concentrations of DOP did not differ significantly among landscape ages, hillslope positions or sampling dates (ANOVA: age: $F_{3,92}$=0.32, p=0.81; hillslope position: $F_{2,90}$=0.36, p=0.70; sampling date: $F_{4,80}$=1.53, p=0.20; Figure 3.5b). DOP typically made up 60% of total dissolved phosphorous in soil and stream water. Lysimeter concentrations of phosphate did not differ significantly among landscape ages, hillslope positions, or sampling dates (ANOVA: age: $F_{3,102}$=0.71, p=0.55; hillslope position: $F_{2,100}$=0.87, p=0.42; sampling date: $F_{4,90}$=1.22, p=0.31; Figure 3.6b). Soil water concentrations of phosphate sampled with perforated needles also did not differ significantly among landscape ages or sampling dates (ANOVA: age: $F_{3,157}$=1.68, p=0.42; sampling date: $F_{4,145}$=2.13, p=0.080; Figure 3.5b). However needle-sampled concentrations of phosphate in soil water decreased significantly from the upslope to the streamside hillslope position (ANOVA: $F_{2,155}$=5.67, p=0.004; Tukey's HSD: α=0.05; Figure 3.6a).

Nitrate concentrations in needle-sampled soil water were not significantly different among landscape ages, hillslope positions, or sampling dates (ANOVA: age: $F_{3,158}$=16.77, p=0.50; hillslope position: $F_{2,156}$=2.38, p=0.096; sampling date: $F_{4,146}$=1.53, p=0.20; Figure 3.7a). Lysimeter concentrations of nitrate also did not differ significantly among landscape ages, hillslope positions, or sampling dates (ANOVA: age: $F_{3,103}$=1.36,

p=0.26; hillslope position: $F_{2,101}$=1.78, p=0.17; sampling date: $F_{4,91}$=1.32, p=0.27; Figure 3.7b). However, there was a significant age by hillslope position interaction in lysimeter nitrate concentrations with different patterns among landscape ages in nitrate concentrations within hillslopes (ANOVA: $F_{6,95}$=2.64, p=0.019; Tukey's HSD: α=0.05; Figure 3.7b).

As expected, bicarbonate concentrations in both needle- and lysimeter-sampled soil water were significantly higher on the two younger (less acidic) landscape ages than the two older landscape ages when averaging across hillslope positions and sampling dates (ANOVA: needle: $F_{3,155}$=11.91, p=0.019; lysimeter: $F_{3,92}$=10.79, p<0.001; Tukey's HSD: α=0.05; Figure 3.8). Concentrations of free soil water bicarbonate showed significant differences among sampling dates, with the highest values at the beginning and end of the summer and the lowest values during the middle of the summer (ANOVA: $F_{4,143}$=3.92, p=0.005; Tukey's HSD: α=0.05). When averaging across landscape ages and sampling dates, needle-sampled soil water concentrations of bicarbonate were also significantly higher at streamside hillslope positions than at upslope and vegetation boundary hillslope positions, as expected (ANOVA: $F_{2,153}$=9.40, p<0.001; Tukey's HSD: α=0.05; Figure 3.8a). However, concentrations of bicarbonate in lysimeters did not differ significantly among sampling dates or among hillslope positions (ANOVA: sampling date: $F_{4,80}$=0.49, p=0.75; hillslope position: $F_{2,90}$=2.80, p=0.064; Figure 3.8b). There was a significant age by transect interaction in needle-sampled soil water bicarbonate concentrations (ANOVA: $F_{6,147}$=2.67, p=0.017; Tukey's HSD: α=0.05; Figure 3.8a) with concentrations increasing down the hillslope on some landscape ages and remaining relatively constant within hillslopes on other landscape ages.

Stream Water

Stream temperatures did not vary significantly among sampling dates or among landscape ages (ANOVA: sampling date: $F_{3,49}$=0.13, p=0.88; landscape age: $F_{3,52}$=3.02, p=0.27; Table 3.2). Stream pH increased throughout the summer with significantly higher values in the last week than in the first week of sampling (ANOVA: $F_{3,49}$=4.90, p=0.007; Tukey's HSD: α=0.05; Table 3.2). However, stream pH did not vary significantly with landscape age (ANOVA: $F_{3,52}$=0.32, p=0.81; Table 3.2).

Despite the differences observed among terrestrial ecosystems, no differences in stream water chemistry were observed at the watershed scale. Concentrations of DOC in stream water were significantly higher during the second week of sampling than during all other weeks of sampling (ANOVA: $F_{3,57}$=13.80, p<0.001; Tukey's HSD: α=0.05) and stream water concentrations of DON were significantly higher during the first week of sampling than during the third week of sampling (ANOVA: $F_{3,51}$=6.49, p<0.001; Tukey's HSD: α=0.05). Therefore, the ratio of DOC:DON in stream water was significantly higher during the second week of sampling than during any other week (ANOVA: $F_{3,51}$=10.98, p<0.001; Tukey's HSD: α=0.05). There were no significant differences in stream water concentrations of DOC or DON or in the ratio of DOC:DON among landscape ages (ANOVA: DOC: $F_{3,57}$=0.91, p=0.51; DON: $F_{3,51}$=2.73, p=0.20; DOC:DON: $F_{3,51}$=1.28, p=0.44; Figure 3.2a, 3.3a, and 3.4a). The concentration of DOP in stream water was not significantly different among either landscape ages or sampling dates (ANOVA: age: $F_{3,51}$=3.66, p=0.27; sampling date: $F_{3,49}$=2.33, p=0.14; Figure 3.5a).

The concentration of phosphate in stream water were also not significantly different among either landscape ages or sampling dates (ANOVA: age: $F_{3,52}$=6.98,

p=0.24; sampling date: $F_{3,49}$=0.42, p=0.74; Figure 3.6a). Similarly, stream water nitrate concentrations were not significantly different among either landscape ages or sampling dates (ANOVA: age: $F_{3,52}$=3.74, p=0.22; sampling date: $F_{3,49}$=2.64, p=0.060; Figure 3.7a). Bicarbonate concentrations in stream water were significantly different among sampling dates with significantly higher concentrations in the first week than in the second week (ANOVA: $F_{2,21}$=3.70, p=0.042; Figure 3.8a), but stream water bicarbonate concentrations were not significantly different among landscape ages (ANOVA: $F_{3,23}$=4.59, p=0.087; Figure 3.8a).

Discussion

In all sites soil water dissolved organic carbon (DOC), dissolved organic nitrogen (DON), and phosphate concentrations were significantly higher in upslope samples while concentrations of bicarbonate in soil water were significantly higher in riparian samples, indicating significant transformations of C and N within hillslopes. High pH sites on younger glacial drift had significantly higher soil water bicarbonate concentrations and significantly lower concentrations of DON in soil water than older, more weathered soils. Unlike previous laboratory results, there was no consistent pattern of DOC concentrations in soil water with landscape age. Despite differences in rates of soil organic matter processing and in soil water DON and bicarbonate concentrations among landscapes, watershed concentrations of inorganic and organic carbon and nutrients did not differ among landscape ages during summer conditions. Our results suggest that under current permafrost and soil conditions DOM availability is highly variable within the hillslope, but within-stream processing masks landscape ages effects at the watershed scale.

Variation within hillslopes

Our research indicates that topographic variation within arctic hillslopes is an important control on availability of DOM, and nutrients, likely leading to differences in microbial and plant productivity within arctic hillslopes. Concentrations of DOC, DON, and phosphate in soil water decreased moving down hillslopes potentially due to chemical stabilization of DOM or phosphate, plant and microbial uptake of DON and phosphate, or mineralization of DOM by microbial communities within the hillslope. Combined with previous research on inorganic nutrient availability within hillslopes (Giblin et al. 1991, Nadelhoffer et al. 1991), our results suggest lower nutrient availability at downslope positions due to decreases in inorganic phosphorus, organic nitrogen, and inorganic nitrogen availability. In addition, DOC:DON ratios decreased down the hillslope, suggesting that within hillslope processing changes the composition and stoichiometry of the bulk DOM pool as water moves down arctic hillslopes.

If streamside hillslope positions are flushed more frequently, dilution would explain lower concentrations of DOC and DON, but not higher concentrations of bicarbonate in downslope samples. Greater connectivity between downslope hillslope positions and streams has been suggested (Stieglitz et al. 2003). However, concentrations of bicarbonate increased within the hillslope from upslope sites to downslope sites, suggesting either a buildup of weathering products within the hillslope, or increased soil respiration rates at streamside hillslope positions. Streamside hillslope positions also had higher temperatures and thaw depths than upslope positions which may result in a longer active season or faster rates of microbial activity downslope.

Variation among hillslopes

Bicarbonate concentrations in soil water were higher on younger, less weathered landscape ages, consistent with higher rates of carbonate weathering on younger landscapes than older landscapes. Carbonate minerals in younger landscapes provide a relatively large pool of easily weathered minerals for bicarbonate production, whereas on landscapes older than 50,000 years since glaciation, the carbonate minerals have been exhausted, greatly suppressing weathering rates. This is consistent with previous results showing higher concentrations of bicarbonate in lakes and streams on younger than on older landscapes (Engstrom et al. 2000, Keller et al. 2007).

Landscape age controls on laboratory DON and DOC production in arctic soils appear to influence concentrations of DON in soil water, but not concentrations of DOC. Dissolved organic nutrient pools/fluxes do not always have the same controls as the bulk pool of DOM within ecosystems (Kaushal and Lewis 2003, McDowell 2003, Kaushal and Lewis 2005). In our study, higher DOC production in soils from older landscapes observed in laboratory incubations do not appear to translate into hillslope or watershed scale differences in concentrations of DOC among landscape ages. However, landscape age did affect the rate of DOC and DON removal from soil water within hillslopes, such that DOM disappearance occurred more quickly on older landscape ages than on younger landscape ages. This indicates that rates of DOC consumption are higher on older landscape ages, consistent with previous research showing higher microbial activity on older, more weathered landscapes (Hobbie and Gough 2002, Hobbie et al. 2002, Hobbie and Gough 2004, Chapter 1, Chapter 2). However, we found no significant differences in the biodegradability of DOC among landscape ages (Chapter 4).

In addition to changes in hillslope DOC dynamics among landscape ages, concentrations of DON in soil water were higher on older, more weathered landscape ages which exhibit higher DON production in laboratory incubations (Hobbie et al. 2002, Chapter 1, Chapter 2). As nitrogen is limiting in many arctic soils and plants obtain most of their nitrogen in the organic form through either direct uptake of amino acids or through mychorrizae (Kielland 1994, Lipson and Nasholm 2001, Nordin et al. 2004, Weintraub and Schimel 2005a, b, Hobbie and Hobbie 2006*)*, higher DON availability on older landscapes ages may lead to higher plant productivity on older landscape ages. This is consistent with higher rates of plant productivity on older landscape ages (Gough et al. 2000, Hobbie and Gough 2002, 2004).

Variation among watersheds

Despite clear differences observed in laboratory incubations, and for DON for soil water, effects of landscape age on concentrations of organic matter and nutrients were not evident in stream biogeochemistry during this study. Faster rates of soil organic matter processing, more DOC and DON production, lower soil water bicarbonate concentrations, and higher concentrations of DON in soil water were observed on older landscapes compared to younger ones. However, watershed concentrations of inorganic and organic carbon and nutrients did not differ among landscape ages. Similarly soil pH was significantly different among landscape ages, but stream pH did not differ among landscape ages. This surprising result could be related to other factors that override or mask the influence of landscape age on stream biogeochemistry including variation in hydrology, riparian vegetation, and in hyporheic-zone or within-stream processing of organic matter and nutrients.

Hydrology and within-stream processing are unlikely to homogenize stream chemistry relative to differences in soil water chemistry. We chose hillslopes within watersheds of similar slope and aspect to minimize variation in hydrology. It is not possible to completely eliminate variation in hydrologic flow paths among watersheds, but time since glaciations should not affect watershed hydrology in areas of similar topography. Processing of DOM within hyporehic zones and within streams can also greatly affect fluxes of OM and nutrients within aquatic ecosystems in temperate and arctic ecosystems (Harvey et al. 1997, Dawson et al. 2001, Edwardson et al. 2003, Webster et al. 2003, Bernhardt et al. 2005). However, differences among landscape ages in within-stream or hyporehic-zone processing of organic matter and nutrients are unlikely to occur in such a way that would mask differences in biogeochemical processing within hillslopes.

Since riparian ecosystems can have a large impact on organic matter and nutrient inputs to streams (Naiman and Decamps 1997*)*, variation among watersheds in riparian vegetation could mask differences in soil water biogeochemistry among landscape ages. It was not possible to constrain watersheds to one type of riparian vegetation (wet sedge or riparian willow shrub tundra) so chose an equal number of watersheds older and younger than 50,000 years since glaciations with each riparian vegetation type. There is large variation in biogeochemical cycling among riparian vegetation types with wet sedge tundra having lower biomass, lower NPP, lower phosphorus mineralization, and higher N availability than riparian shrub tundra (Giblin et al. 1991, Nadelhoffer et al. 1991, Shaver et al. 1996). Therefore, biogeochemical processing within riparian vegetation could negate differences among landscape ages in soil organic matter processing.

Implications

In addition to previous research on variation in biogeochemical cycling of organic matter and nutrients within soils, our research indicates that while landscape age influences gaseous carbon fluxes from soil and terrestrial productivity within hillslopes (Gough et al. 2000, Hobbie and Gough 2002, Hobbie et al. 2002, Hobbie and Gough 2004, Chapter 1, Chapter 2), it does not affect aquatic fluxes of DOM and nutrients. At the plot scale, heterogeneity among landscape ages leads to higher dissolved and gaseous fluxes of carbon from soils on older landscapes and should be included in models of terrestrial carbon cycling. At the hillslope scale, decreases in concentrations of DOC, phosphate, and DON and increases in concentrations of bicarbonate in soil water downslope suggest that hillslope processes such as chemical weathering, mineralization of organic matter, and plant or microbial nutrient uptake alter forms of organic matter and nutrients within hillslopes. Therefore, these hillslope processes should be included when modeling transport of carbon and nitrogen, productivity, and decomposition within arctic terrestrial ecosystems. However, at the watershed scale, heterogeneity among landscape age does not appear to influence fluxes of carbon and nitrogen to downstream aquatic ecosystems and the Arctic Ocean. Thus other factors such as riparian zone functioning are exerting a strong control over stream water biogeochemistry in arctic watersheds during summertime. Over wider ranges of conditions, effects of soil structure, permafrost cover and age are evident (Kawahigashi et al. 2004, Streigl et al. 2005, Frey et al 2005, Frey et al 2007, Frey and McClelland 2009). It is unknown how riparian functions might change as permafrost watersheds thaw and riparian zone vegetation and hydrology change. Currently, however, it does not appear to be necessary to include landscape age

as a factor in large scale modeling of arctic carbon and nutrient fluxes in aquatic ecosystems during summer conditions.

Chapter 4: Decomposition of dissolved organic carbon across a hillslope chronosequence in the Kuparuk River region, Alaska

Summary

The proportion and character of dissolved organic matter (DOM) exported from arctic watersheds depends upon the balance between DOM production, biodegradation, and transport within thawed soil layers, all of which may be affected by large variation in geology, topography, and vegetation throughout the circumpolar region. Significant differences in production of DOM and decomposition of soil organic matter exist among landscapes with different glaciation histories in the Kuparuk River region of northern Alaska, with younger landscapes having lower rates of microbial activity. In addition to variation among landscape ages, significant differences in soil water DOM concentrations exist within hillslope toposequences in the region, with higher concentrations in upslope positions and lower concentrations in streamside positions. We hypothesized that lower biodegradability of DOM in younger landscapes compared to older, more weathered landscapes explains lower observed rates of soil respiration on these younger landscapes. We also hypothesized that within hillslope decomposition of labile DOM leads to both lower observed concentrations of DOM *in situ* and to lower biodegradability of DOM in streamside hillslope positions.

To test this hypothesis we examined the biodegradability of water-extracted DOM from soils within hillslopes across a chronosequence of landscape ages near the Kuparuk River using four direct and indirect indices of DOM biodegradability. Soil extract DOM concentrations did not differ among landscape ages, but were significantly higher in upslope hillslope positions than streamside hillslope positions. DOM fluorescence

(fluorescence index) was significantly lower in upslope hillslope positions, but fluorescence index did not vary significantly among landscape ages. There were no significant differences among landscape ages or hillslope positions in DOM specific UV absorbance, rates of DOM derived respiration, or decomposition of DOM, suggesting that variation in biodegradability of DOM is not an important factor leading to observed variation in organic matter processing during summer. It appears that DOM in seasonally thawed soils is highly recalcitrant throughout the landscape in the Kuparuk River region so that differences in geochemistry are most likely to influence DOM during summer.

Introduction

Since terrestrial ecosystems are the primary source of dissolved organic matter (DOM) exported from high latitudes (Benner et al. 2004), an understanding of arctic terrestrial DOM dynamics is necessary to predict future trends in DOM inputs to aquatic ecosystems. DOM is produced in soils through the release of plant and microbial exudates and the biotic or abiotic breakdown of soil organic matter. DOM may be 1) mineralized by microbes to carbon dioxide, methane, and inorganic nutrients, 2) stabilized within terrestrial ecosystems through sorption to mineral soil layers, or 3) transported down hillslopes to aquatic ecosystems (Kalbitz et al. 2000, Kalbitz et al. 2003). Therefore, the proportion and character of DOM export from arctic watersheds depends upon the balance between DOM production, biodegradation, and abiotic reactivity (affecting sorption to mineral soil components).

Dissolved organic matter is an important substrate for microbial activity in soils and aquatic ecosystems where it can be mineralized to carbon dioxide or methane, or storage in soils and aquatic sediments. Thus DOM can mediate the rate, timing and spatial location of gaseous carbon to the atmosphere, making DOM a significant component of landscape carbon budgets (Kling 1991, Kalbitz et al. 2000, Cole et al. 2007). Terrestrially derived DOM represents 30-75% of energy inputs to streams worldwide and is an important component of aquatic food webs (Hessen et al. 2004, Gueguen et al. 2006, Guo and Macdonald 2006). Therefore, the proportion of DOM which is easily degraded can affect gaseous carbon fluxes from terrestrial and aquatic ecosystems as well as fluxes of DOM from terrestrial to aquatic ecosystems.

Dissolved organic matter is also an important source of organically bound nutrients to aquatic and terrestrial ecosystems, particularly in arctic ecosystems where the majority of nutrients exist in organic forms (Kling 1995, Lipson and Nasholm 2001, Kawahigashi et al. 2004, Weintraub and Schimel 2005b, Bronk et al. 2007). In aquatic ecosystems, DON is an important source of N for phytoplankton (Bronk et al. 2007). Arctic plants satisfy 60-80% of their N demand through direct uptake of organic N in the form of amino acids or indirect uptake of organic N through mycorrhizae (Kielland 1994, Lipson and Nasholm 2001, Hobbie and Hobbie 2006). In soils and aquatic systems, DON can be mineralized by microbes to inorganic N, providing N to plants and algae; therefore a better understanding of the availability of DON for microbial uptake or mineralization (to inorganic N) is necessary to make predictions of current and future arctic terrestrial primary productivity.

In soils, DOM biodegradation depends both on DOM quality (determined by its source) and on environmental factors affecting soil microbial activity (i.e. temperature and soil moisture), stabilization of DOM in soils (i.e. soil geochemistry), and contact between microbes and soil water (i.e. water table depth, hydraulic conductivity) (Kalbitz et al. 2003, Marschner and Kalbitz 2003, Bengtsson and Torneman 2004, Weintraub and Schimel 2005b, Judd et al. 2006). DOM is a complex mixture of dissolved organic compounds with varying size and chemical composition (e.g. elements, size, charge, structural complexity, and functional groups) (Kalbitz et al. 2000). Typically, hydrophilic DOM molecules such as carbohydrates, organic acids and proteins can be mineralized more readily by microbes than DOM that is highly condensed, is hydrophobic, or has many aromatic rings such as lignin-derived compounds (Kalbitz et al. 2003, Marschner

and Kalbitz 2003). Although controls on DOM biodegradability have been relatively well studied in temperate forests, less is known about their controls in arctic systems.

As water and dissolved materials move through soils in terrestrial ecosystems the biodegradability and concentration of DOM is altered through contact with microbes and soil (Qualls and Haines 1992, Kalbitz et al. 2000, Michalzik et al. 2001, Qualls et al. 2002, Kalbitz et al. 2003, Marschner and Kalbitz 2003). As a result, aquatic DOC and DON concentration and biodegradability are higher in seasonally frozen watersheds during spring floods when frozen soils prevent contact between flowing water and plants, soil microbes, and soil particles (Michaelson et al. 1998, Stepanauskas et al. 2000, Jones et al. 2005, Kaushal and Lewis 2005, Finlay et al. 2006). As the growing season progresses and soils thaw, interactions between DOM, soil, and microbes become relatively more important. Yet, little is known about how factors such as topography and geochemistry contribute to heterogeneity in these interactions at the landscape scale.

In addition, the residence time of water and dissolved materials in soils increases as permafrost thaws (Hinzman et al. 2005), potentially increasing DOM mineralization and retention in soils and altering fluxes of DOM to aquatic ecosystems with future climate warming. DOM export in some arctic watersheds has been shown to increase with increased temperatures through increased leaching of thawed permafrost and direct stimulation of microbial activity (Frey and Smith 2005, Frey et al. 2007b) while in other watersheds DOM export has shown no change or a decrease with warming (Kawahigashi et al. 2004, Streigl et al. 2005, McClelland et al. 2007). It has been hypothesized that differences in the effects of climate on DOM export among arctic watersheds may be due large variation in geology, vegetation, and permafrost extent within the major Arctic

drainage basins (Kawahigashi et al. 2004, Frey and Smith 2005, Streigl et al. 2005, Frey and McClelland 2009). All of these sources of variability may affect terrestrial inputs of DOM to rivers through their influence on DOM production, biodegradability, and stabilization within soils. Yet relatively few studies have examined landscape patterns in biodegradability of DOM in permafrost dominated watersheds.

To improve understanding of DOM export from arctic terrestrial ecosystems we examined spatial patterns of DOM biodegradability within and among hillslopes of different glaciation histories in arctic watersheds using both direct and indirect measures of DOM biodegradability. The area around Toolik Lake, AK (in the northern foothills of the Brooks Range) is an ideal location to study the effects of spatial variation in topography and geology on DOM biodegradability. First, considerable small-scale (<1 km) topographic variation exists that has substantial effects on ecosystem processes, with up to 10-fold variation in primary productivity accompanying large variation in inorganic nutrient availability and decomposition rates within hillslopes between upslope plant communities and streamside plant communities (Giblin et al. 1991, Shaver et al. 1996, Shaver et al. 2006). Previous research on growing season DOM within hillslopes demonstrated that DOM concentrations decreased significantly down hillslopes, highlighting the importance of within-hillslope transformations of C and N (Chapter 3), as mineralization of labile DOM within the hillslope before reaching downslope sites would explain lower concentrations of DOM at downslope positions.

Second, Pleistocene expansion and contraction of glaciers in the Brooks Range created a mosaic of landscape ages (and therefore extent of weathering) with similar parent material within relatively small (<1 km) regions (Bockheim et al. 1998, Hamilton

2002), providing an opportunity to study effects of variation in soil geochemistry while holding parent material, vegetation, climate, and topography constant. Previous research in the region, has shown higher exchangeable base cations and pH as well as lower rates of DOM production, N mineralization, litter decomposition and microbial respiration on younger (<50,000 years old), less weathered surfaces than on older, more weathered surfaces (Bockheim et al. 1998, Hobbie and Gough 2002, Hobbie et al. 2002, Hobbie and Gough 2004, Keller et al. 2007, Chapter 1, Chapter 2). Differences in soil geochemistry among landscape ages likely influence stabilization of DOM, because polyvalent base cations can bind negatively charged molecules of DOM to negatively charged soil organic matter or clay minerals, making that DOM unavailable to microbes (Oades 1988, Kalbitz et al. 2000, Chapter 2). However, previous research suggests that higher rates of microbial activity on older landscapes cannot be explained entirely by lower chemical stabilization on older landscapes (Chapter 2). Therefore we hypothesized that higher rates of microbial activity on older landscapes may additionally be caused by greater bioavailability of DOM, perhaps resulting from differences in vegetation and microbial communities on these landscapes compared to younger ones. However, little is known about how landscape age influences the biodegradability of DOM at the peak of the growing season when interactions between DOM and both soil particles and soil biota are likely at their maximum. By examining patterns in DOM biodegradability among landscape ages we aimed to determine whether higher microbial respiration in soils from older landscape ages results from greater biodegradability of DOM.

To examine landscape patterns in biodegradability of DOM in permafrost dominated watersheds we examined the biodegradability of water-extracted DOM from

soils within hillslopes across a chronosequence of landscape ages near Toolik Lake, AK. We hypothesized that a) within hillslopes, downslope sites will have smaller concentrations of labile DOC than upslope sites due to mineralization of less complex, more labile compounds by microbes as DOM moves downhill along the slope, while b) among hillslopes of different ages, soil from younger, less-weathered landscapes will have relatively smaller concentrations of labile DOM than soils from older landscapes, partly explaining low respiration rates from these soils.

Methods

We examined spatial patterns of DOM biodegradability within and among hillslopes of different glaciation histories in the arctic using four indices of biodegradability: a) specific UV absorbance, b) fluorescence index, c) oxygen consumption, and d) DOM mineralization. To study variability among landscape ages in biodegradability of DOM, we worked in three replicate watersheds on four landscape ages near Toolik Lake, AK, ranging from 11,000-13,000 years to 120,000-600,000 years before present. To determine topographic variability in biodegradability of DOM in each of these watersheds, we characterized upslope, vegetation boundary, and streamside hillslope positions on each hillslope.

Site Characteristics

We chose three hillslope study sites contained entirely on glacial drift within each of four glaciations and therefore landscape ages: Itkillik III (11,000-13,000 years before present), Itkillik II (11,000-50,000 years before present), Itkillik I (50,000-120,000 years before present), and Sagavanirktok (120,000-600,000 years before present) (Table 1, Figure 4.1). Drift deposited from these four glaciations came from the Brooks Range and

is of similar mineralogy (Bockheim et al. 1998, Hamilton 2002). To minimize differences in climate, sites were all located within 15 miles of the Toolik Lake Biological Field Station along the Dalton Highway in northern Alaska. We chose hillslopes of similar slope (1-15^{o}) and aspect (20^{o} W of N to 10^{o} E of N) to minimize differences in soil temperature, hydrology, and thaw depth related to topography. To minimize the influence of calcium-rich road dust on soil geochemistry, all of our hillslopes were located at least 0.5km from all roads. Site selection was done in ARCGIS (ESRI, Redlands, CA) using data layers provided by Toolik Field Station GIS (http://www.uaf.edu/toolik/gis/).

Field Data and DOM characteristics

At each hillslope, we measured air temperature and depth of the organic horizon before collecting one 10x10cm sample of the entire organic horizon (between the bottom of living moss and the mineral soil or top of the permafrost, whichever was shallower) to calculate bulk density. We measured soil pH by shaking a 5g sub-sample of organic soil in 60mL of nanopure water for one hour and measuring the pH of the resulting solution. A second sub-sample of soil was used to measure gravimetric soil moisture content by drying soil for 48hrs at 60^{o}C.

We measured concentrations of DOM and nutrients in soil water, soil water extracts, and stream water. We collected soil water and soil samples for extraction at three locations equally spaced along three 15m transects at each hillslope in each site. The "tussock" transect was within the upslope tussock tundra vegetation, the "vegetation boundary" transect was along the boundary between the tussock tundra vegetation, and the "streamside" transect was directly adjacent to the stream. A 250mL soil water sample from the saturated zone was collected using a 50mL syringe and perforated metal tube at

each location. From each site we collected three replicate samples of stream water from the stream at the bottom of each hillslope for comparison with soil water data.

For soil water extracts, we collected three soil core samples (5cm diameter) of the entire organic layer within each transect on a hillslope across all landscape ages for a total of 108 cores. After we removed the large roots and homogenized the soil samples, we stored them at 4^{o}C until extraction. We extracted porewater DOM from the homogenized organic soil samples by shaking 50g (wet weight) of soil in 750mL of nanopure water for two hours at 180 oscillations per minute and filtered the resulting solution through a Geotech 0.45µm dispos-a-filter (Geotech Environmental Equipment, Denver, CO). We determined our extraction procedure with a pilot experiment to obtain DOC concentrations in extracts of approximately 10mg/L.

Soil water, water extracts, and stream water samples were analyzed for dissolved organic carbon and total dissolved nitrogen (TDN) concentrations (TOC-V CSH and TNM-1, Shimadzu, Columbia, MD), nitrate (NO_3^-) plus nitrite (NO_2^-) concentrations (Lachat, QuickChem 8500 Flow Injection Analyzer, Loveland, CO, cadmium reduction (Wood et al. 1967)), ammonium (NH_4^+) concentrations (Lachat, QuickChem 8500 Flow Injection Analyzer, Loveland, CO, phenol hypochlorite, (Solórzano 1969)), and phosphate (PO_4^-) concentrations (Cary 50 Bio UV-Vis Spectrophotometer, Varian, Palo Alto, CA, colorometrically (Eaton et al. 1995). Total dissolved phosphorous (TDP) in stream water samples was analyzed by digesting samples using potassium persulfate following the method of Valderrama (1981) before analyzing the resulting digest for phosphate using the method described above. We calculated dissolved organic

phosphorous (DOP) in all water samples as TDP less PO_4^- and DON as TDN less the sum of NO_3^- and NH_4^+.

We used four methods to characterize DOM biodegradability in soil extracts. We analyzed soil extracts rather than soil water in order to have adequate sample volume for analyses and minimize time between sample collection and the experiment. We measured UV absorbance of soil extracts at 254nm (Abs_{254}), 280nm (Abs_{280}), and 400nm (Abs_{400}) using a spectrophotometer (Cary 50 UV-Vis Spectrophotometer, Varian, Palo Alto, CA). These measurements were used to calculate specific UV absorbance (SUVA) by dividing UV absorbance at a given wavelength by the concentration of DOC in the sample (i.e. $SUVA_{254}$ is Abs_{254} divided by the concentration of DOC in the sample). $SUVA_{254}$ and $SUVA_{280}$ have been used as indicators of the source of DOC and the recalcitrance of DOC in previous studies (Kalbitz et al. 2003, Weishaar et al. 2003, McDowell et al. 2006, Fellman et al. 2008). Higher SUVA values indicate more aromatic compounds and usually, but not always, more recalcitrant DOC (Kalbitz et al. 2003, Weishaar et al. 2003, McDowell et al. 2006). Surface waters typically have $SUVA_{254}$ values between 2 and 4 $L*mg\ C^{-1}*m^{-1}$ (Weishaar et al. 2003). We also examined the ratio of Abs_{254} to Abs_{400} as this has been shown to be an indicator of the proportion of high molecular weight, unsaturated structures and thus high values indicate low DOM biodegradability (Trulleyova and Rulik 2004).

We also used a second method, the fluorescence index (FI), as an index of bioavailability. Lower FI typically indicates a greater proportion of aromatic compounds in the DOC mixture (McKnight et al. 2001). We calculated FI as emission at 450nm divided by emission at 500nm of soil extracts DOC excited at 370nm following the

method of McKnight et al (2001) using a fluorimeter (Horiba Scientific, FluoroMax-3 Spectrofluorimeter, Edison, NJ). This FI has been used to indicate if DOC is more microbially or terrestrially derived in aquatic systems (McKnight et al. 2001). For example, ,microbially derived DOC found in Antarctic lakes has an FI of 1.7-2.0 while plant and soil derived DOC in small temperate forested watersheds have an FI of 1.3-1.4 with most surface waters in between these extremes (McKnight et al. 2001).

Incubation Experiment

As an additional index of bioavailability, we conducted an 11 month soil incubation experiment on three replicate soil extract samples from each of the three hillslope positions at all 12 study sites to determine the decomposition rate of DOC from different landscapes and hillslope positions. Soil extracts (450mL) from three replicate soil samples from each of three hillslope positions (upslope, vegetation boundary, streamside) at each of three sites on four distinct landscape ages were placed in 500mL amber glass bottles with screw cap lids and stored in the dark at 11^{o}C (for a total of 108 bottles). In addition we incubated three replicate blank bottles with only microbial community inoculations but no soil DOM extract, three replicate bottles with 10mg/L glycine-C, and three replicate bottles with 10mg/L glucose-C. Incubation bottles were sub-sampled to measure DOC concentrations (using the method previously described) after 7, 21, 70, 126, 176, and 304 days.

To measure DOC derived respiration, on day 0, day 126, day 176, and day 304 we also collected two sub-samples of water from each incubation bottle for dissolved oxygen analysis. One of these sub-samples was fixed immediately with a 1% $HgCl_2$ solution. The other was fixed with $HgCl_2$ after 2-7 days (the minimum amount of time necessary to

measure detectable changes in oxygen concentration). Samples were then analyzed for oxygen concentrations using Membrane Induction Mass Spectrometry on a Pfeiffer Vacuum Prisma residual gas analyzer (Pfeiffer Vacuum, Prisma, Nashua, NH). We calculated respiration rates as the difference in oxygen concentration between the initial and second water sample divided by the number of hours between the times the two samples were fixed. On day 304 of the experiment we also incubated two subsamples of each soil water extract for all site x hillslope position combinations (120 samples) at room temperature for one week fixing one sample with $HgCl_2$ at the start of the week and fixing one sample with $HgCl_2$ at the end of the week and analyzing both for changes in oxygen concentration to determine if respiration rates were limited by temperature. Cumulative respiration rates were calculated by multiplying the average daily respiration rates for two sampling dates by the number of dates between sampling and summing across the entire length of the incubation.

At the end of the incubation experiment we measured $SUVA_{254}$, $SUVA_{280}$, Abs_{254}/Abs_{400}, and FI on subsamples of water to examine possible changes in the bioavailability of dissolved organic carbon after 11 months. Final SUVA and FI values were compared with SUVA and FI values from initial extracts.

Statistical Analysis

To analyze differences in soil characteristics among landscape ages and hillslope positions and we used split-plot one-way analysis of variance (ANOVA) with landscape age as a whole plot factor, site (hillslope) number as a random effect, hillslope position as a sub-plot factor, and replicate as a random effect. We used a similar split-plot one-way ANOVA to analyze differences in concentrations of carbon, nitrogen and phosphorous in

soil water and extracts and to analyze differences in SUVA, FI, respiration rate, and DOC consumption in soil extracts among hillslope positions and landscape ages. To compare differences in SUVA, FI, and nutrient concentrations between the beginning and end of the experiment we used a paired t-test. We compared the fit of three nonlinear models to model DOC decomposition rate, a single exponential (1), double exponential (2), and asymptotic model (3).

$$X = e^{-k * t} \qquad (1)$$

$$X = (1-A) * e^{-k1 * t} + A * e^{-k2 * t} \qquad (2)$$

$$X = (1-A) * e^{-k * t} + A \qquad (3)$$

where X is the % initial DOC remaining , k is the decomposition rate constant, t is the sampling time in days, and A is the size of the slow pool of organic matter. To compare between models we used AICc (Anderson et al. 2000):

$$AICc = n * \ln(RSS/n) + 2 * K + 2 * K * (K+1) / (n - K - 1)$$

where n is the number of time points, K is the number of parameters in the model and RSS is the residual sum of squares for each model run. K was equal to one for the single exponential model, three for the double exponential model, and two for the asymptotic model. Models were ranked in order from the lowest to highest AICc. All statistical analyses were run using JMP software (JMP 7, SAS, Cary, NY).

Results

Site Characteristics, Soil and Stream Water

There were no significant differences in bulk density, gravimetric soil moisture, thaw depth, or organic layer depth among the landscape ages (ANOVA: Bulk Density: $p=0.25$, $F_{3,8}=1.67$; Soil Moisture: $p=0.74$, $F_{3,8}=0.43$; Thaw Depth: $p= 0.63$, $F_{3,86}=0.60$;

Organic Layer Depth: $p=0.25$, $F_{3,8}=1.68$; Table 4.1); however, thaw depth was significantly different among all three hillslope positions, increasing down the hillslope from upslope to streamside hillslope positions ANOVA: $p<0.001$, $F_{3,84}=27.58$, Tukey's HSD $\alpha=0.05$; Table 4.2). There were no significant differences among ages in air temperature or soil temperature at either 5cm or 10cm depths (ANOVA: Air: $p=0.047$, $F_{3,7}=4.50$, Tukey's HSD $\alpha=0.05$ NSD among ages; 5cm Depth: $p=0.60$, $F_{3,96}=0.66$; 10cm Depth: $p= 0.79$, $F_{3,96}=0.35$). Soil temperature at 10cm depth was significantly higher at streamside hillslope positions than in tussock or vegetation boundary hillslope positions (ANOVA: $p<0.001$, $F_{3,94}=9.97$, Tukey's HSD $\alpha=0.05$, Table 4.2); however, there were no significant differences in soil temperature at 5cm between hillslope positions (ANOVA: $p=0.65$, $F_{2,94}=0.44$; Table 4.1). Soil pH did not differ significantly among landscape ages (ANOVA: $p=0.098$, $F_{3,96}=2.95$; Table 1).

In contrast to a previous study (Chapter 3), there were no significant differences in soil water DOC or DON concentrations among landscape ages (ANOVA: DOC: $p=0.64$, $F_{3,96}=0.60$; DON: $p=0.17$, $F_{3,95}=2.20$; Figure 4.2 and 4.3). Similar to previous observations (Chapter 3), concentrations of DOC within landscape ages decreased significantly moving down hillslopes, but the magnitude of that change depended on landscape age (ANOVA: hillslope position: $p=0.003$, $F_{2,94}=17.17$; age x hillslope position: $p=0.046$, $F_{6,88}=2.26$; Figure 4.2).

Incubation of soil extracts

Similar to soil water samples, initial soil extracts showed no significant differences in DOC concentration among landscape ages (ANOVA: $p=0.18$, $F_{3,96}=1.68$; Figure 4.3). However, DOC concentrations in extracts were significantly different among

hillslope positions across all landscape ages, with lower concentrations of dissolved organic carbon at down slope sites (ANOVA: $p=0.014$, $F_{2,94}=4.49$, Tukey's HSD $\alpha=0.05$, Figure 4.3). There were no significant differences among landscape ages or hillslope positions in the ratio of DOC:DON in initial soil extracts (ANOVA: age: $p=0.52$, $F_{3,96}=0.82$, hillslope positions: $p=0.31$, $F_{2,94}=1.18$).

SUVA values from soil extracts in our study were within the range of SUVA values from surface waters (2-4 L mg C^{-1} m^{-1}) (Weishaar et al 2003, McDowell et al 2006) and wetlands in southeast Alaska (3.2 -4.6 L mg C^{-1} m^{-1}) (Fellman et al. 2008) with our values on the high end of spectrum similar to those from surface waters dominated by more recalcitrant DOC (Weishaar et al 2003, Fellman et al 2008). Contrary to expectations, there were no significant differences in $SUVA_{254}$ or $SUVA_{280}$ of initial soil extracts among either landscape ages (ANOVA: $SUVA_{254}$: $p=0.82$, $F_{3,96}=0.30$; $SUVA_{280}$: $p=0.77$, $F_{3,96}=0.37$; Figure 4.4) or hillslope positions (ANOVA: $SUVA_{254}$: $p=0.63$, $F_{2,94}=0.47$; $SUVA_{280}$: $p=0.65$, $F_{2,94}=0.43$; Figure 4.4). Similarly, there were no significant differences among hillslope positions or landscape ages in Abs_{254}/Abs_{400} (ANOVA: age: $p=0.38$, $F_{3,96}=1.17$; hillslope position: $p=0.61$, $F_{2,94}=0.49$; Figure 4.4) of initial soil extracts. Nor were their significant differences in the $SUVA_{254}$, $SUVA_{280}$, or Abs_{254}/Abs_{400} of soil extracts after 10 months of incubation among landscape ages (ANOVA: $SUVA_{254}$: $p=0.77$, $F_{3,96}=0.37$; $SUVA_{280}$: $p=0.88$, $F_{3,96}=0.22$; Abs_{254}/Abs_{400}: $p=0.63$, $F_{3,96}=0.60$; Figure 4.5) or among hillslope positions (ANOVA: $SUVA_{254}$: $p=0.075$, $F_{2,94}=4.12$; $SUVA_{280}$: $p=0.05$, $F_{2,94}=5.19$; Abs_{254}/Abs_{400}: $p=0.80$, $F_{2,94}=0.22$; Figure 4.5). There were no significant differences in $SUVA_{254}$, $SUVA_{280}$, or Abs_{254}/Abs_{400} between initial and final samples of DOM from the experiment (Paired t-

test: $SUVA_{254}$: p=0.20, t_{119}=1.28; $SUVA_{280}$: p=0.67, t_{119}=-0.43; Abs_{254}/Abs_{400}: p=0.80, t_{119}=0.26; Figure 4.4 and 4.5).

Fluorescence index values of initial soil extracts were similar to FI values for terrestrially derived DOC which is relatively recalcitrant (1.3-1.4) (McKnight et al 2001) and similar to DOC extracted from wetlands in southeast Alaska (1.3-1.42) (Fellman et al 2008). FI values were significantly different among hillslope positions (ANOVA: p=0.04, $F_{2,94}$=5.47; Figure 4.6), but were not significantly different among landscape ages (ANOVA: p=0.92, $F_{3,96}$=0.16; Figure 4.6). During the course of the experiment FI increased (Paired t-test: p<0.001, t_{119}=15.39; Figure 4.6). There were no significant differences among either landscape ages or among hillslope positions in FI of final DOM samples (ANOVA: age: p=0.91, $F_{3,96}$=0.18; hillslope position: p=0.14, $F_{2,94}$=2.81; Figure 4.6).

Contrary to our hypotheses, initial respiration rates, measured as dissolved oxygen consumption over seven days, did not show significant differences among either landscape ages (ANOVA: p=0.77, $F_{3,91}$=0.37; Figure 4.7) or hillslope positions (ANOVA: p=0.16, $F_{2,89}$=1.86; Figure 4.7). Nor were there differences among oxygen consumption rates after 126 days or after 176 days among either landscape ages (ANOVA: day 126: p=0.33, $F_{3,88}$=1.31; day 176: p=0.27, $F_{3,94}$=1.58; Figure 4.7) or hillslope positions (ANOVA: day 126: p=0.47, $F_{2,86}$=0.86; day 176: p=0.44, $F_{2,92}$=0.96; Figure 4.7). At the end of the experiment there were no significant differences in oxygen consumption rate among hillslope positions (ANOVA: p=0.62, $F_{2,82}$=0.52; Figure 4.6). Oxygen consumption rates were significantly different among landscape ages at the end of the experiment; however, there was no trend in oxygen consumption with age

(ANOVA: $p=0.025$, $F_{3,84}=5.28$; Tukey's HSD $\alpha=0.05$; Figure 4.7). Respiration rates were significantly lower at the end of the experiment than at the beginning of the experiment (Paired t-test: $p<0.001$, $t_{100}=7.069$; Figure 4.7). Respiration rates at the end of the experiment were significantly higher at room temperature than at 11^{o}C, indicating temperature limitation of DOC decomposition (Paired t-test: $p<0.001$, $t_{102}=-9.00$; data not shown). There were no significant differences among landscapes in cumulative respiration rates (ANOVA: $p=0.21$, $F_{3,96}=1.88$; Figure 4.7); however, there were significantly higher cumulative respiration rates in samples from the upslope tussock tundra hillslope position than in samples from the hillslope positions at the boundary between the upslope tussock tundra and streamside vegetation (ANOVA: $p=0.033$, $F_{2,84}=6.32$; Figure 4.7).

Over the course of 10 months, 10-25% of DOC was decomposed on average across all landscape ages (Figure 4.8). Similar to patterns in microbial respiration in extracts, decomposition of DOC throughout the experiment did not differ significantly among landscape ages or hillslope positions in either total amount (ANOVA: age: $p=0.78$, $F_{3,96}=0.37$; hillslope position: $p=0.10$, $F_{2,94}=2.35$; Figure 4.8) or as a percent of initial DOC concentrations (ANOVA: age: $p=0.60$, $F_{3,96}=0.66$; hillslope position: $p=0.54$, $F_{2,94}=0.62$; Figure 4.8). In approximately one third of the cases there was no significant difference between the two models (asymptotic vs. single exponential), the single exponential model was a significantly better fit for the data in approximately one third of the cases, and the asymptotic model was a significantly better fit for the data in the remaining third of the cases (Table 4.3). We do not present data from a double exponential model because that model did not fit the data in most cases (data not shown).

There were no significant differences in the decomposition rate constant modeled with a single exponential model among either landscape ages or among hillslope positions (age: $p=0.77$, $F_{3,96}=0.37$; hillslope positions: $p=0.62$, $F_{2,94}=0.48$; Figure 4.8). When we modeled decomposition rates using an asymptotic model there were also no significant differences among landscape ages or among hillslope positions (data not shown).

Discussion

Our results indicate that biodegradability of DOM remained relatively constant throughout the landscape, with no differences among landscape ages or among hillslope positions. Although we hypothesized that DOM would be more labile on older landscape ages due to differences in plant and microbial communities, we found no differences in biodegradability of summertime DOM among landscape ages. Therefore higher observed rates of microbial respiration on older landscape ages (Hobbie et al. 2002, Hobbie and Gough 2004, Chapter 3, Chapter 4) cannot be explained by a more labile substrate on older landscape ages. These findings are not consistent with previous work on biodegradability of tundra DOM during springtime snowmelt which did find significant differences among landscape ages (Michaelson et al. 1998). For topography, we hypothesized that DOM would be less labile in downslope hillslope positions due to degradation of labile DOM within the hillslope, but we found no differences in DOM biodegradability among hillslope positions. Therefore, degradation of labile DOM within the hillslope does not appear to explain higher concentrations of DOM at upslope sites. The lack of variation in lability of DOM within hillslopes indicates that chemical stabilization of DOM is a more important driver of DOM concentrations than biological breakdown of DOM within hillslopes.

Summertime DOM in this region appears to be uniformly recalcitrant throughout the landscape despite several factors that could potentially lead to variability. In relation to temperate studies of DOM biodegradability, rates of decomposition reported here are similar to those found for DOM in soil extracts from hardwood and spruce forest floors, but are much slower than for DOM found in agricultural soils (McDowell et al. 2006). Roehm et al (2009) examined soil extracts from subarctic mire in Sweden and found much higher bioavailability of terrestrial DOM (21-56% in 12 days) than we found in our study. Similarly, biodegradability of DOM in our soil extracts was lower than exhibited biodegradability of DOM from wetlands in SE Alaska (23-42% in 30 days) (Fellman et al. 2008). The high specific UV absorbance (near 4 at 250nm) of DOM in soil extracts also indicates a high proportion of aromatic compounds which often indicates more recalcitrant DOM (Kalbitz et al. 2003, Weishaar et al. 2003, McDowell et al. 2006). Similarly, the fluorescence index of DOM in soil extracts (near 1.3) typically indicates more recalcitrant DOM (McKnight et al. 2001). Spectral properties of DOM were also not significantly altered throughout the course of a 10 month incubation experiment.

Extrapolating results from the laboratory incubations suggests that the majority of DOM is moving into streams before it can be degraded within the terrestrial landscape. For example, if we assume a 100 day growing season, decomposition rates similar to those reported here, and a mean residence time of water in the landscape of 100 days, less than 15% of DOM would be degraded before reaching aquatic ecosystems, so the majority of DOM is likely to be flushed into aquatic ecosystems before it is processed in the hillslope. Holmes et al. (2008) found that 10% or less of the summertime DOM in three rivers in the Kuparuk Region (the Kuparuk, the Coleville, and the Sagavanirktok)

was labile. They proposed that this was due to microbial processing within hillslopes; however, our data indicate that DOC produced by leaching from vegetation and soils in summertime is already very recalcitrant. However, DOM may undergo photo-oxidation within aquatic ecosystems, producing labile DOM which can represent an important source of energy and nutrients for aquatic microbes (Kling 1995, Judd and Kling 2002, Judd et al. 2006, Judd et al. 2007).

In contrast to the recalcitrant nature of DOM in arctic watersheds in mid-summer shown here, DOM in tundra watersheds appears to be more labile throughout the landscape (rivers and soils) during the spring freshet when the majority of DOM fluxes occur. Michaelson et al (1998) found that 36-46% of the DOM in tundra soil cores was labile during thaw. They also observed that the proportion of labile DOM decreased in thawed soil cores after a 34 day incubation along with the proportion of hydrophilic neutral compounds (Michaelson et al. 1998). Similarly, up to 40% of the DOM is labile in three rivers in Northern Alaska (the Kuparuk, the Colville, and the Sagavanirktok) during the snowmelt flush (Holmes et al. 2008). Previous research on bacterial utilization of DOM within a small tundra catchment at Toolik Lake, AK also demonstrated decreases in the biodegradability of DOM from a springtime experiment to a mid-growing season experiment (Judd et al. 2006). In addition, Raymond et al (2007) found that DOC exported during spring runoff is significantly younger than DOC exported from major arctic rivers during summertime base flow. These seasonal changes in DOM source and biodegradability have been demonstrated to lead to changes in the bacterioplankton communities of Toolik Lake (Crump et al. 2003). More labile DOM during the spring freshet and soil thaw period may be due to the flushing of labile DOM

produced by both microbial and freeze-thaw processes throughout the fall, winter, and spring (Schimel and Clein 1996, Larsen et al. 2002, Grogan et al. 2004). Free-thaw cycling in soils has been shown to produce peaks in microbial activity thought to result from decomposition of labile compounds such as carbohydrates resulting from the lysis of plant and microbial cells (Schimel and Clein 1996, Larsen et al. 2002, Grogan et al. 2004). If freeze-thaw processes during the fall, winter, and spring release labile DOM which is removed from terrestrial ecosystems during snowmelt this labile DOM would not be available to support summertime microbial productivity.

Our study suggests that DOM production and transport are more important than DOM degradation in explaining variation in DOM concentrations among landscape ages and hillslope positions in arctic soils. Our results indicate that there is little variation in DOM degradation within tundra ecosystems during maximum thaw depth when DOM has the greatest potential to interact with soils. Therefore, it does not appear that differences in DOM biodegradability lead to variation in DOM concentrations among landscape ages nor does not appear that degradation of DOM within hillslopes leads to decreases in DOM concentration moving down hillslopes. Previous research demonstrates that geochemical variation among landscape ages leads to significant differences in the production of DOM with higher DOM production on older landscapes than younger, less weathered landscapes (Chapter 1, Chapter 2), which do not lead to significant differences in soil water DOM concentrations among landscape ages (Chapter 3). However, it does appear that transport of DOM or hydrologic connectivity within hillslopes may lead to topographic variation in soil water concentrations of DOM (Chapter 3). Judd and Kling (2002) found that the amount of DOM produced and

exported from soils depended on both the vegetation type and the amount and frequency of water flushing in soils. This would indicate that hydrologic transport is an important control on watershed DOM fluxes within hillslopes (Judd and Kling 2002).

Table Legends

Table 1.1: Mean (± SE) characteristics of two to four sites on each of the four landscape ages from the Upper Kuparuk River region included in this study. Age and vegetation type are from Hamilton (2002). Age differences ($p<0.05$) are indicated with superscript capitol letters.

Table 1.2: Results of statistical tests used to determine correlations between rates of microbial activity (respiration, dissolved organic carbon production, and dissolved organic nitrogen production) and relevant predictor variables (dissolved organic carbon in leachates, total soil nitrogen, soil carbon to nitrogen ratios, and microbial biomass carbon).

Table 1.3: Results from analysis of covariance (ANCOVA) to determine relationships between rates of microbial activity (dissolved organic carbon production, dissolved organic nitrogen production, and microbial respiration) and relevant predictor variables (landscape age, dissolved organic carbon, total soil nitrogen, soil carbon to nitrogen ratios, or microbial biomass).

Table 1.4: Mean (± SE) characteristics of water from surface pools and soil water from tension lysimeters on each of three landscape ages. Significant differences among landscape ages are indicated by superscript capitol letters ($p<0.05$).

Table 2.1: Mean (± SE) geochemical characteristics of soil used for this study from two to four sites on each of four landscape ages near Toolik Lake, AK. Age data are from Hamilton (2002) and pH and exchangeable calcium data are from Chapter 1.

Table 2.2: Results from regression to determine relationships between dissolved organic nitrogen production, and microbial respiration and dissolved organic carbon grouped by

landscape age and averaged across all treatments or grouped by treatment and averaged across all landscape ages.

Table 3.1: Mean (± standard error) pH, soil temperature, and thaw depth for three replicate samples at three hillslope positions in small watersheds underlain by four distinct landscape ages.

Table 3.2: Mean (± standard error) stream pH and temperature for eight streams in watersheds underlain entirely by four distinct landscape ages.

Table 3.3: Average vegetation absolute percent cover (n=4) at each stream with all plants included.

Table 4.1: Mean (± SE) characteristics of four sites on each of four landscape ages in the Upper Kuparuk River region included in this study averaged across hillslope positions. Vegetation type and age were assigned according to Hamilton (2002).

Table 4.2: Mean (± SE) characteristics of each hillslope positions averaged across four landscape ages in the Upper Kuparuk River region included in this study.

Table 4.3: Using a difference of 3 AICc to indicate significant difference.

Table 1.1

Glaciation	Years Before Present	Vegetation Type	# of Sites	Soil T (^{o}C at 10cm)	July Thaw Depth (cm)	Organic Horizon Depth (cm)	Bulk Density (g soil/ cm^3)	Organic Horizon Carbon Stocks (kg/m^2)	Organic Horizon Nitrogen Stocks (kg/m^2)	pH (in water)	Soil Moisture
Itkillik II	11,000-50,000	Moist Non-Acidic Tundra	4	6.0 ± 1.2	29.7 ± 2.0	14.4 ± 1.2	0.66 ± 0.09	36302 ± 6050	1749 ± 196^{A}	6.5^{A}	456 ± 107
Itkillik I	50,000-120,000	Moist Acidic Tundra	3	3.0 ± 1.5	32.0 ± 6.0	12.5 ± 4.6	0.29 ± 0.08	18512 ± 6953	626 ± 225^{B}	5^{B}	1490 ± 956
Sagavanirktok	120,000-600,000		4	1.4 ± 0.4	28.4 ± 1.7	13.9 ± 1.2	0.54 ± 0.11	27598 ± 6549	716 ± 212^{B}	4.5^{B}	535 ± 54
Anaktuvuk	4.8 million		2	3.1 ± 0.8	24.5 ± 0.2	15.0 ± 2.5	0.38 ± 0.12	47160 ± 20807	1095 ± 674^{AB}	4.5^{B}	345 ± 13

Table 1.2

	Predictor	Correlation (Pearson's r)	p
Respiration (per gram soil carbon)			
	Dissolved Organic Carbon (per g soil C)	0.75	<0.001
	Total Soil Nitrogen	-0.62	<0.001
	Soil Carbon to Nitrogen Ratio	0.58	<0.001
	Microbial Biomass Carbon (per g soil)	0.035	0.84
Dissolved Organic Carbon (per gram soil carbon)			
	Total Soil Nitrogen	-0.75	<0.001
	Soil Carbon to Nitrogen Ratio	0.79	<0.001
	Microbial Biomass Carbon (per g soil)	-0.17	0.30
Dissolved Organic Nitrogen (per gram soil carbon)			
	Dissolved Organic Carbon (per g soil C)	0.5	0.001
	Total Soil Nitrogen	-0.36	0.026
	Soil Carbon to Nitrogen Ratio	0.33	0.043
	Microbial Biomass Carbon (per g soil)	-0.21	0.20

Table 1.3

Predictor		**R^2**	**p**	**F**
Respiration (per g soil)				
ANCOVA:	Landscape Age		0.64	0.58
	Dissolved Organic Carbon		<0.001	25.43
	DOC X LA		0.054	3.39
	Whole Model	0.94		
ANCOVA:	Landscape Age		0.041	3.36
	Total Soil Nitrogen		0.021	6.62
	TSN X LA		0.94	0.15
	Whole Model	0.86		
ANCOVA:	Landscape Age		0.065	2.81
	Soil Carbon to Nitrogen Ratio		0.035	5.38
	C:N X LA		0.65	0.57
	Whole Model	0.87		
ANCOVA:	Landscape Age		0.003	8.64
	Microbial Biomass Carbon		0.75	0.11
	MBC X LA		0.049	3.61
	Whole Model	0.91		
Dissolved Organic Carbon (per g soil)				
ANCOVA:	Landscape Age		0.67	0.52
	Total Soil Nitrogen		0.25	1.79
	TSN X LA		0.78	0.36

Predictor		**R^2**	**p**	**F**
Dissolved Organic Carbon (per g soil)				
ANCOVA:	Whole Model	0.86		
ANCOVA:	Landscape Age		0.59	0.66
	Soil Carbon to Nitrogen Ratio		0.041	5.22
	C:N X LA		0.27	1.49
	Whole Model	0.89		
ANCOVA:	Landscape Age		0.029	4.60
	Microbial Biomass Carbon		0.11	3.08
	MBC X LA		<0.001	11.89
	Whole Model	0.96		
Dissolved Organic Nitrogen (per g soil)				
ANCOVA:	Landscape Age		0.36	1.14
	Dissolved Organic Carbon		0.16	2.28
	DOC X LA		0.92	0.17
	Whole Model	0.71		
ANCOVA:	Landscape Age		0.61	0.62
	Total Soil Nitrogen		0.18	2.03
	TSN X LA		0.52	0.78
	Whole Model	0.74		
ANCOVA:	Landscape Age		0.50	0.82
	Soil Carbon to Nitrogen Ratio		0.31	1.13
	C:N X LA		0.63	0.59

Predictor		**R^2**	**p**	**F**
Dissolved Organic Nitrogen (per g soil)				
ANCOVA:	Whole Model	0.73		
ANCOVA:	Landscape Age		0.15	2.01
	Microbial Biomass Carbon		0.87	0.027
	MBC X LA		0.58	0.69
	Whole Model	0.71		

Table 1.4

		Soil Pond Water						
Glaciation	Sites	pH	T (^{o}C)	DIC (g/L)	DOC (mg/L)	DON (mg/L)	Nitrate (µg/L)	Ammonium (µg/L)
Itkillik II	2	7.01 ± 0.28^{A}	16.29 ± 2.31	15.22 ± 1.24^{A}	10.59 ± 1.29	0.46 ± 0.32	12.13 ± 5.60	71.89 ± 22.14
Itkillik I	2	6.63 ± 0.29^{A}	6.47 ± 2.41	3.96 ± 1.13^{AB}	8.42 ± 0.80	0.01 ± 0.20	6.94 ± 5.91	78.14 ± 21.73
Sagavanirktok	4	4.98 ± 0.20^{B}	7.85 ± 1.71	3.48 ± 0.98^{B}	10.90 ± 0.76	0.12 ± 0.21	4.40 ± 4.85	44.12 ± 20.21
		Soil Water (Lysimeters)						
Landscape Age	n				DOC (mg/L)	DON (mg/L)	Nitrate (µg/L)	Ammonium (µg/L)
Itkillik II	4				14.88 ± 2.40	1.03 ± 0.21	14.07 ± 5.23	81.58 ± 12.11
Itkillik I	3				20.37 ± 2.78	1.14 ± 0.21	6.11 ± 5.23	74.03 ± 13.99
Sagavanirktok	4				16.25 ± 2.40	0.75 ± 0.18	2.34 ± 4.53	66.56 ± 12.11

Table 2.1:

Glaciation	Years Before Present	Number of Sites	pH (in water)	Exchangeable Calcium (cmoles/kg soil)
Itkillik II	11,000-50,000	4	6.5	78.6 ± 7.7
Itkillik I	50,000-120,000	3	5	23.6 ± 8.9
Sagavanirktok	120,000-600,000	4	4.5	11.5 ± 7.7
Anaktuvuk	4.8 million	2	4.5	26.3 ± 10.9

Table 2.2:

Respiration by DOC						
Glaciation	**Treatment**	**p**	**t**	**slope**	**intercept**	**R^2**
Averaged across All Treatments and Landscape Ages						
All	All	<0.001	4.87	3.55 ± 0.73	10.27 ± 1.11	0.094
Grouped by Landscape Age Across All Treatments						
Itkillik II	All	0.15	1.44			0.029
Itkillik I	All	0.030	2.23	4.92 ± 2.20	13.26 ± 2.64	0.087
Sagavanirktok	All	<0.001	4.19	4.11 ± 1.12	8.33 ± 2.12	0.20
Anaktuvuk	All	0.097	1.71			0.081
Grouped by Treatment Across All Landscape Ages						
All	Unmanipulated Soil	<0.001	5.00	9.87 ± 1.97	8.11 ± 2.10	0.48
All	Calcium Removal	0.022	2.4	5.07 ± 2.12	10.57 ± 3.00	0.13
All	High Calcium pH 6.5	<0.001	5.89	8.05 ± 1.37	6.55 ± 1.60	0.48

		Respiration by DOC				
Glaciation	**Treatment**	**p**	**t**	**slope**	**intercept**	**R^2**
All	High Calcium pH 4	0.61	-0.50			0.007
All	Low Calcium pH 6.5	<0.001	6.04	9.83 ± 1.63	4.98 ± 2.74	0.50
All	Low Calcium pH 4	0.62	-0.50			0.010
		DON by DOC				
Glaciation	**Treatment**	**p**	**t**	**slope**	**intercept**	**R^2**
Averaged across All Treatments and Landscape Ages						
All	All	<0.001	5.84	0.089 ± 0.015	0.040 ± 0.023	0.15
Grouped by Landscape Age Across All Treatments						
Itkillik II	All	<0.001	5.33	0.13 ± 0.024	0.032 ± 0.033	0.30
Itkillik I	All	0.36	0.93			0.022
Sagavanirktok	All	0.057	1.94			0.063
Anaktuvuk	All	0.073	1.86			0.10

DON by DOC						
Glaciation	**Treatment**	**p**	**t**	**slope**	**intercept**	**R^2**
Grouped by Treatment Across All Landscape Ages						
All	Unmanipulated Soil	0.064	1.93			0.11
All	Calcium Removal	<0.001	5.22	0.19 ± 0.037	0.15 ± 0.054	0.48
All	High Calcium pH 6.5	<0.001	4.66	0.043 ± 0.009	0.012 ± 0.011	0.41
All	High Calcium pH 4	0.015	2.58	0.11 ± 0.041	0.030 ± 0.077	0.18
All	Low Calcium pH 6.5	0.084	1.77			0.082
All	Unmanipulated Soil	0.064	1.93			0.11

Table 3.1

Age	Stream	Transect	Week	Soil pH	Soil Temperature (^{o}C)	Thaw Depth (cm)
Itkillik III	A	Above Upslope	4	5.77 (±) 0.16		
		Upslope	0		4.99 (±) 0.57	19.8 (±) 2.2
			1		9.12 (±) 1.45	12.2 (±) 5.1
			3		10.24 (±) 1.48	19.0 (±) 5.3
			4	5.77 (±) 0.16	7.41 (±) 1.53	22.3 (±) 5.3
		Vegetation Boundary	0		4.05 (±) 0.57	20.7 (±) 2.6
			1		3.58 (±) 1.51	26.7 (±) 5.1
			3		7.11 (±) 1.54	32.9 (±) 5.3
			4		7.34 (±) 1.59	32.8 (±) 5.3
		Streamside	0		6.49 (±) 0.55	45.0 (±) 2.1
			1		2.45 (±) 1.44	51.2 (±) 5.1
			3		7.84 (±) 1.54	62.4 (±) 5.3
			4		7.91 (±) 1.52	64.3 (±) 5.3

Age	Stream	Transect	Week	Soil pH	Soil Temperature (^{o}C)	Thaw Depth (cm)
Itkillik III	B	Above Upslope	5	5.95 (±) 0.16		
		Upslope	0		4.99 (±) 0.59	19.8 (±) 2.2
			1		6.12 (±) 1.45	21.0 (±) 5.1
			2		8.13 (±) 1.45	29.3 (±) 5.2
			3		10.10 (±) 1.48	33.8 (±) 5.3
			5	5.59 (±) 0.16	9.78 (±) 1.44	37.0 (±) 5.2
		Vegetation Boundary	0		4.05 (±) 0.57	20.7 (±) 2.6
			1		5.49 (±) 1.51	22.6 (±) 5.1
			2		3.36 (±) 1.51	23.5 (±) 5.2
			3		7.23 (±) 1.54	27.7 (±) 5.3
			5		8.68 (±) 1.50	33.5 (±) 5.1
		Streamside	0		6.49 (±) 0.55	45.0 (±) 2.1
			1		3.53 (±) 1.44	46.4 (±) 5.1
			2		6.77 (±) 1.45	50.3 (±) 5.2

Age	Stream	Transect	Week	Soil pH	Soil Temperature (^{o}C)	Thaw Depth (cm)
Itkillik III	B	Streamside	3		7.87 (±) 1.47	52.8 (±) 5.3
			5		7.92 (±) 1.44	60.0 (±) 5.1
Itkillik II	C	Above Upslope	5	5.83 (±) 0.17		
		Upslope	0		4.99 (±) 0.59	19.8 (±) 2.2
			2		6.94 (±) 1.48	14.8 (±) 8.3
			3		7.57 (±) 1.54	20.8 (±) 8.3
			5	5.71 (±) 0.18	8.06 (±) 1.51	30.8 (±) 8.25
		Vegetation Boundary	0		4.05 (±) 0.57	20.7 (±) 2.6
			2		8.50 (±) 1.49	46.8 (±) 10.4
			3		10.49 (±) 1.48	52.7 (±) 10.5
			5		10.99 (±) 1.44	64.8 (±) 10.4
		Streamside	0		6.49 (±) 0.55	45.0 (±) 2.1
			2		2.80 (±) 1.45	41.5 (±) 6.7
			3		7.13 (±) 1.47	40.8 (±) 6.8

Age	Stream	Transect	Week	Soil pH	Soil Temperature (^{o}C)	Thaw Depth (cm)
			5		7.33 (±) 1.44	34.8 (±) 6.6
Itkillik II	D	Above Upslope	4	5.74 (±) 0.18		
		Upslope	0		4.05 (±) 0.56	20.7 (±) 2.6
			3		9.15 (±) 1.54	18.1 (±) 8.3
			4	5.80 (±) 0.17		20.2 (±) 8.4
		Vegetation Boundary	0		10.10 (±) 1.48	33.8 (±) 5.3
			3		12.40 (±) 1.48	55.4 (±) 10.5
			4			53.9 (±) 10.5
		Streamside	0		6.49 (±) 0.55	45.0 (±) 2.1
			3		3.64 (±) 1.47	40.8 (±) 6.8
			4			45.2 (±) 6.8
Itkillik I	E	Above Upslope	5	5.76 (±) 0.16		
		Upslope	0		4.99 (±) 0.60	19.8 (±) 2.1
			1			21.8 (±) 4.9

Age	Stream	Transect	Week	Soil pH	Soil Temperature (^{o}C)	Thaw Depth (cm)
Itkillik I	E	Upslope	2		7.04 (±) 1.44	24.6 (±) 5.0
			3		8.75 (±) 1.47	39.0 (±) 5.1
			5	5.78 (±) 0.16	9.99 (±) 1.43	29.2 (±) 4.9
		Vegetation Boundary	0		4.05 (±) 0.56	20.7 (±) 2.6
			1			26.3 (±) 4.9
			2		4.67 (±) 1.39	27.1 (±) 5.0
			3		6.94 (±) 1.42	33.7 (±) 5.1
			5		6.78 (±) 1.38	37.0 (±) 5.0
		Streamside	0		6.49 (±) 0.55	45.0 (±) 2.1
			1			41.9 (±) 4.9
			2		6.54 (±) 1.39	51.4 (±) 5.0
			3		9.51 (±) 1.42	41.6 (±) 5.1
			5		9.62 (±) 1.38	64.3 (±) 4.9
Sagavanirktok	F	Above Upslope	4	5.82 (±) 0.16		

Age	Stream	Transect	Week	Soil pH	Soil Temperature (^{o}C)	Thaw Depth (cm)
Sagavanirktok	F	Upslope	0		4.98 (±) 0.59	19.8 (±) 2.2
			1		1.26 (±) 1.80	22.0 (±) 8.1
			3		5.68 (±) 1.63	30.6 (±) 7.7
			4	5.72 (±) 0.16	4.67 (±) 1.86	30.0 (±) 8.2
		Vegetation Boundary	0		4.05 (±) 0.57	20.7 (±) 2.6
			1		1.34 (±) 1.77	
			3		5.50 (±) 1.61	17.2 (±) 9.3
			4		4.19 (±) 1.84	14.3 (±) 9.7
		Streamside	0		6.49 (±) 0.55	45.0 (±) 2.1
			1		12.56 (±) 1.75	66.8 (±) 7.1
			3		14.01 (±) 1.58	66.4 (±) 6.6
			4		13.81 (±) 1.81	75.1 (±) 7.2
Sagavanirktok	G	Above Upslope	5	5.48 (±) 0.16		
		Upslope	0		4.99 (±) 0.59	19.8 (±) 2.2

Age	Stream	Transect	Week	Soil pH	Soil Temperature (^{o}C)	Thaw Depth (cm)
Sagavanirktok	G	Upslope	1			35.9 (±) 8.1
			2		2.01 (±) 1.79	34.7 (±) 8.2
			3		4.24 (±) 1.63	40.8 (±) 7.7
			5	6.06 (±) 0.16	4.54 (±) 1.79	46.5 (±) 8.2
		Vegetation Boundary	0		4.05 (±) 0.57	20.7 (±) 2.6
			2		3.00 (±) 1.78	
			3		6.45 (±) 1.61	
			5		6.03 (±) 1.77	20.4 (±) 9.6
		Streamside	0		6.49 (±) 0.55	45.0 (±) 2.1
			1		14.40 (±) 1.76	49.0 (±) 7.1
			2		13.25 (±) 1.75	63.5 (±) 7.2
			3		4.24 (±) 1.63	40.8 (±) 7.7
			5		15.81 (±) 1.74	63.6 (±) 7.2
Sagavanirktok	H	Above Upslope	5	5.83 (±) 0.16		

Age	Stream	Transect	Week	Soil pH	Soil Temperature (^{o}C)	Thaw Depth (cm)
		Upslope	0		4.99 (±) 0.60	19.79 (±) 2.2
			1		3.77 (±) 1.80	23.0 (±) 8.1
			3		9.95 (±) 1.6	33.2 (±) 7.8
			5	5.71 (±) 0.16	4.36 (±) 1.79	42.5 (±) 8.2
		Vegetation Boundary	0		4.05 (±) 0.57	20.7 (±) 2.7
			1		0.78 (±) 1.77	7.3 (±) 9.7
			3		2.06 (±) 1.61	14.8 (±) 9.3
			5		5.61 (±) 1.77	31.1 (±) 9.6
		Streamside	0		6.49 (±) 0.55	45.0 (±) 2.1
			1		10.60 (±) 1.75	59.8 (±) 7.1
			3		13.18 (±) 1.58	66.3 (±) 7.2
			5		16.40 (±) 1.74	56.9 (±) 7.2

Table 3.2

Age	Stream	Week	Stream pH	Stream Temperature (^{o}C)
Itkillik I	A	0	6.7 (±) 0.1	11.8 (±) 0.5
		1	6.6 (±) 0.2	
		3	7.2 (±) 0.2	16.7 (±) 0.7
	B	0	6.7 (±) 0.1	11.8 (±) 0.5
		2	6.8 (±) 0.2	
		3	7.0 (±) 0.2	14.0 (±) 0.7
Itkillik II	C	0	6.7 (±) 0.1	11.8 (±) 0.5
		2	6.9 (±) 0.2	
		3	7.1 (±) 0.2	
	D	0	6.7 (±) 0.1	11.8 (±) 0.5
		1	6.0 (±) 0.3	13 (±) 1.1
Itkillik I	E	0	6.7 (±) 0.1	11.8 (±) 0.5
		2	6.7 (±) 0.2	
		3	6.7 (±) 0.2	10.7(±) 0.7
Sagavanirktok	F	0	6.7 (±) 0.1	11.8 (±) 0.5
		1	5.7 (±) 0.2	12.3 (±) 0.7
		3	6.2 (±) 1.2	
	G	0	6.7 (±) 0.1	
		2	7.1 (±) 0.1	
	H	0	6.7 (±) 0.1	
		1	6.4 (±) 0.2	

Table 3.3

	< 50,000 Years Since Glaciation				> 50,000 Years Since Glaciation			
	Itkillik III		Itkillik II		Itkillik I	Sagavanirktok		
Plant	Stream A	Stream B	Stream C	Stream D	Stream E	Stream F	Stream G	Stream F
Andromeda polyfolia	<1	<1			<1	<1		
Arctostaphylos alpinum	1	5						
Betula nana	5	<1		10	7	3	8	7
Carex bigelowii	4	4	15	6	4	5		1
Carex 2			<1					
Cassiope tetragona	<1	5				1		
Dryas integrifolia			1					
Dryas octopetala			5					
Dryas 3	<1	3						
Empetrum nigrum	<1					6		
Equisetum arvense		1						

	< 50,000 Years Since Glaciation				> 50,000 Years Since Glaciation			
	Itkillik III		Itkillik II		Itkillik III	Itkillik II		
Plant	Stream A	Stream B	Stream A	Stream B	Stream A	Stream B	Stream A	Stream B
Eriophorum angustifolium			1				<1	<1
Eriophorum vaginatum	19	9	3	11	17		14	<1
fern			<1					
grass 1								<1
grass 2				<1				
leaf 1		<1						
leaf 2		1						
leaf 3		<1						
Ledum palustre	1	<1		<1	2	2	<1	2
Lupinus arcticus		<1						
Oxytropis cf.								<1

	< 50,000 Years Since Glaciation				> 50,000 Years Since Glaciation			
	Itkillik III		Itkillik II			Itkillik III		
Plant	Stream A	Stream B	Plant	Stream A	Stream B	Plant	Stream A	Stream B
Pedicularis lapponica					<1	<1	<1	
Pedicularis rosette						<1		
Pedicularis 2		<1		<1				
Pedicularis 3	<1	<1						
Petasites cf.			<1			<1		<1
Polygonum bistorta	<1	<1	<1	<1		2		2
Polygonum viviparum			<1					
Pyrola rotundifolia	<1	<1	<1	<1		<1		<1
Pyrola 2		<1						
Rosette						<1		<1
Rubus chamaemorus	2				2	<1	16	2
Salix reticulata	1	1	15			<1		

	< 50,000 Years Since Glaciation				> 50,000 Years Since Glaciation			
	Itkillik III		Itkillik II			Itkillik III		
Plant	Stream A	Stream B	Plant	Stream A	Stream B	Plant	Stream A	Stream B
Salix 2	4	1	3	9	2	5	2	10
Salix 3	<1						5	
Saxifraga sp.		<1	<1					<1
Thalictrum alpinum			<1					
Toffieldia pussila		<1						
Vaccinium uliginosum	5	1	<1	<1	<1	7		
Vaccinium vitis-idea	<1	<1		<1	5	2	2	8
All Mosses	82	76	66	93	68	97	84	97
Moss:								
Aulacomium turgidum	2		<1	9	<1	6	1	9
Aulacomium 2			2					

	< 50,000 Years Since Glaciation				> 50,000 Years Since Glaciation			
	Itkillik III		Itkillik II		Itkillik I	Sagavanirktok		
Moss:	Stream A	Stream B	Stream C	Stream D	Stream E	Stream F	Stream G	Stream F
Dicranum 1	1			5	1	<1	1	
Dicranum 2				3				
Hylocomium splendens	9	15	3	<1	<1	5	<1	19
Polytrichum				4			14	3
Racomitrium	0							
Rhytidium rugosum	1	4	8			2		
Sphagnum	11			15	35	32	40	11
Tomenthypnum nitens	4	3	9	<1		<1		
Lichen:								
Cetraria cucullata		<1	2					
Cladonia					1	<1		

Table 4.1

Glaciation	Years Before Present	Vegetation Type	Air Temp. (°C)	% Moisture	Bulk Density (g/cm3)	pH	Thaw Depth	Soil Temp. at 5cm (°C)	Soil Temp. at 10cm (°C)	Depth of Organic Layer
Itkillik III	11,000-13,000	Moist Non-Acidic Tundra	19.4 ± 0.9	425.0 ± 82.1	0.025 ± 3.0E-3	6.0 ± 0.16[A]	41.0 ± 6.8	10.8 ± 1.8	7.1 ± 1.3	13.8 ± 2.1
Itkillik II	11,000-50,000		21.5 ± 0.9	427.7 ± 82.1	0.019 ± 3.0E-3	6.8 ± 0.17[B]	29.6 ± 6.8	14.3 ± 1.8	8.7 ± 1.4	17.6 ± 2.1
Itkillik I	50,000-120,000	Moist Acidic Tundra	17.2 ± 1.1	505.4 ± 82.2	0.021 ± 3.0E-3	6.1 ± 0.18[A]	39.1 ± 7.9	13.0 ± 1.8	8.1 ± 1.3	16.1 ± 2.1
Sagavanirktok	120,000-600,000		21.8 ± 0.9	375.6 ± 82.3	0.016 ± 3.0E-3	5.5 ± 0.19[A]	40.8 ± 9.0	13.1 ± 1.8	8.9 ± 1.4	21.0 ± 2.1

Table 4.2

Hillslope position	Thaw Depth	Soil Temperature at 5cm (^{o}C)	Soil Temperature at 10cm (^{o}C)
Tussock	29.1 ± 1.8^{A}	12.7 ± 0.5	7.0 ± 0.4^{A}
Vegetation Boundary	35.2 ± 1.8^{B}	13.2 ± 0.5	7.8 ± 0.4^{A}
Streamside	48.4 ± 2.0^{C}	12.6 ± 0.5	9.7 ± 0.4^{B}

Table 4.3:

Model	Fraction of total fits when particular model was best fit (%): each replicate fit separately within a site/hillslope combination
single	34/107 (31.8)
asymptotic	35/107 (32.7)
neither	38/107 (35.5)

Figure Legends

Figure 1.1: Map of our study sites on four landscape ages in the Upper Kuparuk River region in Northern Alaska.

Figure 1.2: Exchangeable polyvalent cations in soils from sites on each of the four landscape ages. Significant differences among landscape ages in exchangeable cations are indicated on the graph as follows: calcium: lowercase letters; magnesium: lowercase italic letters; manganese: lowercase bold letters; total measured exchangeable polyvalent cations: uppercase letters ($p<0.05$). Concentrations of exchangeable aluminum were below the detection limit in soils from the Itkillik II landscape age.

Figure 1.3: Total carbon and nitrogen concentrations of soils from the O horizon from each of the four landscape ages. Significant age effects on soil nitrogen are represented by different lower case letters ($p<0.05$).

Figure 1.4: Microbial biomass carbon and nitrogen normalized per gram soil carbon and the metabolic quotient (cumulative respiration/microbial biomass carbon). Significant age differences are indicated by different lower case letters ($p<0.05$).

Figure 1.5: Cumulative microbial respiration and cumulative dissolved organic carbon production in five month organic soil incubations at $4^{o}C$ normalized per gram soil carbon. Significant age differences are indicated by different lowercase letters ($p<0.05$).

Figure 1.6: Dissolved organic and inorganic nitrogen production in a five month incubation of soils from four landscape ages at $4^{o}C$. Significant age differences are indicated by different lowercase letters ($p<0.05$).

Figure 2.1: Soil total a) C and b) N content as well as c) soil C:N ratio of soils used in the experiment from all treatment and landscape age combinations.

Figure 2.2: Microbial biomass a) C, b) N, and c) C:N ratio estimated from chloroform fumigation extractions.

Figure 2.3: Cumulative soil respiration per gram soil carbon in soils from all four landscape ages and all six treatments. Error bars represent standard error of the mean.

Figure 2.4: Cumulative dissolved organic carbon production per gram of soil carbon in our experiment from all four landscape ages and all six treatments. Error bars represent standard error of the mean.

Figure 2.5: Concentrations of a) ammonium, b) nitrate, and c) dissolved organic nitrogen from all four landscape ages and all six treatments in the experiment.

Figure 2.6: Microbial biomass a) carbon and b) nitrogen and c) microbial carbon to nitrogen ratio at the end of the five month incubation experiment from all age and treatment combinations.

Figure 3.1: (a) Map and (b) diagram of study sites.

Figure 3.2: Mean (averaged over the summer) (± SE) of dissolved organic carbon concentrations of a) soil water (sampled with a perforated needle) and stream water and b) soil water sampled with microlysimeters. Lowercase letters represent significant differences among soil water samples ($p<0.05$).

Figure 3.3: Mean (averaged over the summer) (± SE) of dissolved organic nitrogen concentrations of a) soil water (sampled with a perforated needle) and stream water and b) soil water sampled with microlysimeters. Lowercase letters represent significant differences among soil water samples ($p<0.05$).

Figure 3.4: Mean (averaged over the summer) (± SE) of DOC:DON ratios of soil water (sampled with a perforated needle) and stream water. Lowercase letters represent significant differences among hillslope positions ($p<0.05$).

Figure 3.5: Mean (averaged over the summer) (± SE) of dissolved organic phosphorous concentrations of a) soil water (sampled with a perforated needle) and stream water and b) soil water sampled with microlysimeters.

Figure 3.6: Mean (averaged over the summer) (± SE) of phosphate concentrations of a) soil water (sampled with a perforated needle) and stream water and b) soil water sampled with microlysimeters. Lowercase letters represent significant differences among hillslope positions.

Figure 3.7: Mean (averaged over the summer) (± SE) of nitrate concentrations of a) soil water (sampled with a perforated needle) and stream water and b) soil water sampled with microlysimeters. Lowercase letters represent significant differences among soil water samples.

Figure 3.8: Mean (averaged over the summer) (± SE) of bicarbonate concentrations of a) soil water (sampled with a perforated needle) and stream water and b) soil water sampled with microlysimeters. Lowercase letters represent significant differences among soil water samples.

Figure 4.1: Map of stream sites

Figure 4.2: Dissolved organic carbon concentrations in soil or stream water collected from different hillslope positions at four sites on each of four landscape ages..

Figure 4.3: Concentrations of water-extracted dissolved organic carbon from three replicate organic soil samples collected from different hillslope positions on four distinct landscape ages.

Figure 4.4: Specific UV absorbance (absorbance at a) 254 or b) 280nm/concentration of DOC) and c) the ratio of absorbance at 254nm to absorbance at 400nm of DOC in initial soil extracts.

Figure 4.5: Specific UV absorbance (absorbance at a) 254 or b) 280nm/concentration of DOC) and c) the ratio of absorbance at 254nm to absorbance at 400nm of DOC in soil extracts after a ten month incubation.

Figure 4.6: Fluorescence index (FI) (emission at 450nm divided by emission at 500nm DOC excited at 370nm) of a) initial soil extracts and b) soil extracts after 10 months of incubation.

Figure 4.7: Respiration rate measured as oxygen consumption over 2-7 days (the minimum time required for detectable changes in dissolved oxygen) throughout the 10 month incubation in DOC extracted from a) upslope samples, b) vegetation boundary samples, and c) streamside samples.

Figure 4.8: a) Percent loss of DOC over the course of a 10 month incubation. b) Modeled DOC decomposition rate using a single exponential model. c) Consumption of dissolved organic carbon during a 10 month incubation experiment averaged over all hillslope positions and landscape ages.

Figure 4.9: Soil or stream water a) ammonium, b) nitrate, and c) dissolved organic nitrogen concentrations from different hillslope positions on four sites on each of four landscape ages.

Figure 4.10: a) Dissolved organic phosphorous and b) phosphate concentrations in soil or stream water from different hillslope positions on four sites on each of four landscape ages.

Figure 4.11: a) Ammonium, b) nitrate, and c) dissolved organic nitrogen concentrations in initial soil extracts.

Figure 4.12: a) Ammonium, b) nitrate, and c) dissolved organic nitrogen in soil extracts after 10 months of incubation.

Figure 4.13: a) Dissolved organic phosphorous and b) phosphate concentrations in soil extracts from four sites on each of four landscape ages in both initial soil extracts and in final soil extracts (after 10 months of incubation).

Figure 1.1:

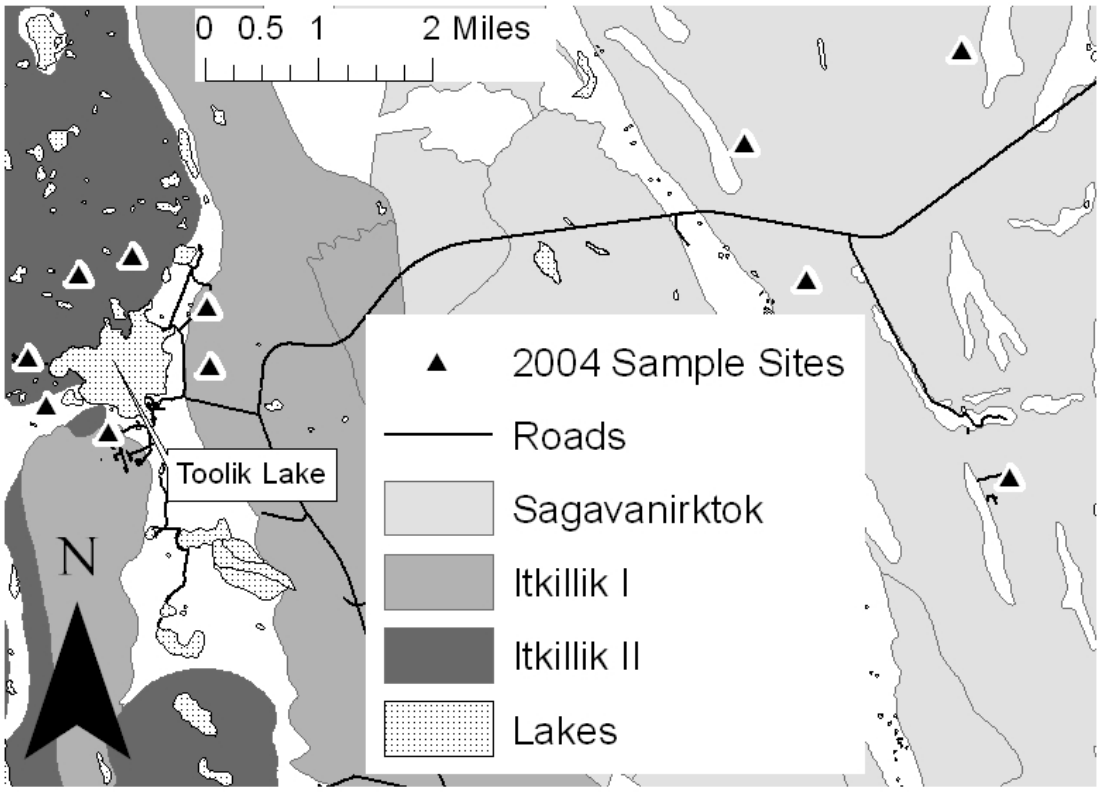
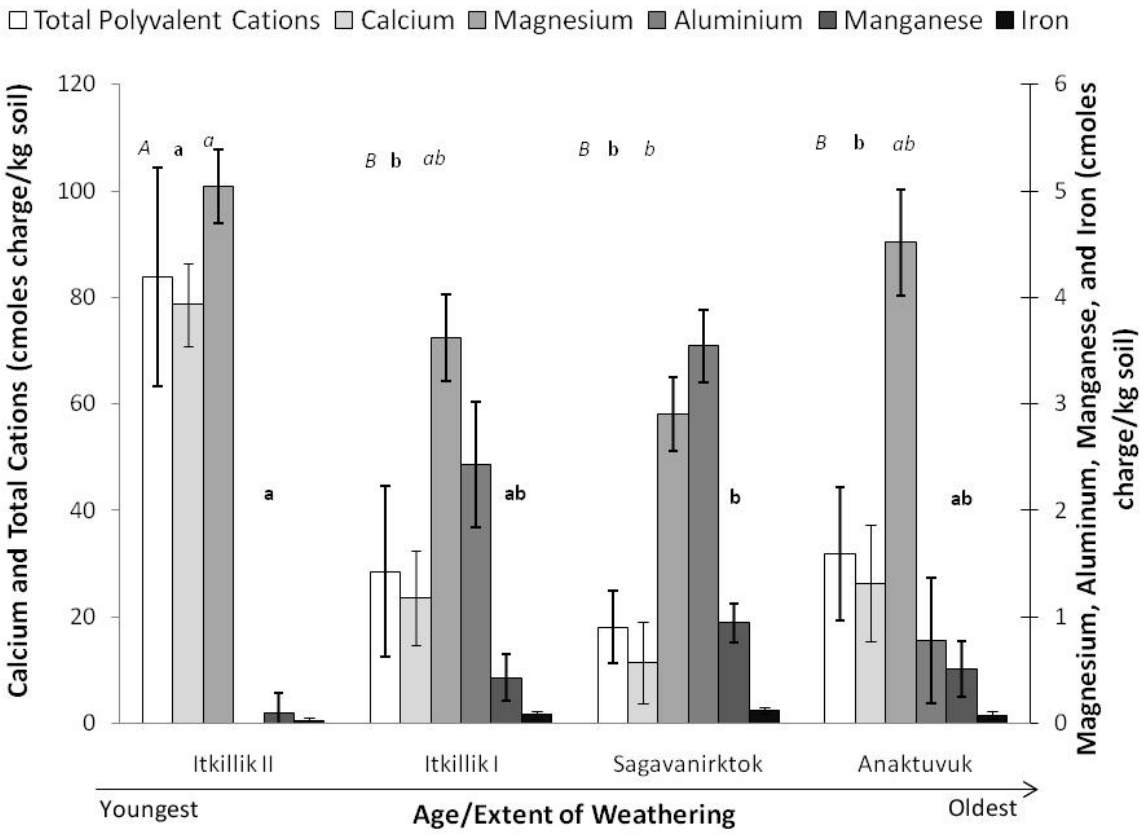
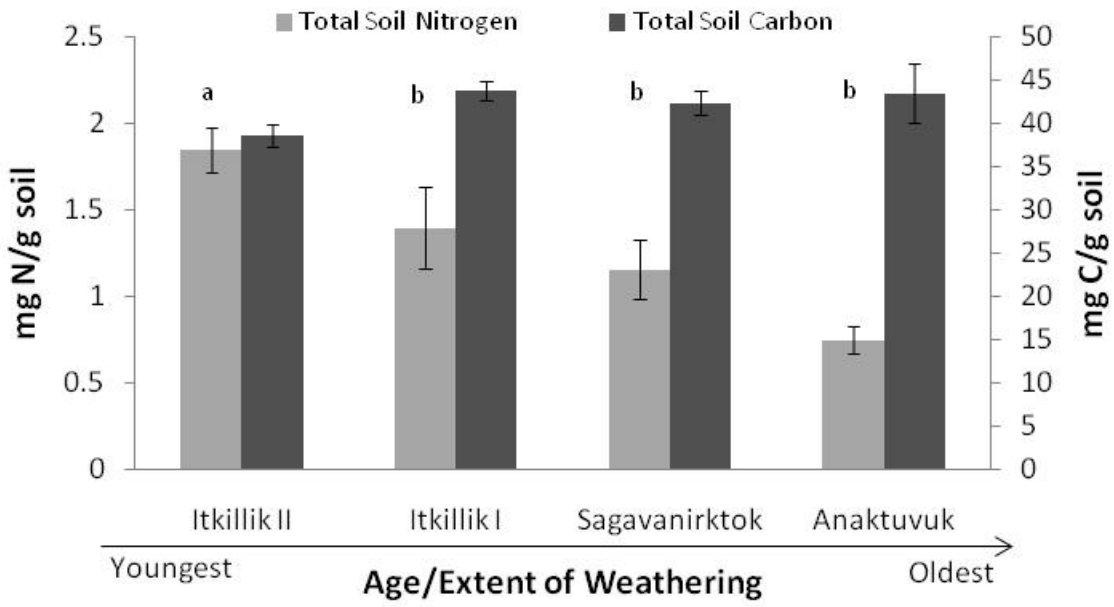

0 0.5 1 2 Miles
2004 Sample Sites
Roads
Sagavanirktok
Itkillik I
Itkillik II
Lakes
Toolik Lake
N

Figure 1.2:



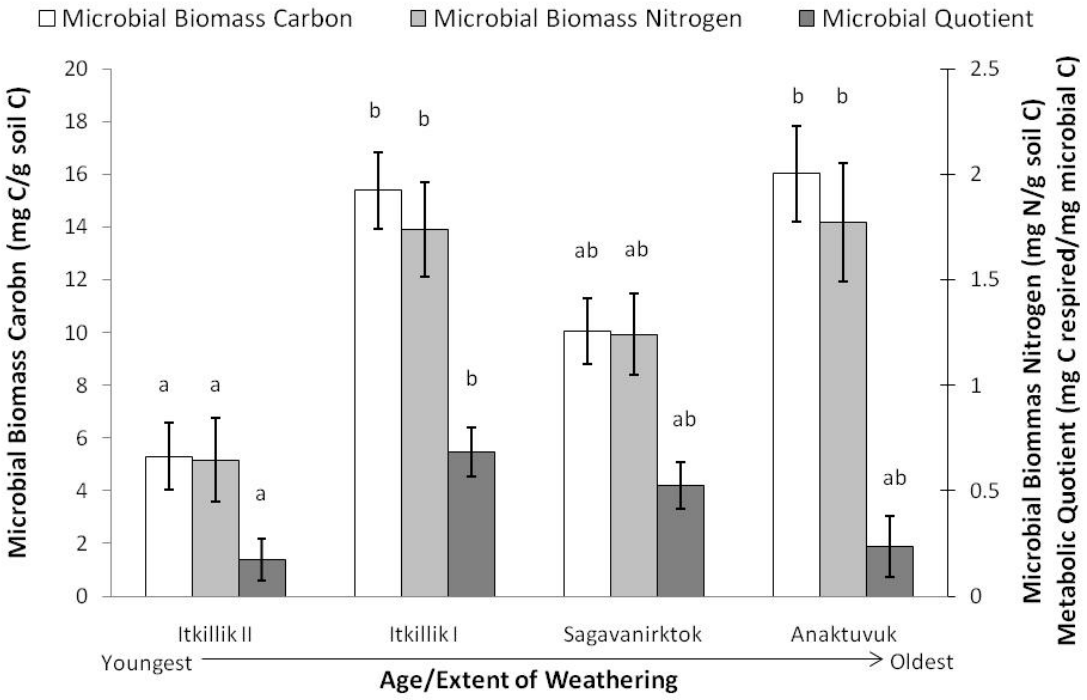
Significant differences among landscape ages in exchangeable cations are indicated on the graph as follows: calcium: lowercase letters; magnesium: lowercase italic letters; manganese: lowercase bold letters; total measured exchangeable polyvalent cations: uppercase letters ($p<0.05$).

Figure 1.3:



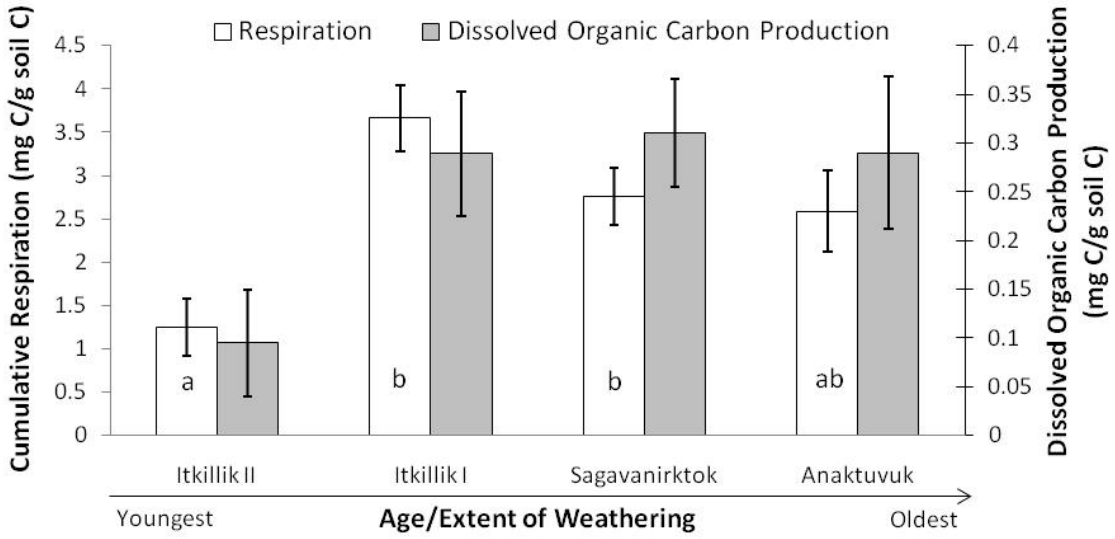
Significant age effects on soil N are represented by different lower case letters ($p<0.05$).

Figure 1.4:



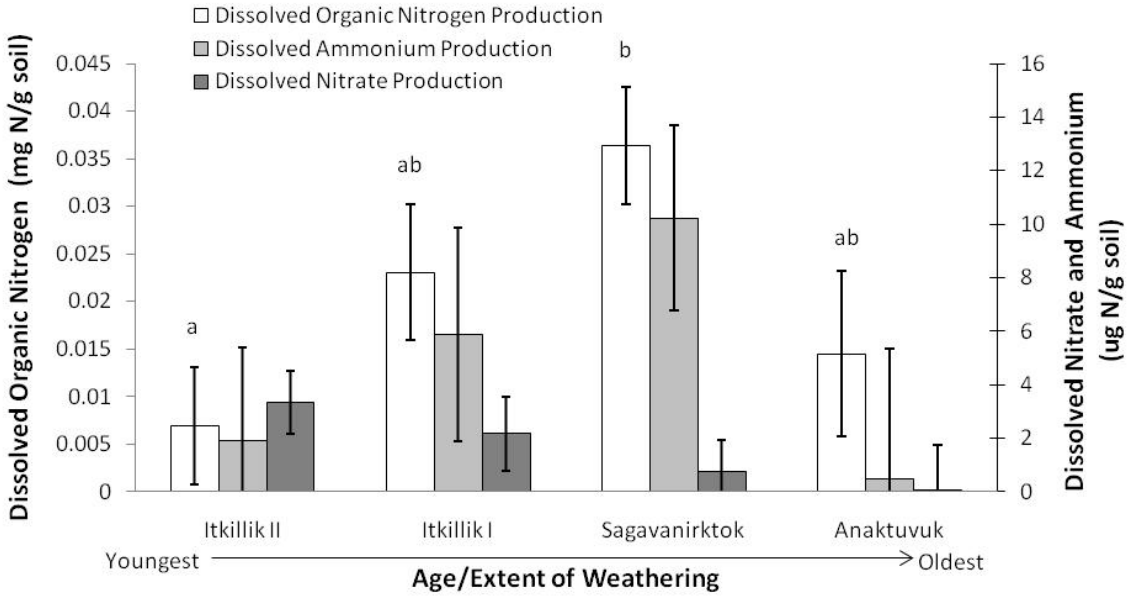
Significant age differences are indicated by different lower case letters ($p<0.05$).

Figure 1.5:



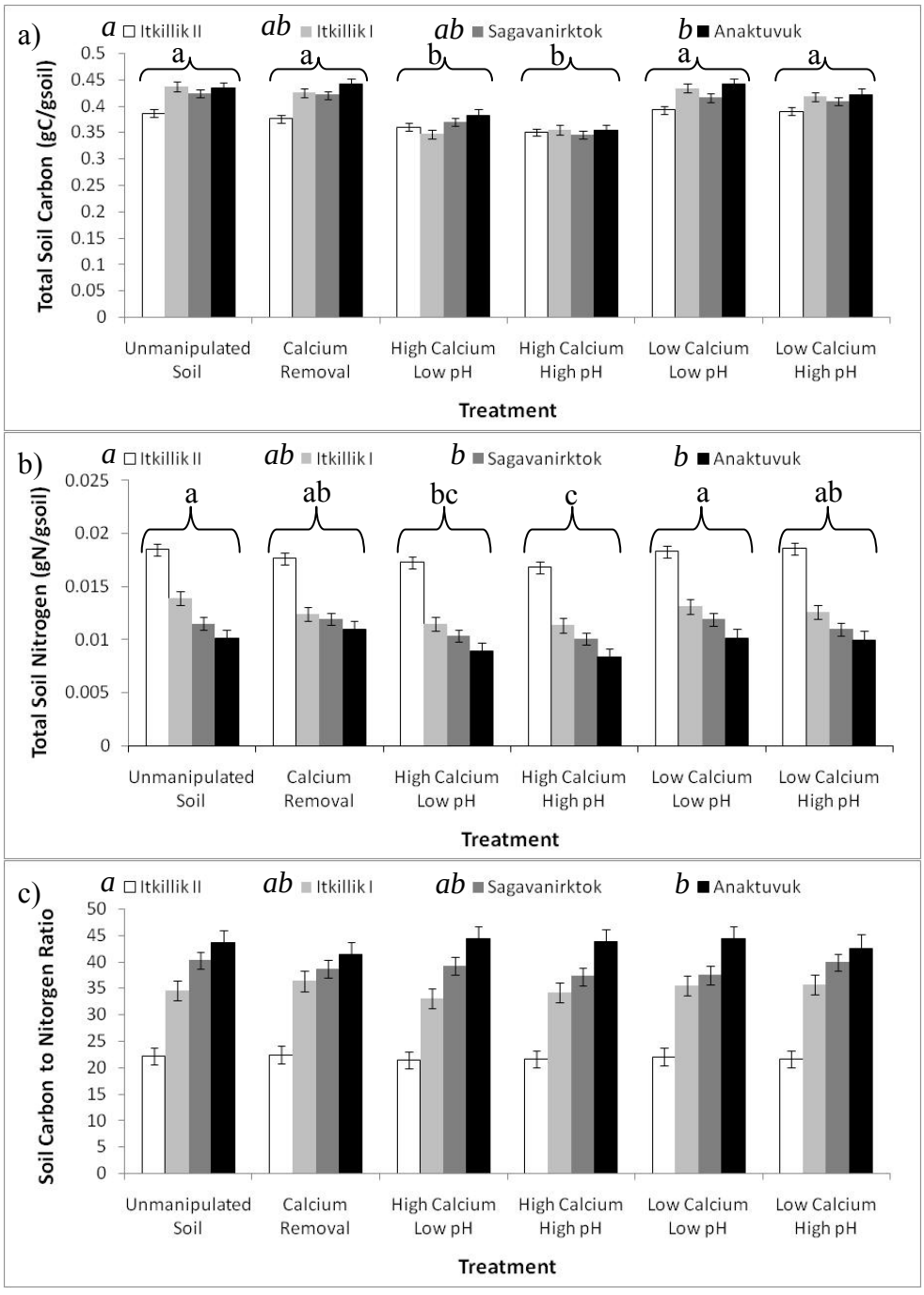
Significant age differences are indicated by different lowercase letters ($p<0.05$).

Figure 1.6:



Significant age differences are indicated by different lowercase letters ($p<0.05$).

Figure 2.1:

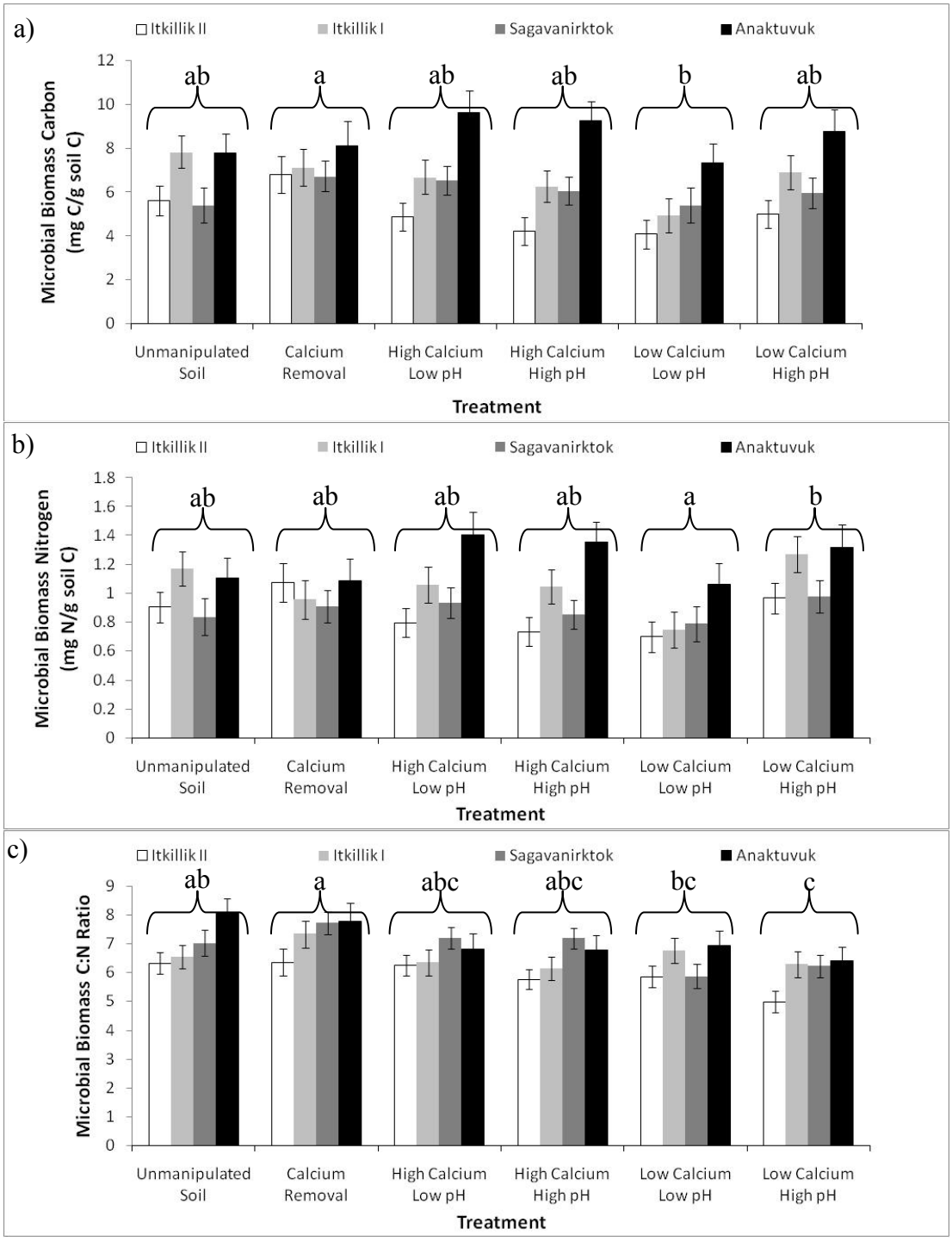


Error bars represent standard errors of the mean.

Significant differences among treatments are represented by lower case letters.

Significant differences among ages are represented by lower case letters in italics.

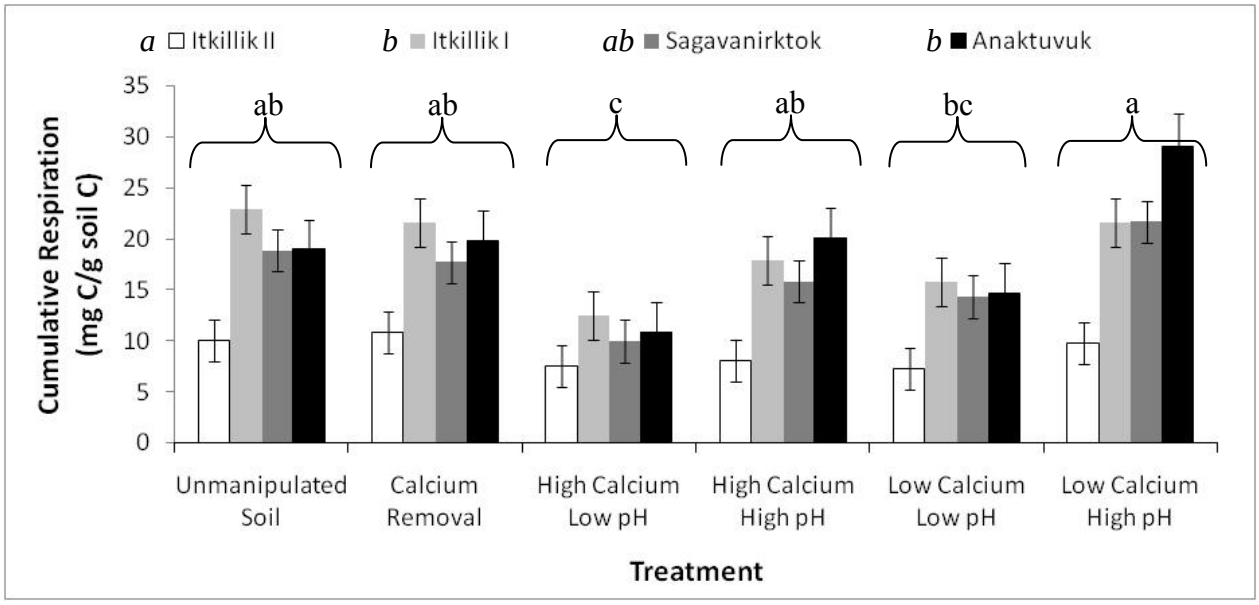
Figure 2.2:



Error bars represent standard errors of the mean.

Significant differences represented by lower case letters.

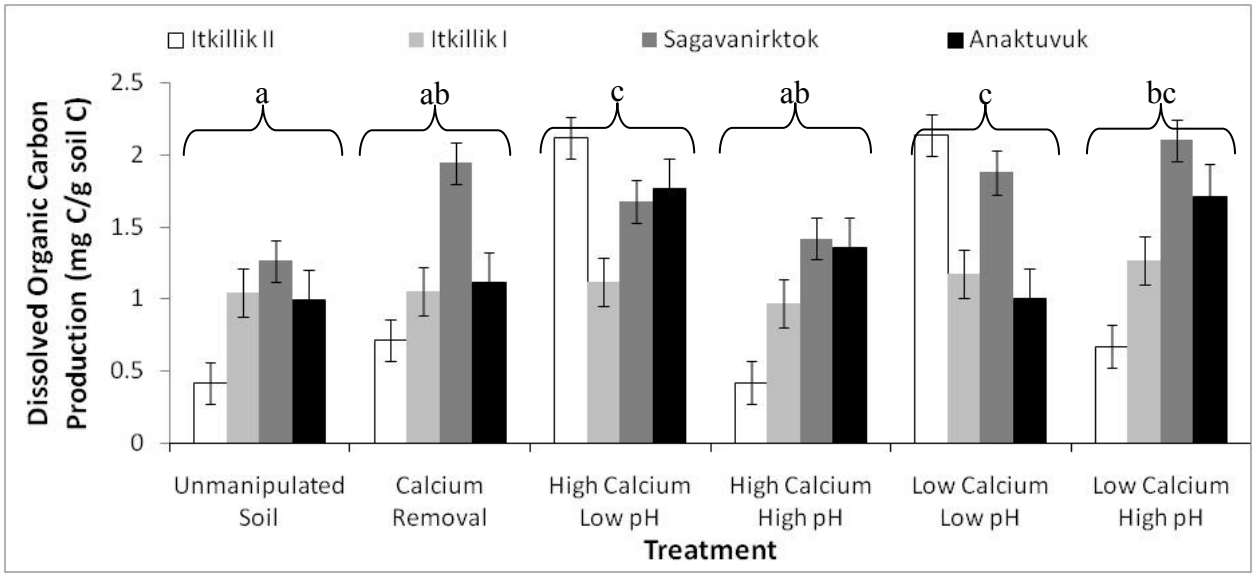
Figure 2.3:



Significant differences among treatments are represented by lower case letters.

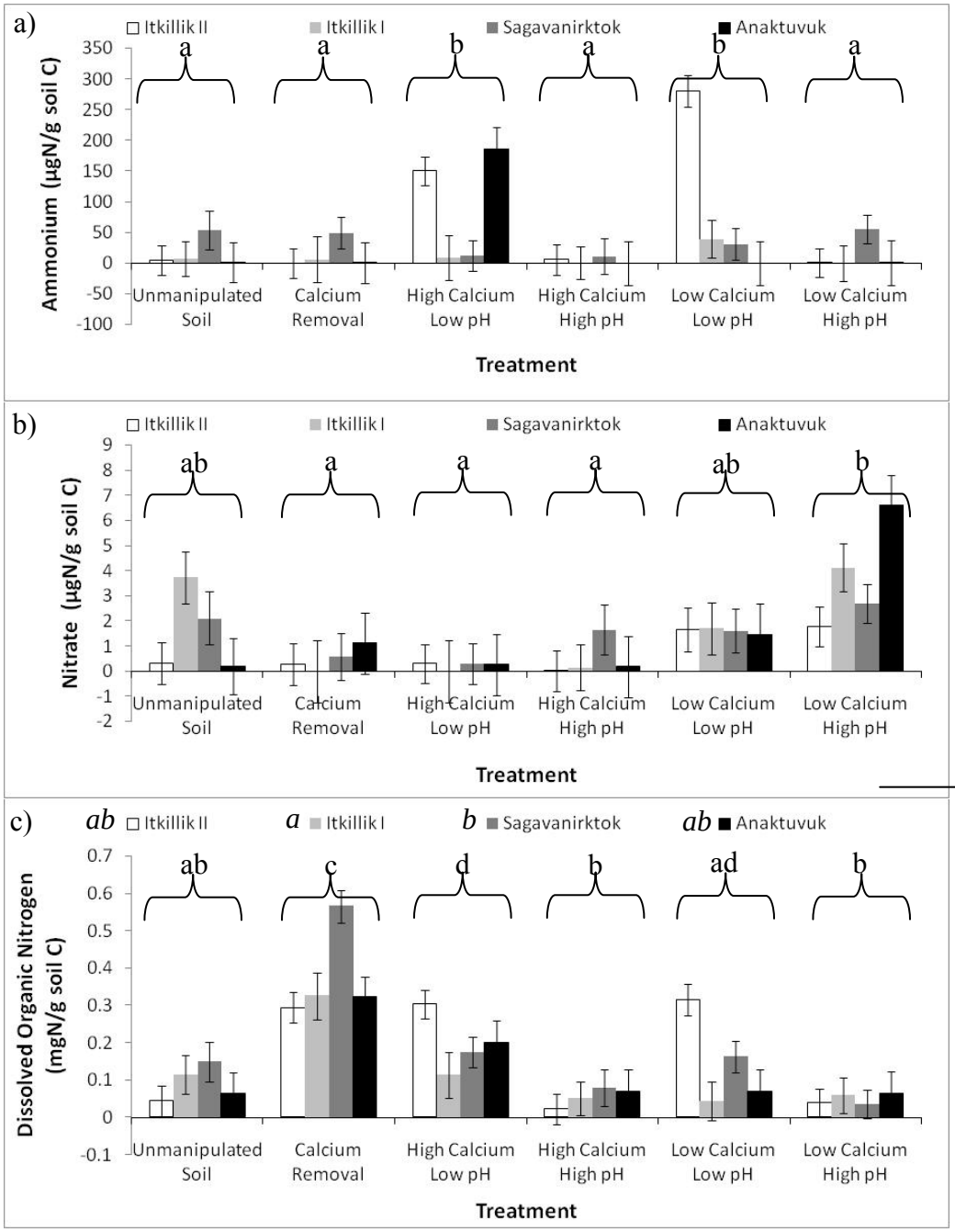
Significant differences among ages are represented by lower case letters in italics.

Figure 2.4:



Significant differences among treatments are represented by lower case letters.

Figure 2.5:

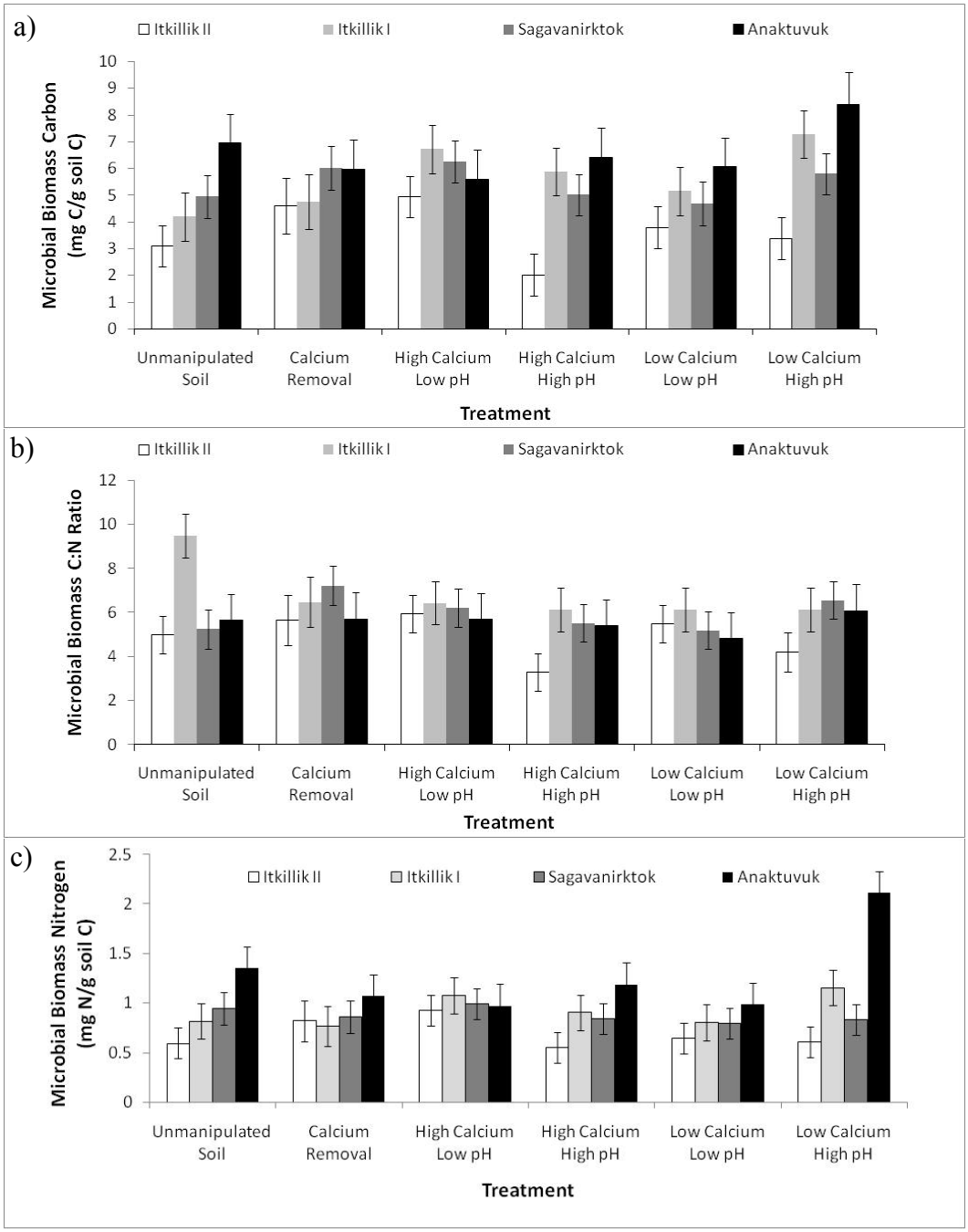


Significant differences among treatments are represented by lower case letters.

Significant differences among ages are represented by lower case letters in italics.

Error bars represent standard error of the mean.

Figure 2.6:



Error bars represent standard error of the mean.

Figure 3.1: (a) Map and (b) diagram of study sites.

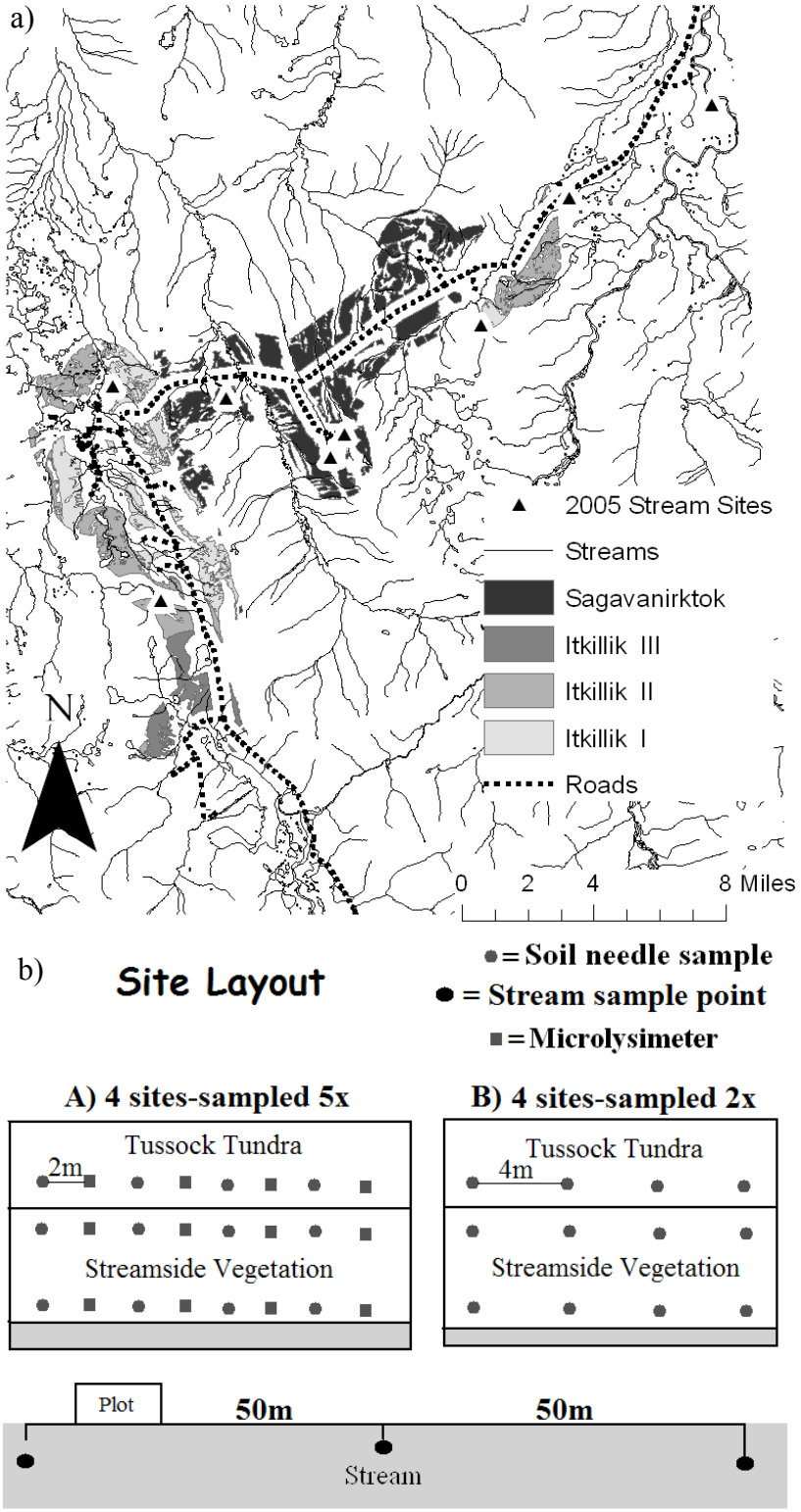
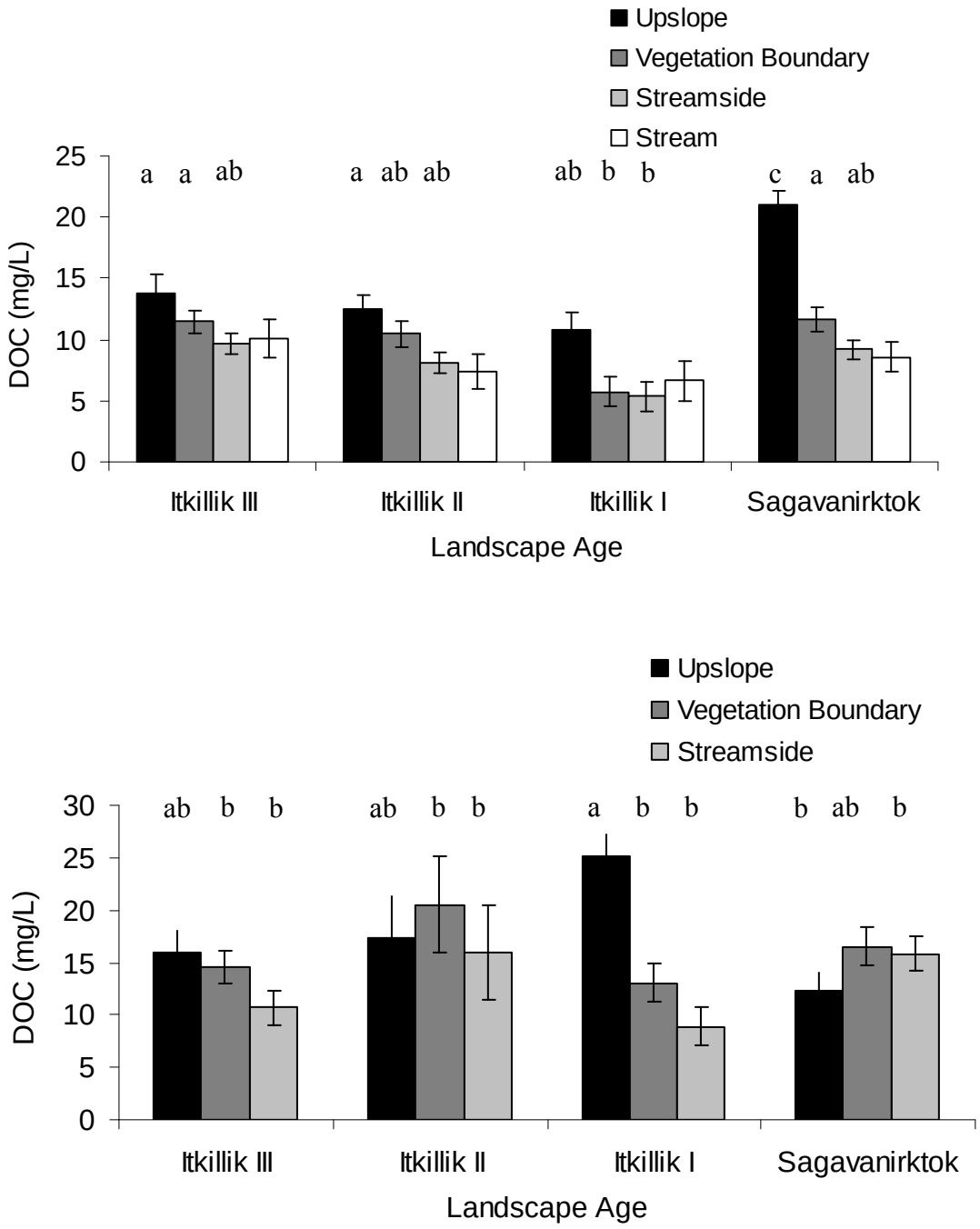
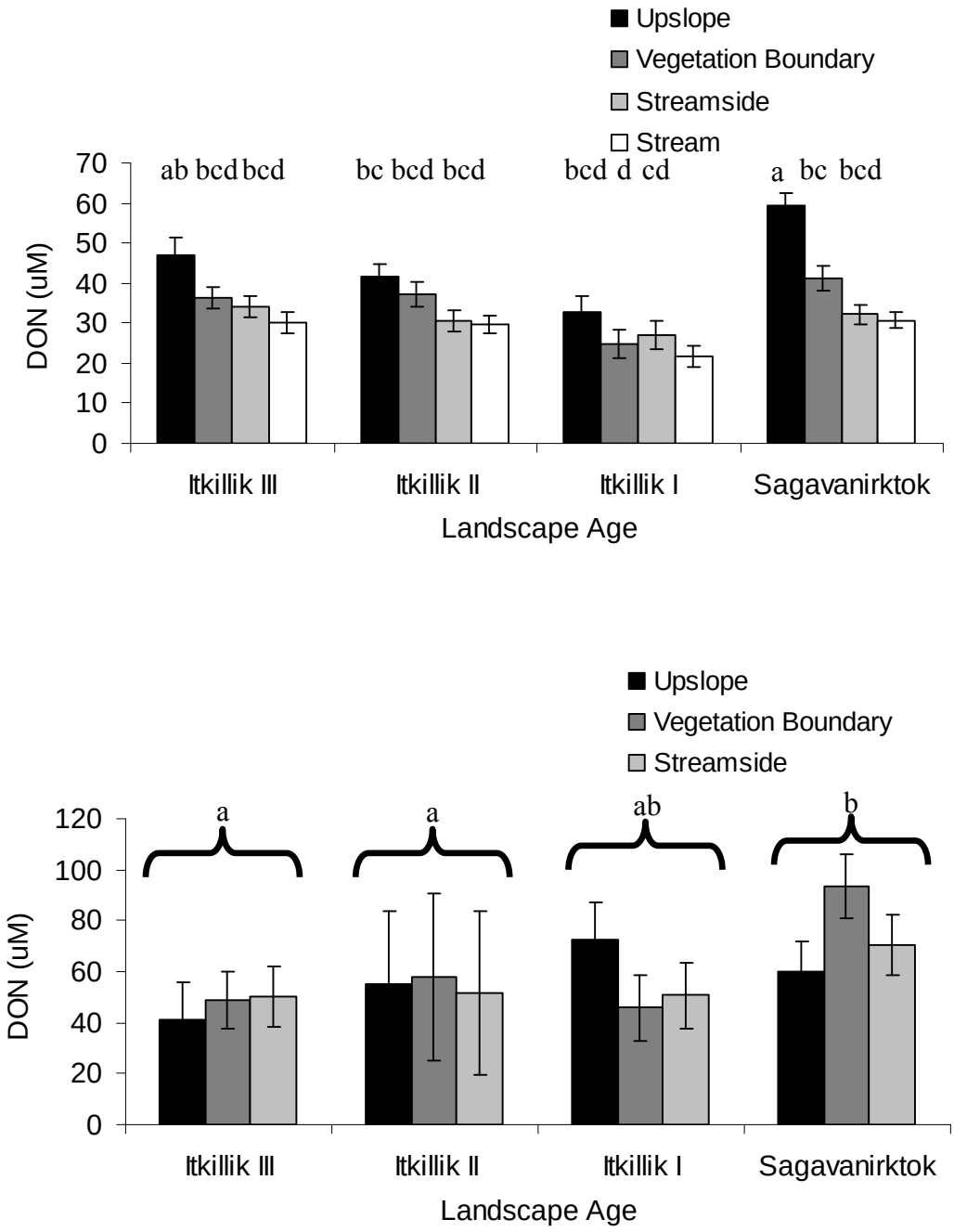


Figure 3.2:



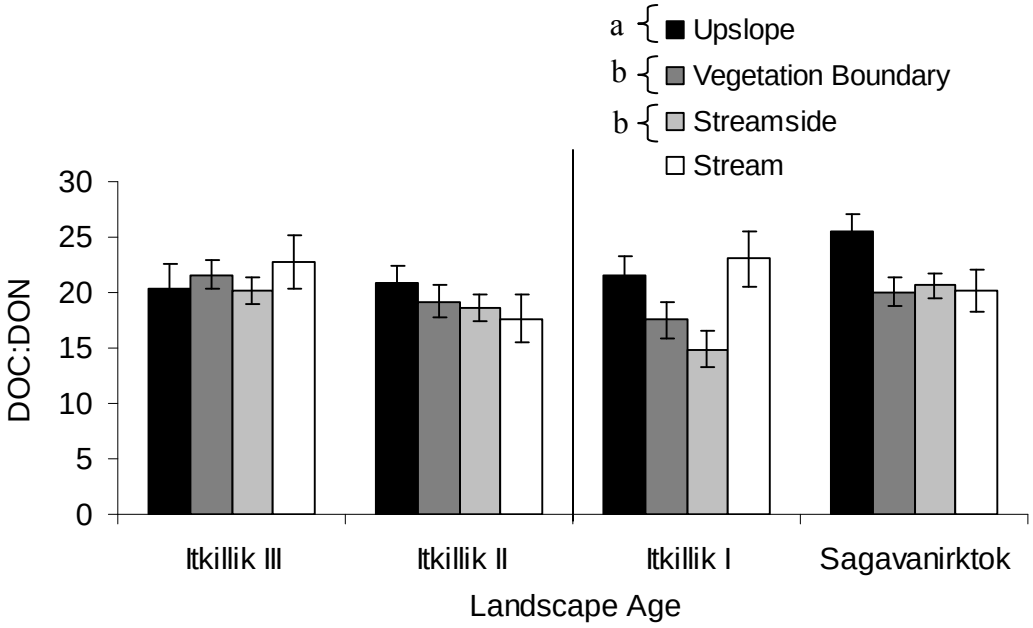
Lowercase letters represent significant differences among soil water samples ($p<0.05$).

Figure 3.3:



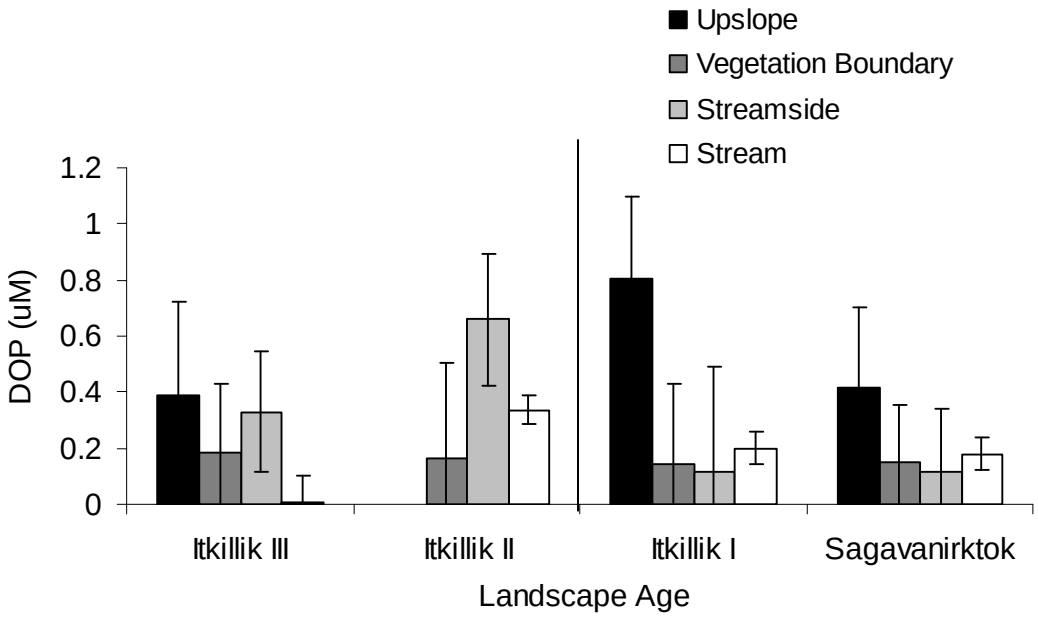
Lowercase letters represent significant differences among soil water samples ($p<0.05$).

Figure 3.4:



Lowercase letters represent significant differences among hillslope positions ($p<0.05$).

Figure 3.5:


Upslope
Vegetation Boundary
Streamside
Stream
DOP (uM)
1.2
1
0.8
0.6
0.4
0.2
0
Itkillik III
Itkillik II
Itkillik I
Sagavanirktok
Landscape Age

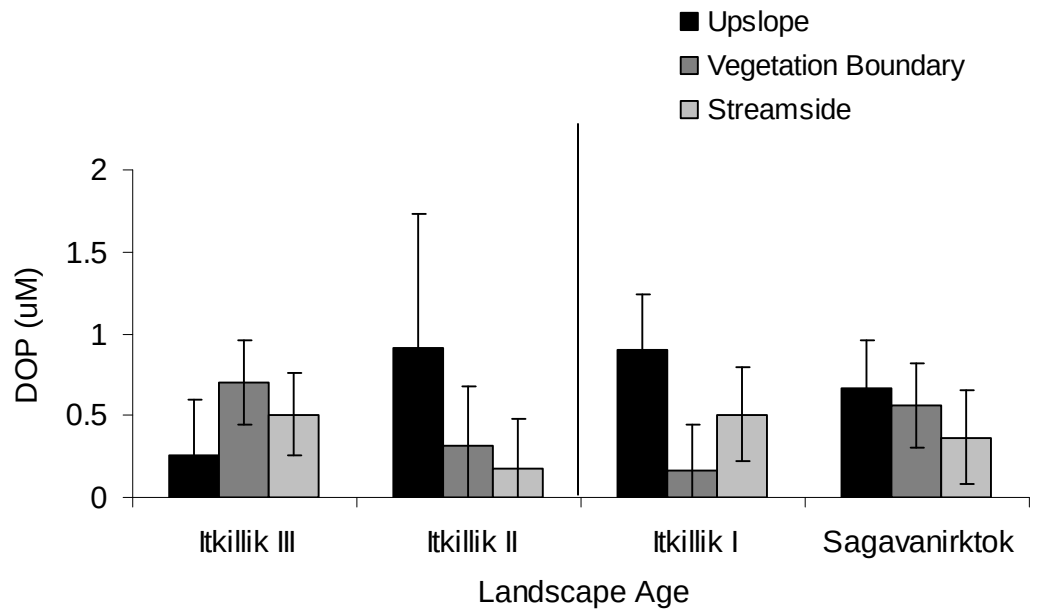
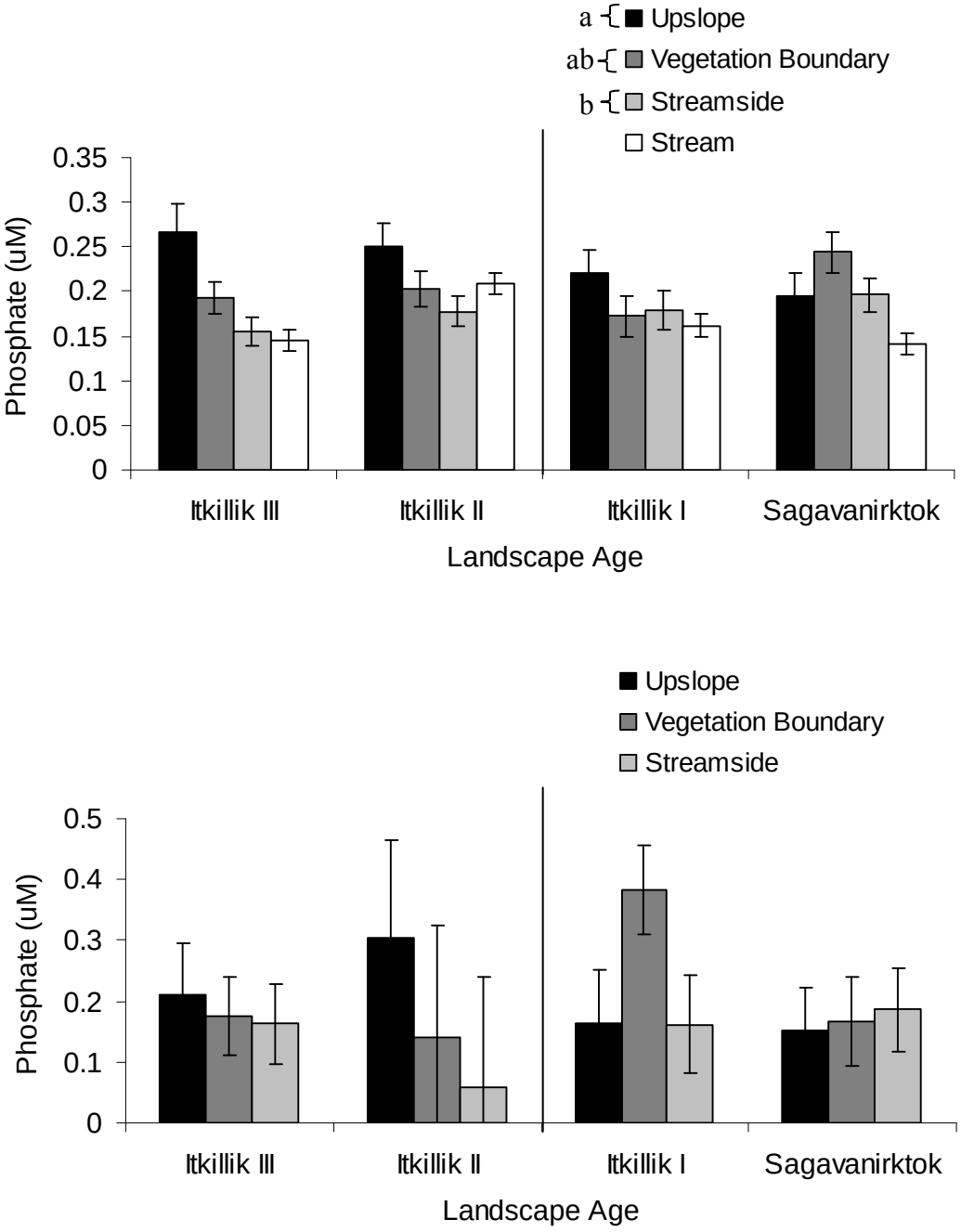
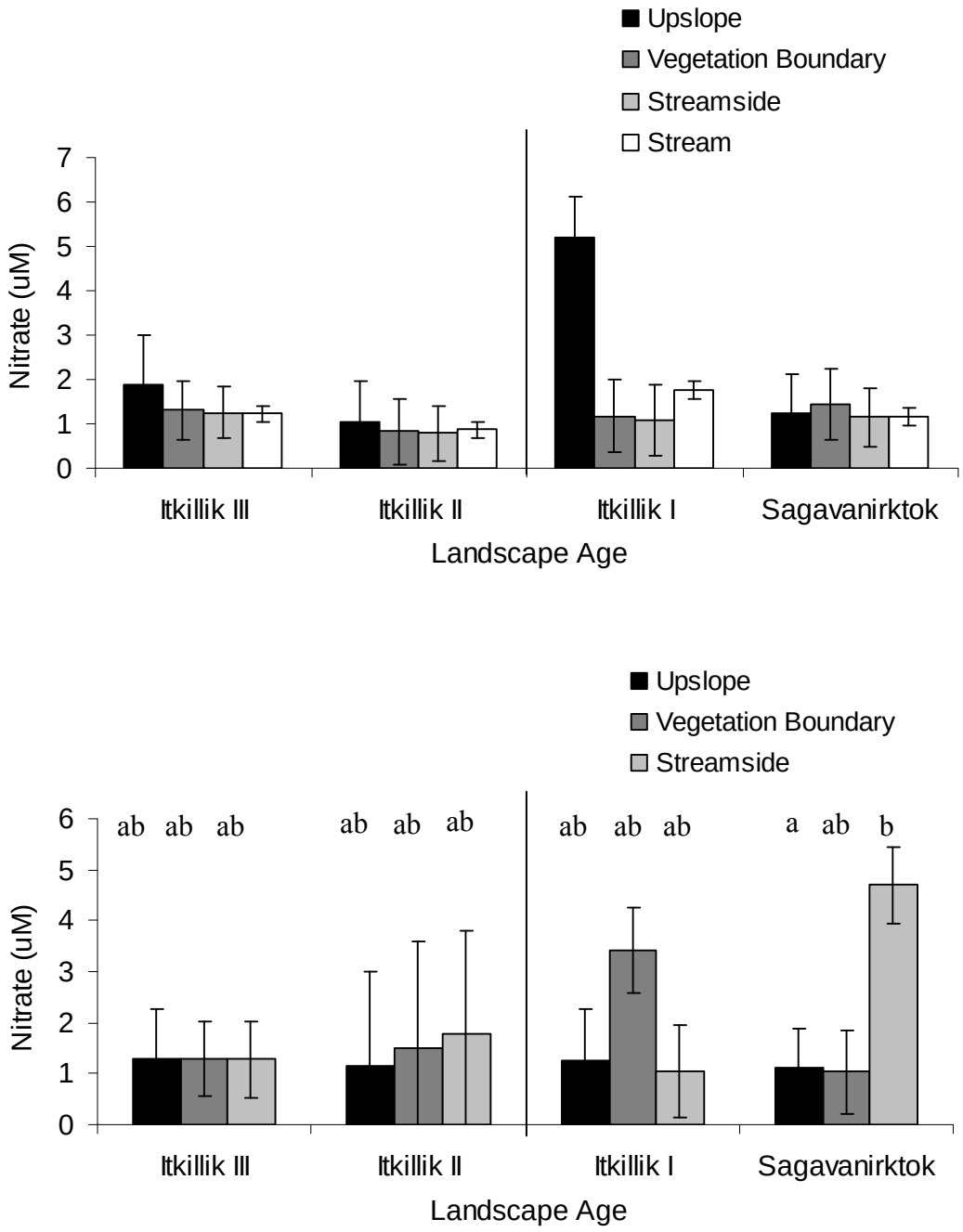

Upslope
Vegetation Boundary
Streamside
DOP (uM)
2
1.5
1
0.5
0
Itkillik III
Itkillik II
Itkillik I
Sagavanirktok
Landscape Age

Figure 3.6:



Lowercase letters represent significant differences among hillslope positions.

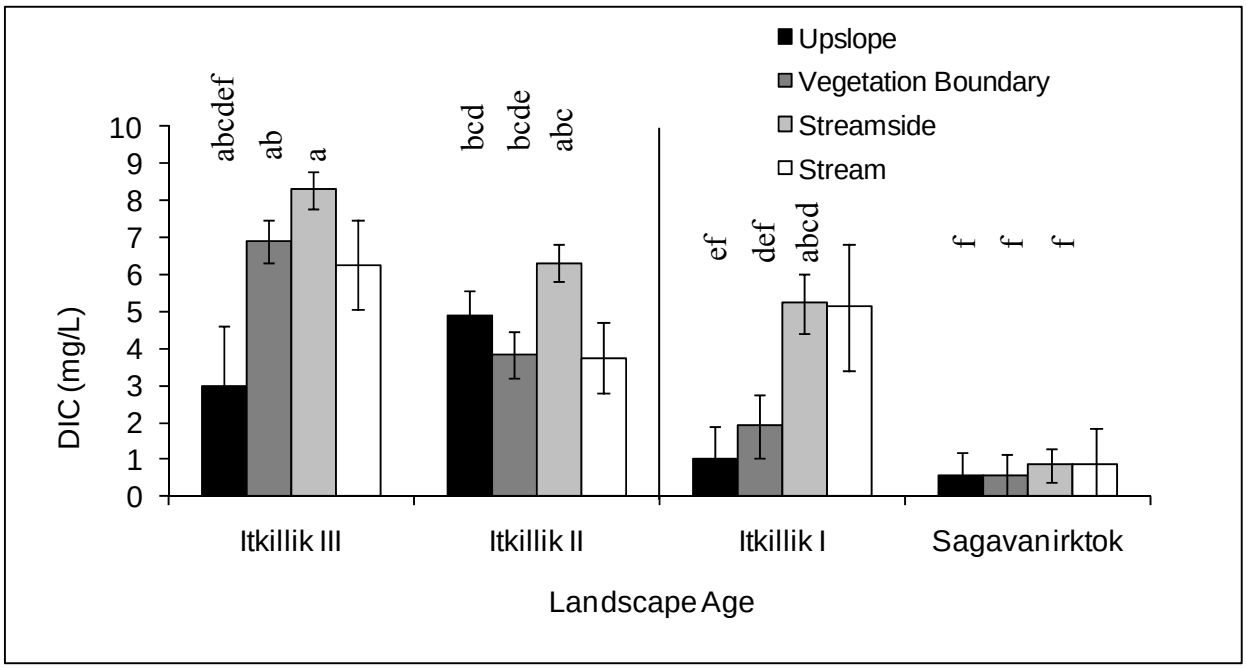
Figure 3.7:



Lowercase letters represent significant differences among soil water samples.

Figure 3.8:

a)


Upslope
Vegetation Boundary
Streamside
Stream
abcdef
ab
a
bcd
bcde
abc
ef
def
abcd
f
f
f
DIC (mg/L)
0
1
2
3
4
5
6
7
8
9
10
Itkillik III
Itkillik II
Itkillik I
Sagavanirktok
Landscape Age

b)

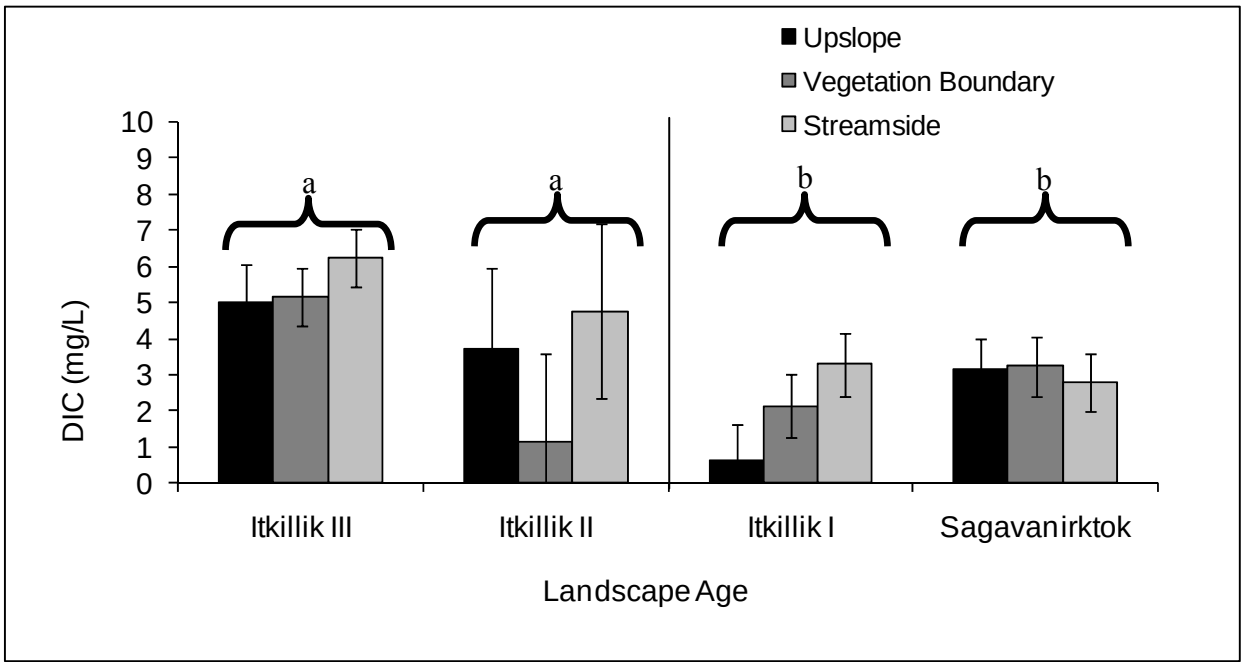

Upslope
Vegetation Boundary
Streamside
a
a
b
b
DIC (mg/L)
0
1
2
3
4
5
6
7
8
9
10
Itkillik III
Itkillik II
Itkillik I
Sagavanirktok
Landscape Age

Figure 4.1: Map of stream sites

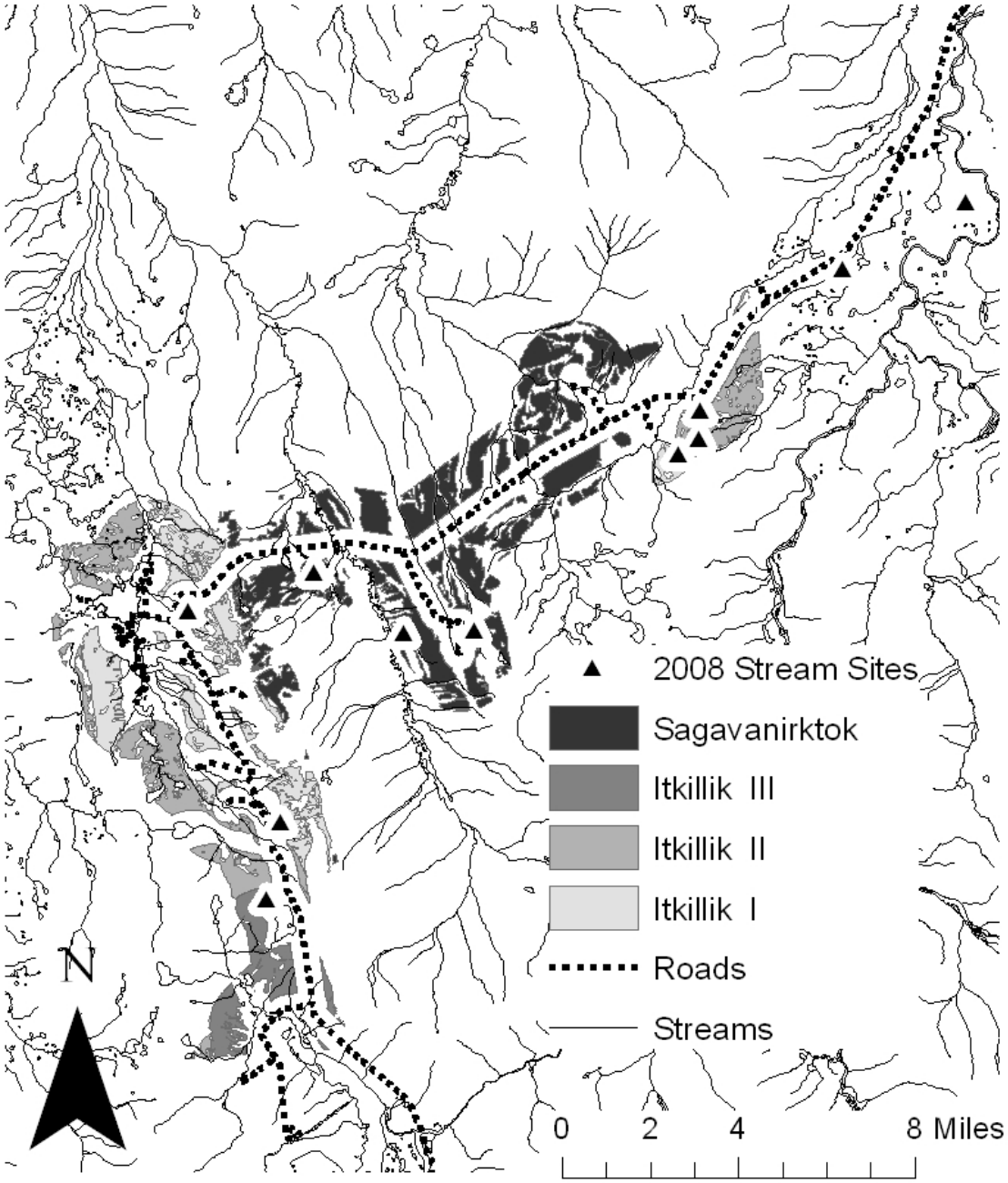
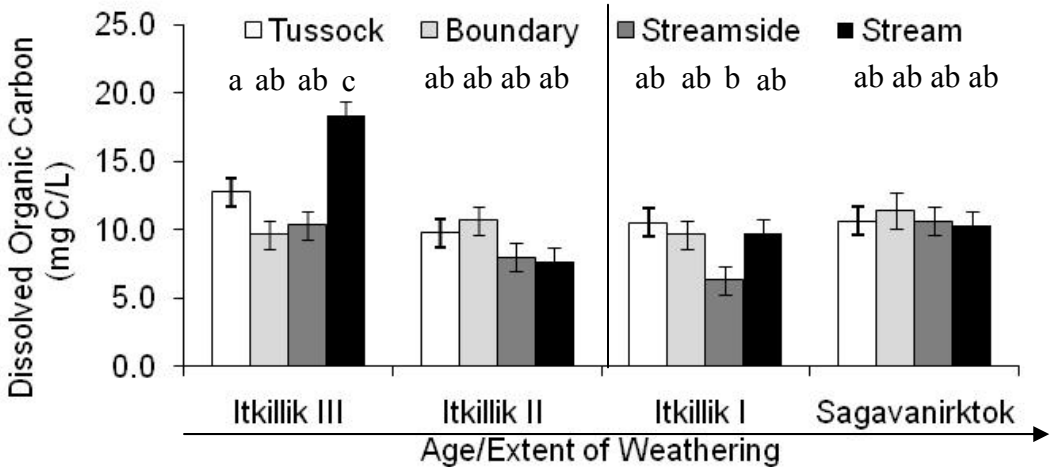
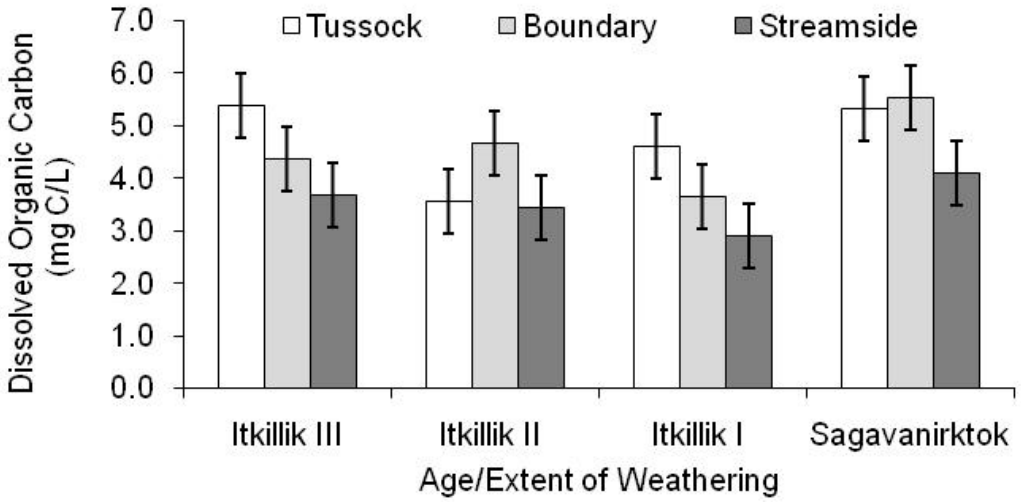


Figure 4.2:



Significant differences among age x transect combinations are represented by lowercase letters.

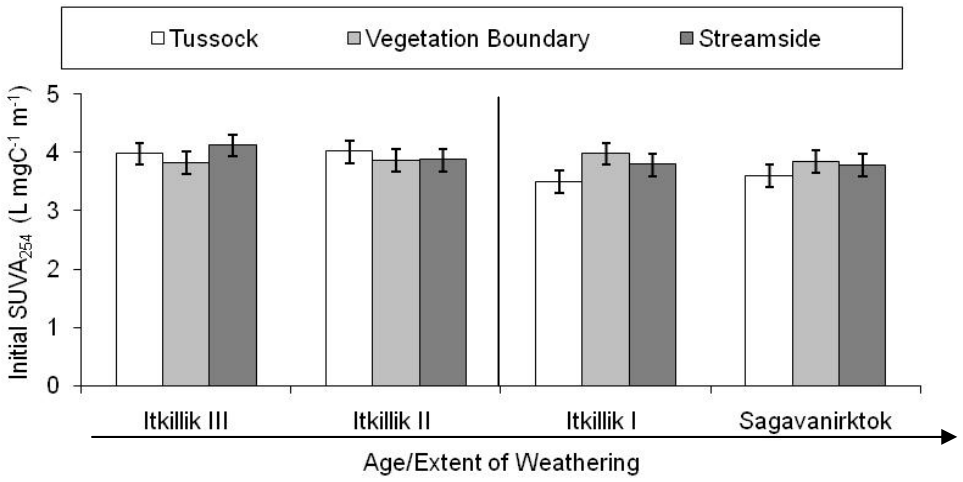
Figure 4.3:



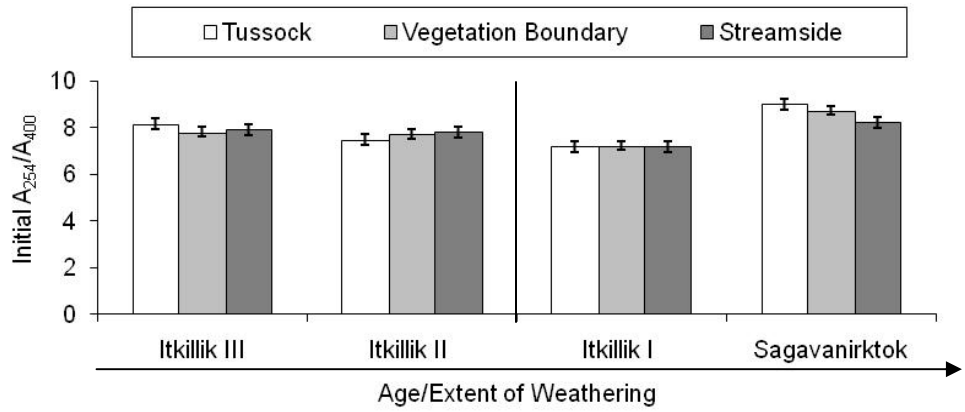
Significant differences between transects are represented by lowercase letters.

Figure 4.4:

a)



b)



c)

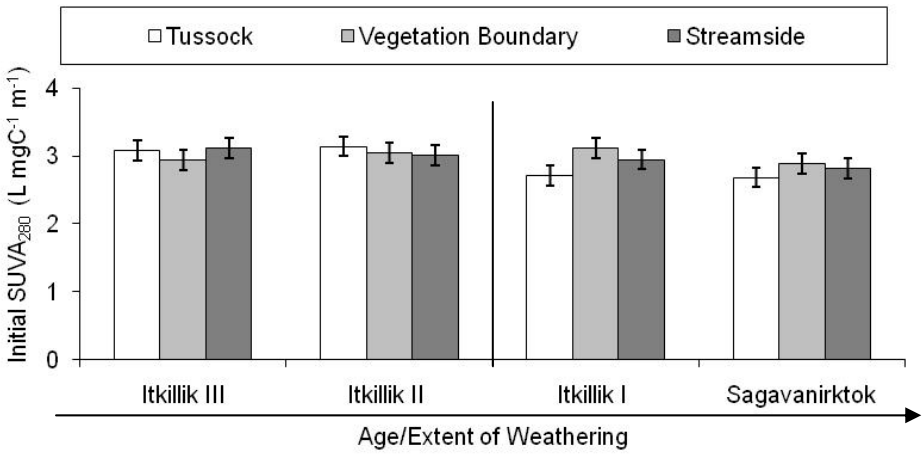
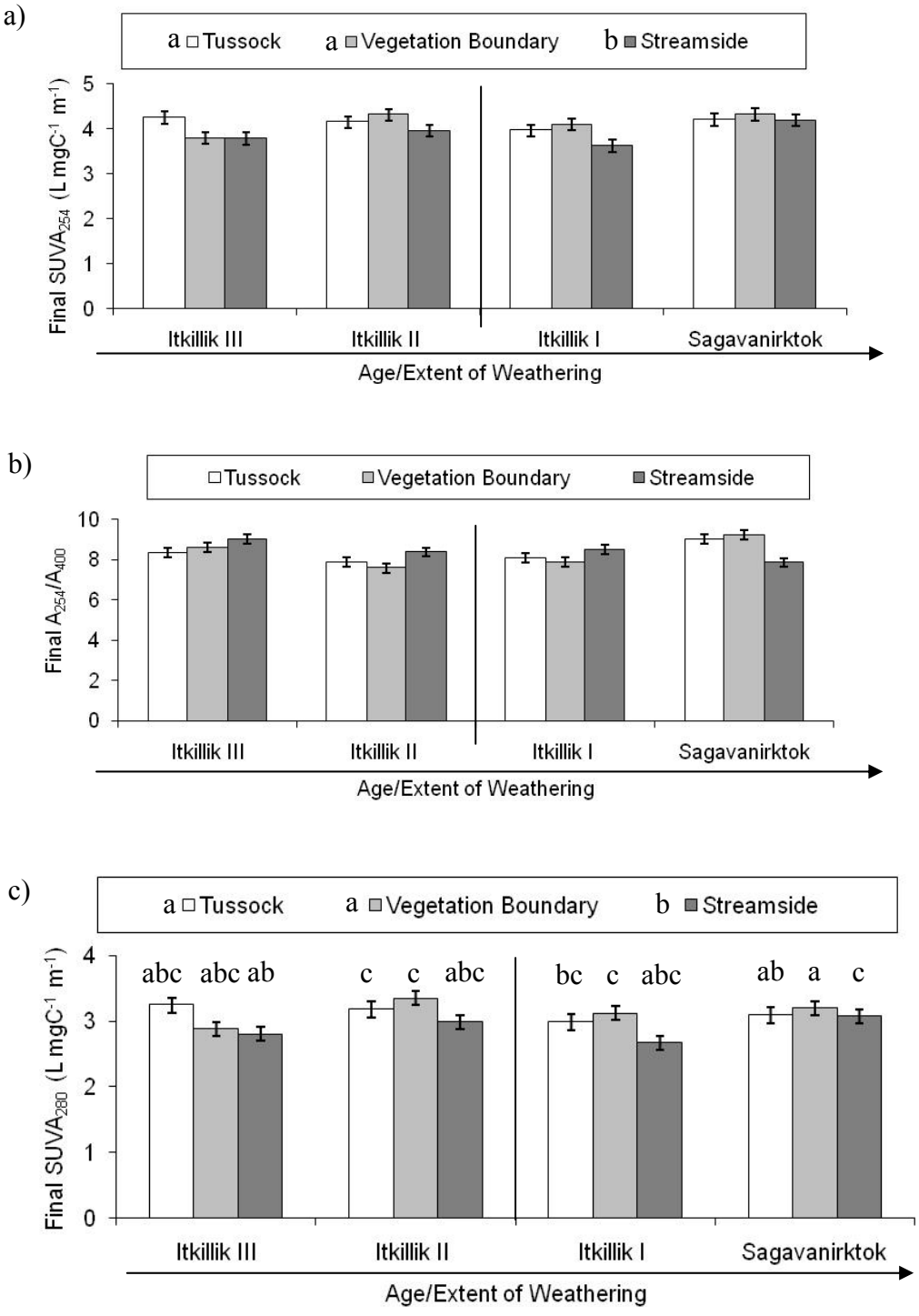


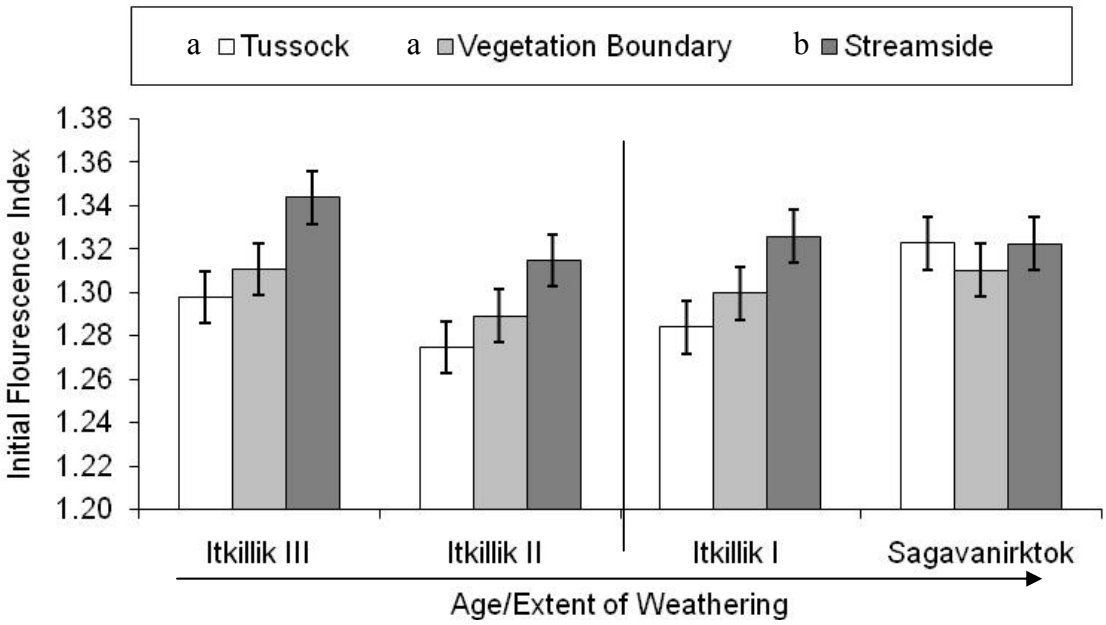
Figure 4.5:



Significant differences among age by transect combinations are represented by lower case letters.

Figure 4.6:

a)


a Tussock
a Vegetation Boundary
b Streamside
Initial Flourescence Index
1.38
1.36
1.34
1.32
1.30
1.28
1.26
1.24
1.22
1.20
Itkillik III
Itkillik II
Itkillik I
Sagavanirktok
Age/Extent of Weathering

b)

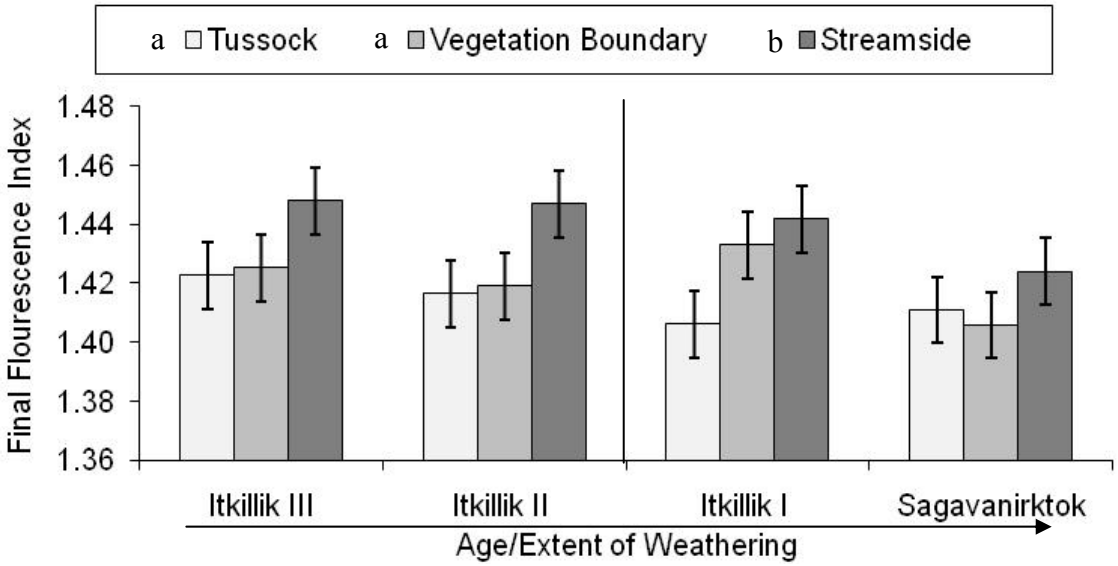
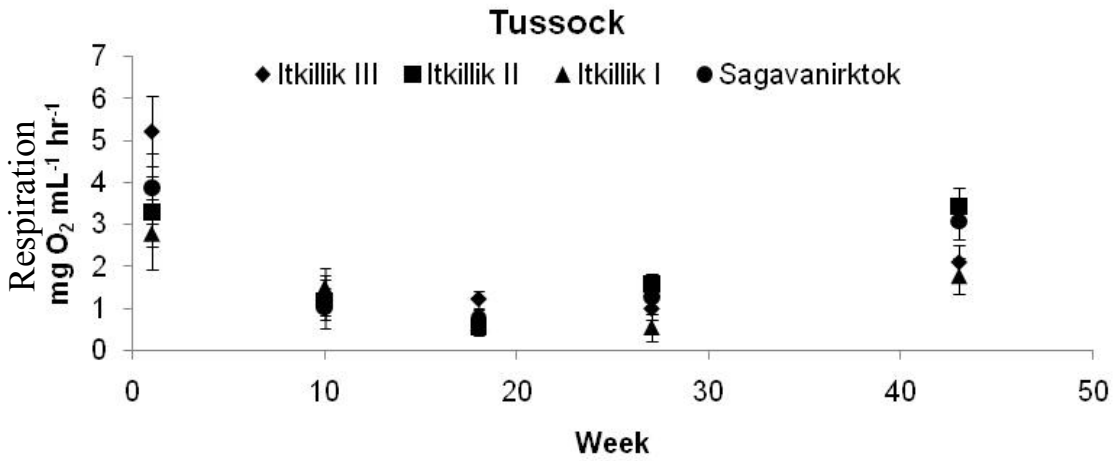
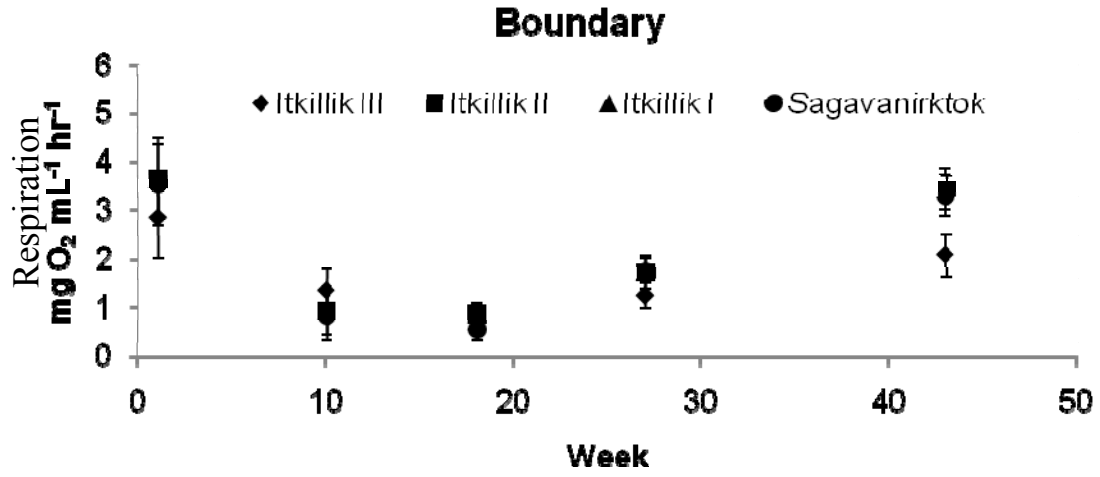

a Tussock
a Vegetation Boundary
b Streamside
Final Flourescence Index
1.48
1.46
1.44
1.42
1.40
1.38
1.36
Itkillik III
Itkillik II
Itkillik I
Sagavanirktok
Age/Extent of Weathering

Figure 4.7:

a)



b)



c)

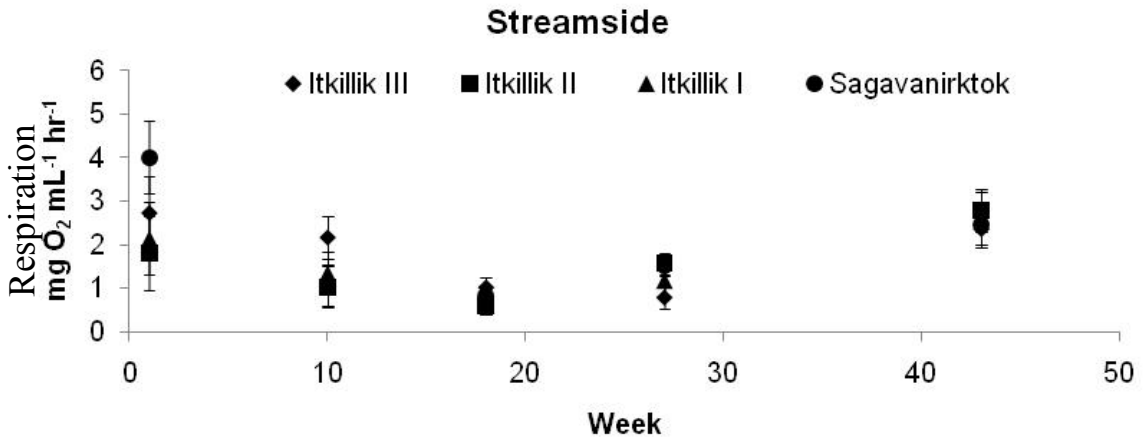


Figure 4.8:

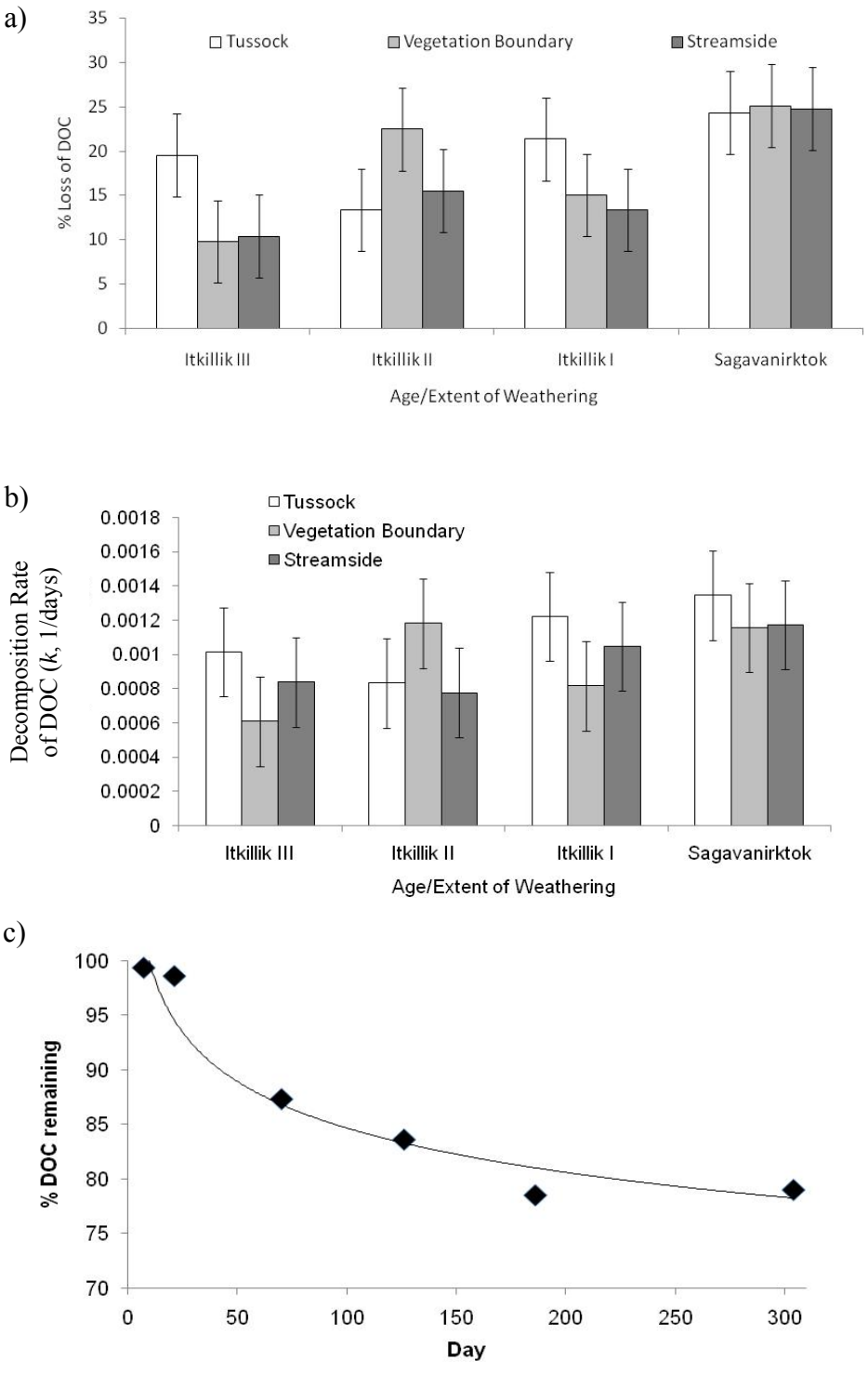
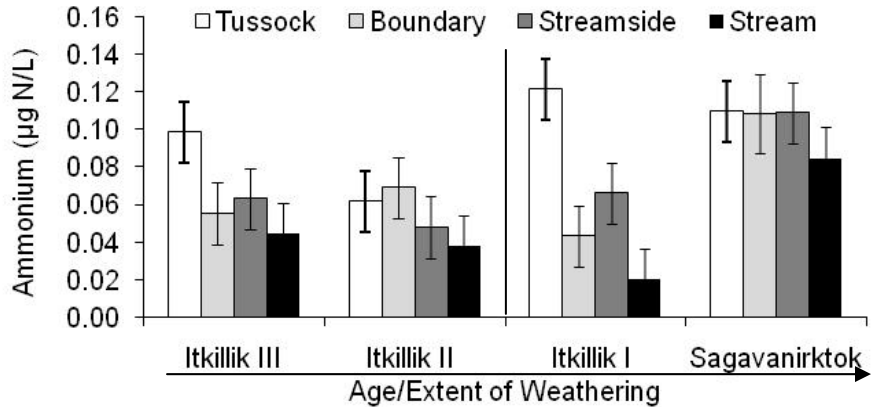
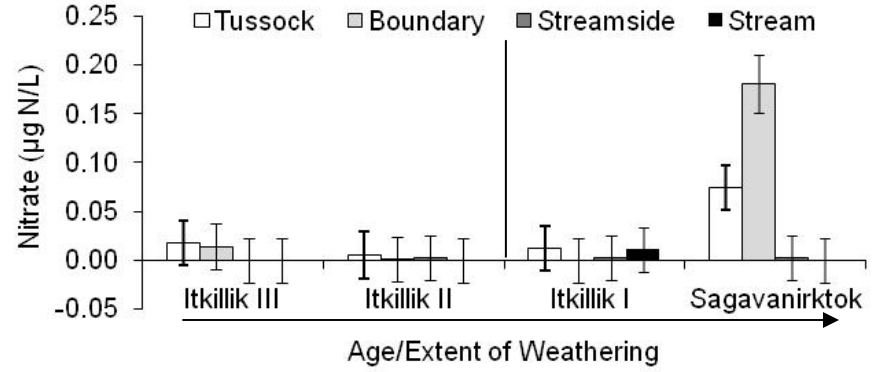

a)
Tussock
Vegetation Boundary
Streamside
% Loss of DOC
35
30
25
20
15
10
5
0
Itkillik III
Itkillik II
Itkillik I
Sagavanirktok
Age/Extent of Weathering
b)
Tussock
Vegetation Boundary
Streamside
Decomposition Rate of DOC (k, 1/days)
0.0018
0.0016
0.0014
0.0012
0.001
0.0008
0.0006
0.0004
0.0002
0
Itkillik III
Itkillik II
Itkillik I
Sagavanirktok
Age/Extent of Weathering
c)
% DOC remaining
100
95
90
85
80
75
70
0
50
100
150
200
250
300
Day

Figure 4.9:

a)



b)



c)

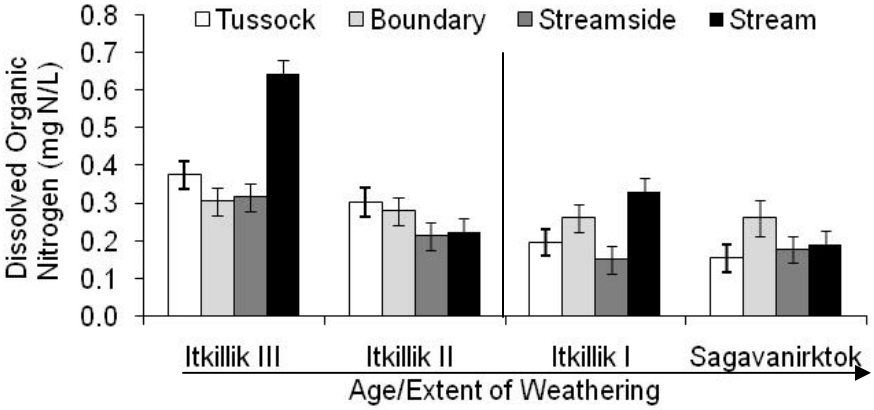
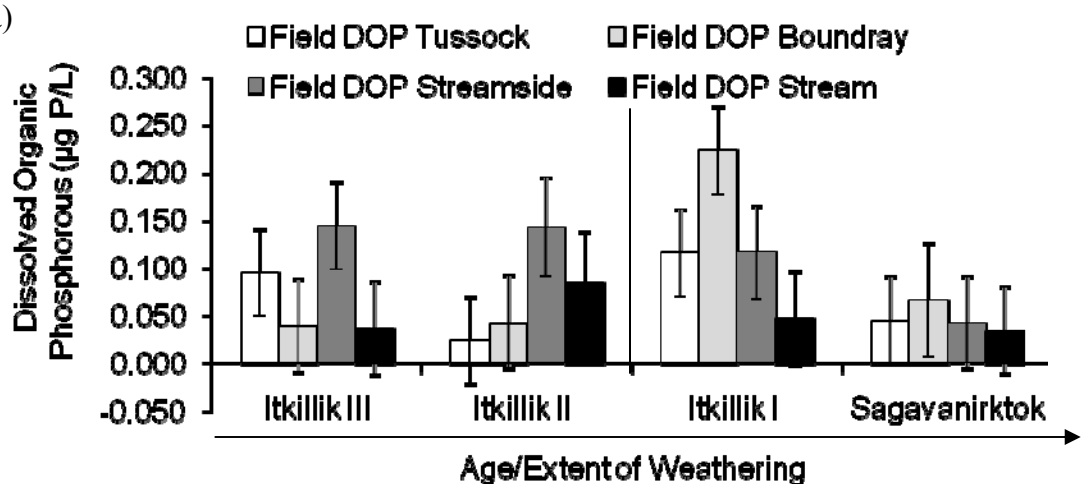


Figure 4.10:

a)



b)

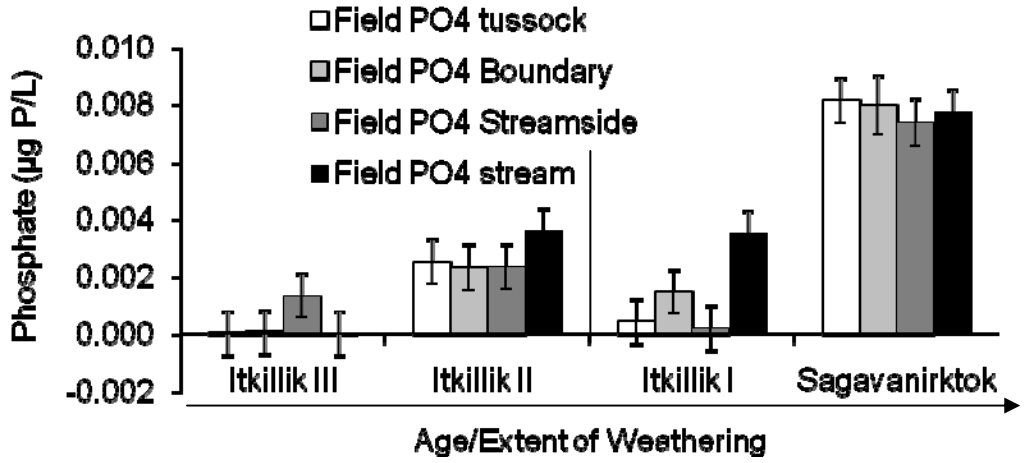
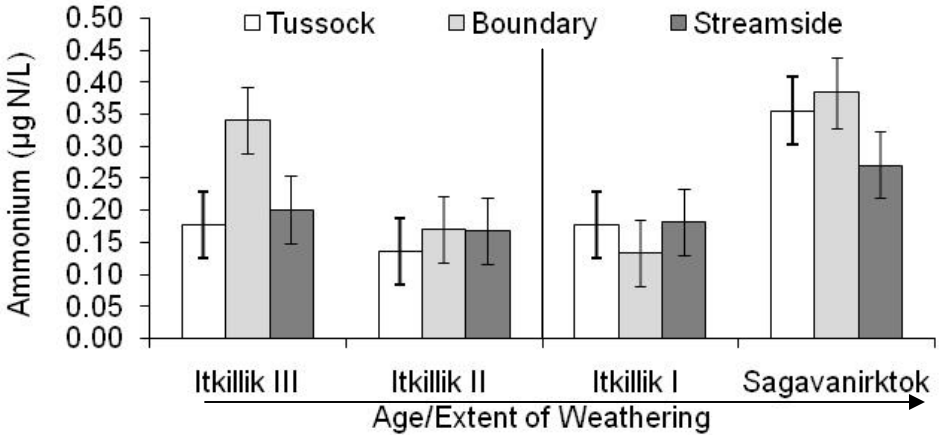
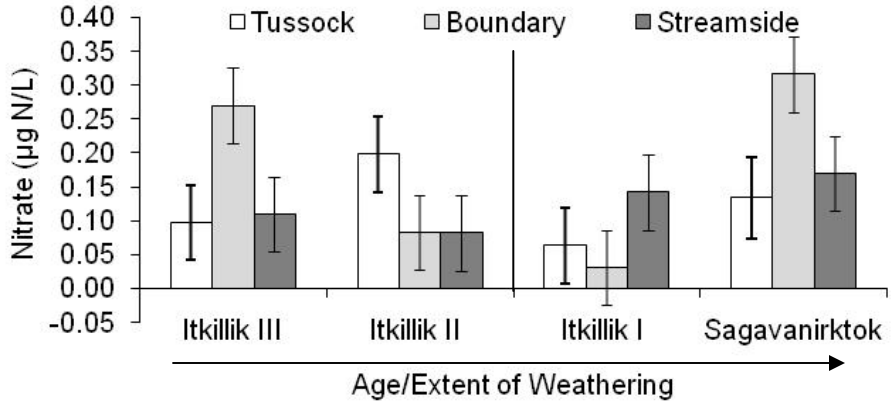


Figure 4.11:

a)



b)



c)

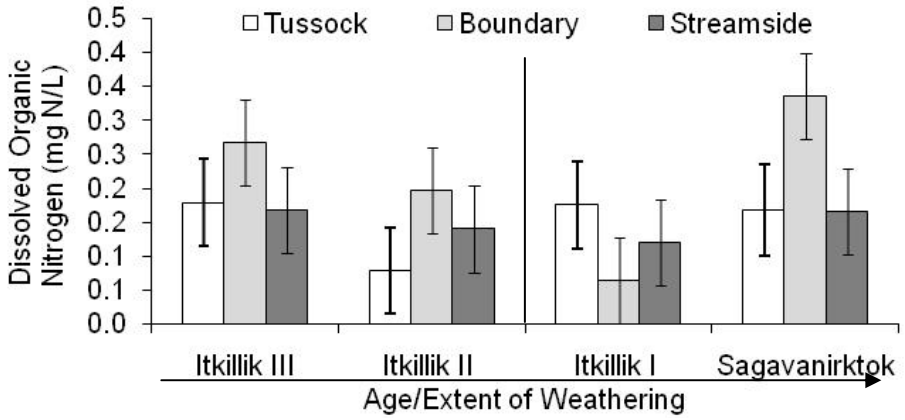


Figure 4.12:

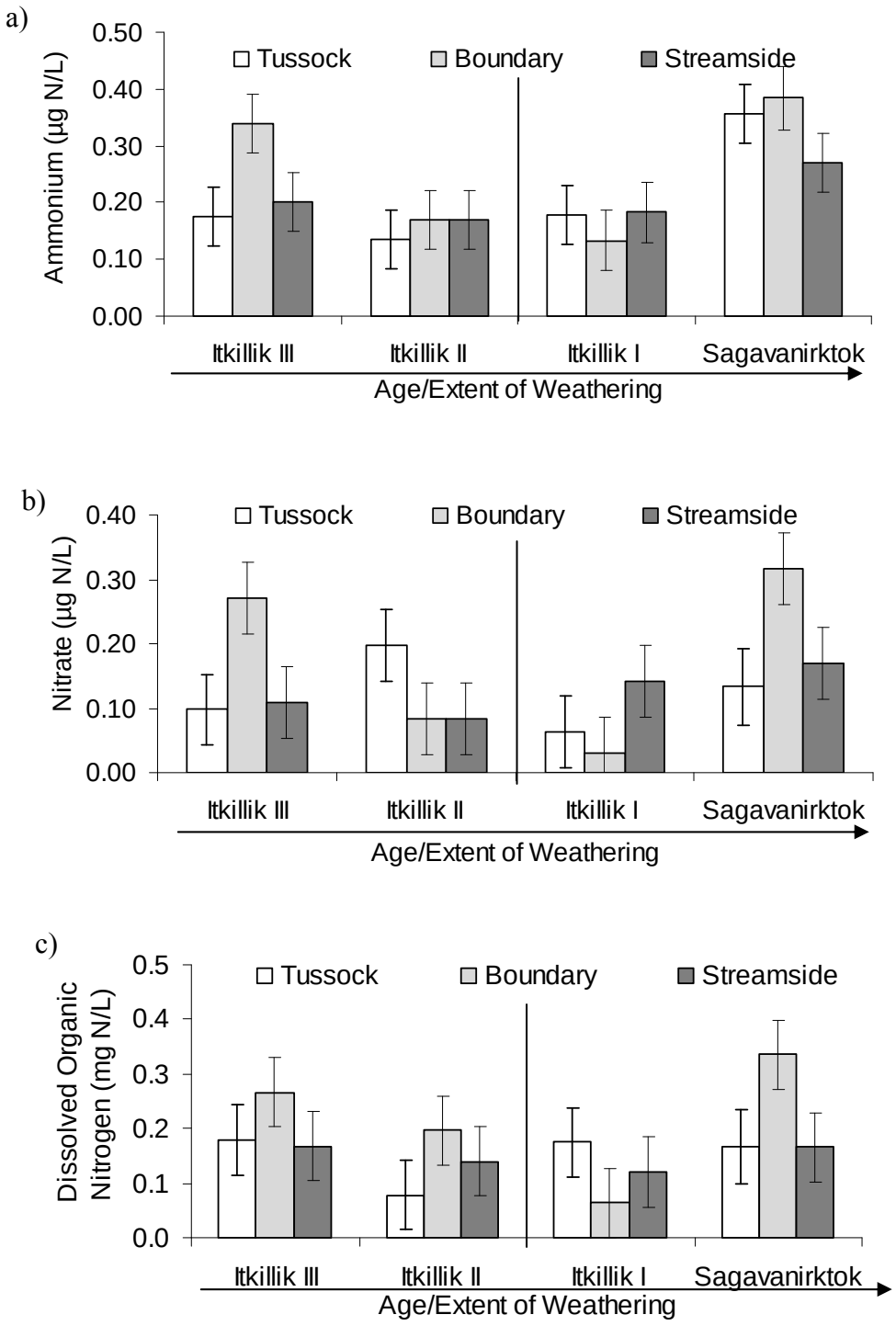
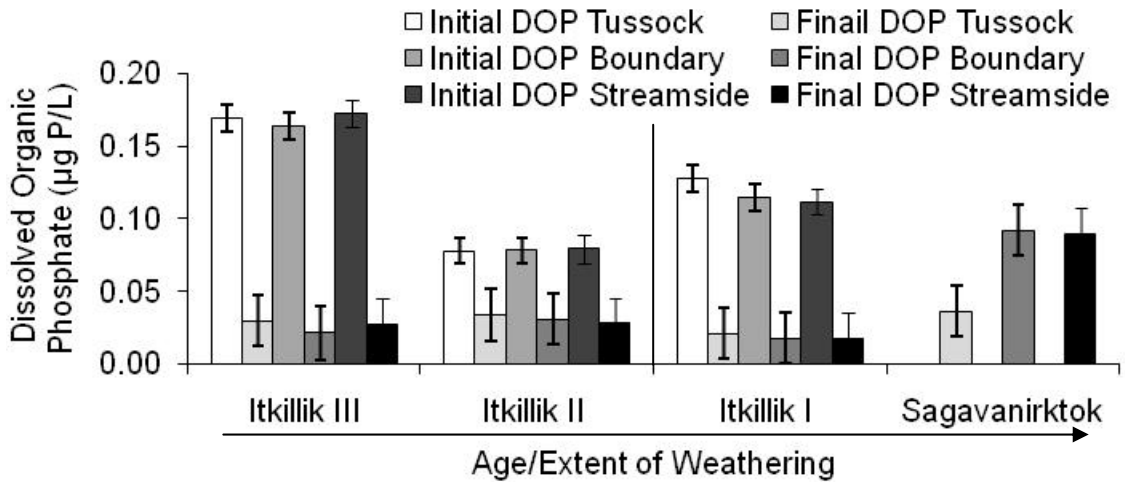
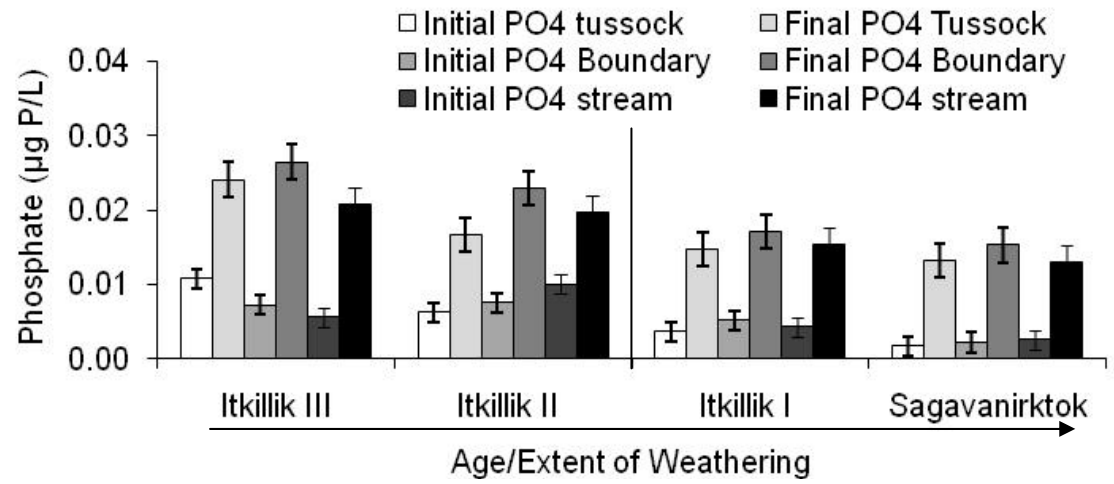

a)
Ammonium (µg N/L)
0.50
0.40
0.30
0.20
0.10
0.00
Tussock
Boundary
Streamside
Itkillik III
Itkillik II
Itkillik I
Sagavanirktok
Age/Extent of Weathering
b)
Nitrate (µg N/L)
0.40
0.30
0.20
0.10
0.00
Tussock
Boundary
Streamside
Itkillik III
Itkillik II
Itkillik I
Sagavanirktok
Age/Extent of Weathering
c)
Dissolved Organic Nitrogen (mg N/L)
0.5
0.4
0.3
0.2
0.1
0.0
Tussock
Boundary
Streamside
Itkillik III
Itkillik II
Itkillik I
Sagavanirktok
Age/Extent of Weathering

Figure 4.13:

a)



b)



References

Aiken, G. R. and E. Cotsaris. 1995. Soil and Hydrology: their effect on NOM. Journal AWWA:36-45.

Anderson, D. R., K. P. Burnham, and W. L. Thompson. 2000. Null hypothesis testing: problems, prevalence, and an alternative. Journal of Wildlife Management **64**:912-923.

Andersson, S., S. I. Nilsson, and P. Saetre. 2000. Leaching of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) in mor humus as affected by temperature and pH. Soil Biology & Biochemistry **32**:1-10.

Beck, T., G. Joergensen, E. Kandeler, E. Makeschin, H. R. Oberholzer, and S. Scheu. 1997. An inter-laboratory comparison of ten different ways of measuring soil microbial biomass C. Soil Biology and Biochemistry **29**:1023-1032.

Bengtsson, G. and N. Torneman. 2004. Dissolved organic carbon dynamics in the peat-streamwater interface. Biogeochemistry **70**:93-116.

Benner, R., B. Benitez-Nelson, K. Kaiser, and R. M. W. Amon. 2004. Export of young terrigenous dissolved orgnaic carbon from rivers to the Arctic ocean. Geophysical Research Letters **31**:L05305.

Benner, R., P. Louchouarn, and R. M. W. Amon. 2005. Terrigenous dissolved organic matter in the Arctic Ocean and its transport to surface and deep waters of the North Atlantic. Global Biogeochemical Cycles **19**.

Berman, T. and D. A. Bronk. 2003. Dissolved organic nitrogen: a dynamic participant in aquatic ecosystems. Aquatic Microbial Ecology **31**:279-305.

Bernhardt, E. S., G. E. Likens, R. O. Hall, D. C. Buso, S. G. Fisher, T. M. Burton, J. L. Meyer, W. H. McDowell, M. S. Mayer, W. B. Bowden, S. E. G. Findlay, K. H. Macneale, R. S. Stelzer, and W. H. Lowe. 2005. Can't see the forest for the stream? - In-stream processing and terrestrial nitrogen exports. Bioscience **55**:219-230.

Brookshire, E. N. J., H. M. Valett, S. A. Thomas, and J. R. Webster. 2005. Coupled cycling of dissolved organic nitrogen and carbon in a forest stream. Ecology **86**:2487-2496.

Bockheim, J. G., D. A. Walker, L. R. Everett, F. E. Nelson, and N. I. Shiklomanov. 1998. Soils and cryoturbation in moist nonacidic and acidic tundra in the Kuparuk River Basin, Arctic Alaska, U.S.A. Arctic and Alpine Research **30**:166-174.

Brookes, P. C., A. Landman, G. Pruden, and D. S. Jenkinson. 1985. Chloroform fumigation and the release of soil nitrogen: a rapid direct extraction method to measure microbial biomass nitrogen in soil. Soil Biology and Biochemistry **17**:837-842.

Callaghan, T. V., and S. Jonasson. 1995. Implications for Changes in Arctic Plant Biodiversity from Environmental Manipulation Experiments. in, Arctic and Alpine Biodiversity: Patterns Causes and Ecosystem Consequences ed. O.L. Lange, H.A. Mooney, Springer Verlag, NY. Ecological Studies Vol. **113**.

Caraco, N. F., and J. J. Cole. 2002. When terrestrial carbon is sent down the river: Importance of allochthonous carbon input to the metabolism of lakes and rivers.*in*

G. A. Polis and M. E. Power, editors. Food Webs at the Landscape Level. University of Chicago Press.

Chapin, F. S., III, and G. R. Shaver. 1989. Differences in growth and nutrient use among arctic plant growth forms. Functional Ecology **3**:73-80.

Chapin III, F.S., N. Fetcher, K. Kielland, K.R. Everett, and A.E. Linkins. 1988. Productivity and nutrient cycling of Alaskan tundra: enhancement by flowing soil water. Ecology **69**(3):693-702.

Chapin III, F. S., L. Moilanen, and K. Kielland. 1993. Preferential use of organic nitrogen for growth by a non-mycorrhizal arctic sedge. Nature **361**:150-153.

Chapin, F. S., III, G. R. Shaver, A. E. Giblin, K. J. Nadelhoffer, and J. A. Laundre. 1995. Responses of Arctic tundra to experimental and observed changes in climate. Ecology **76**:694-711.

Chapin, F. S., M. Sturm, M. C. Serreze, J. P. McFadden, J. R. Key, A. H. Lloyd, A. D. McGuire, T. S. Rupp, A. H. Lynch, J. P. Schimel, J. Beringer, W. L. Chapman, H. E. Epstein, E. S. Euskirchen, L. D. Hinzman, G. Jia, C. L. Ping, K. D. Tape, C. D. C. Thompson, D. A. Walker, and J. M. Welker. 2005. Role of land-surface changes in arctic summer warming. Science **310**:657-660.

Chorover, J., M. K. Amistadi, and O. A. Chadwick. 2004. Surface charge evolution of mineral-organic complexes during pedogenesis in Hawaiian basalt. Geochemica et Cosmochimica Acta **68**:4859-4876.

Cole, J. J. and N. F. Caraco. 2001. Carbon in catchments: connecting terrestrial carbon losses with aquatic metabolism. Marine and Freshwater Research **52**:101-110.

Cole, J. J., Y. T. Prairie, N. F. Caraco, W. H. McDowell, L. J. Tranvik, R. G. Striegl, C. M. Duarte, P. Kortelainen, J. A. Downing, J. J. Middelburg, and J. Melack. 2007. Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. Ecosystems.

Crump, B. C., H. E. Adams, J. E. Hobbie, and G. W. Kling. 2007. Biogeography of bacterioplankton in lakes and streams of an arctic tundra catchment. Ecology **88**:1365-1378.

Crump, B. C., G. W. Kling, M. Bahr, and J. E. Hobbie. 2003. Bacterioplankton community shifts in an arctic lake correlate with seasonal changes in organic matter source. Applied & Environmental Microbiology **69**:2253-2268.

Dalva, M. a. T. R. M. 1991. Sources and sinks of dissolved organic carbon in a freshwater swamp catchment. Biogeochemistry **15**:1-19.

Dawson, J. J. C., C. Bakewell, and M. F. Billet. 2001. Is in-stream processing an important control on spatial changes in carbon fluxes in headwater catchments? The Science of the Total Environment **265**:153-167.

Dittmar, T. 2003. Evidence for terrigenous dissolved organic nitrogen in the Arctic deep sea. Limnol Oceanogr **49**:148-156.

Dittmar, T. and G. Kattner. 2003. The biogeochemistry of the river and shelf ecosystem of the Arctic Ocean: a review. Marine Chemistry **83**:103-120.

Eaton, A. D., L. S. Clesceri, and A. E. Greenberg. 1995. *in* A. D. Eaton, L. S. Cleseri, and A. E. Greenberg, editors. Standard methods for the examination of water and wastewater. American Public Health Association, Washington, DC.

Edwardson, K. J., W. B. Bowden, C. Dahm, and J. Morrice. 2003. The hydraulic characteristics and geochemistry of hyporheic and parafluvial zones in Arctic tundra streams, north slope, Alaska. Advances in Water Resources **26**:907-923.

Elkins, K. M., and D. J. Nelson. 2001. Fluorescence and FT-IR spectroscopic studies of Suwannee river fulvic acid complexation with aluminum, terbium, and calcium. Journal of Inorganic Biochemistry **87**:81-96.

Engstrom, D. R., Sherilyn C. Fritz, James E. Almendinger and Stephen Juggins. 2000. Chemical and biological trends during lake evolution in recently deglaciated terrain. Nature **408**:161-166.

Epstein, H. E., M. P. Calef, M. D. Walker, F. S. Chapin, and A. M. Starfield. 2004. Detecting changes in arctic tundra plant communities in response to warming over decadal time scales. Global Change Biology **10**:1325-1334.

Fellman, J. B., D. V. D'Amore, E. Hood, and R. D. Boone. 2008. Fluorescence characteristics and biodegradability of dissolved organic matter in forest and wetland soils from coastal temperate watersheds in southeast Alaska. Biogeochemistry **88**:169-184.

Finlay, J., J. Neff, S. Zimov, A. Davydova, and S. Davydov. 2006. Snowmelt dominance of dissolved organic carbon in high-latitude watersheds: Implications for characterization and flux of river DOC. Geophysical Research Letters **33**.

Frey, K. E. and J. W. McClelland. 2009. Impacts of permafrost degradation on arctic river biogeochemistry. Hydrological Processes **23**:169-182.

Frey, K. E., J. W. McClelland, R. M. Holmes, and L. C. Smith. 2007a. Impacts of climate warming and permafrost thaw on the riverine transport of nitrogen and phosphorus to the Kara Sea. Journal of Geophysical Research-Biogeosciences **112**.

Frey, K. E., D. I. Siegel, and L. C. Smith. 2007b. Geochemistry of wet Siberian streams and their potential response to permafrost degradation. Water Resources Research **43**:W03406.

Frey, K. E., and L. C. Smith. 2005. Amplified carbon release from vast West Siberian peatlands by 2100. Geophysical Research Letters **32**.

Giblin, A. E., K. J. Nadelhoffer, G. R. Shaver, J. A. Laundre, and A. J. McKerrow. 1991. Biogeochemical diversity along a riverside toposequence in arctic Alaska. Ecological Monographs **61**:415-435.

Gough, L., G. R. Shaver, J. Carroll, D. L. Royer, and J. A. Laundre. 2000. Vascular plant species richness in Alaskan arctic tundra: The importance of soil pH. Journal of Ecology **88**:54-66.

Grogan, P., A. Michelsen, P. Ambus, and S. Jonasson. 2004. Freeze-thaw regime effecs on carbon and nitrogen dynamics in sub-arctic heath tundra mesocosms. Soil Biol. Biochem. **36**:641-654.

Gueguen, C., L. D. Guo, D. Wang, N. Tanaka, and C. C. Hung. 2006. Chemical characteristics and origin of dissolved organic matter in the Yukon River. Biogeochemistry **77**:139-155.

Guo, L. D. and R. W. Macdonald. 2006. Source and transport of terrigenous organic matter in the upper Yukon River: Evidence from isotope (delta C-13, Delta C-14, and delta N-15) composition of dissolved, colloidal, and particulate phases. Global Biogeochemical Cycles **20**.

Hamilton, T. D. 2002. Glacial Geology of the Toolik Lake and Upper Kuparuk River Region. University of Alaska Fairbanks, Institute of Arctic Biology, Fairbanks, AK.

Hansell, D. A., D. Kadko, and N. R. Bates. 2004. Degradation of terrigenous dissolved organic carbon in the western Arctic Ocean. Science **304**:858-861.

Hartley, A. E., C. Neill, J. M. Melillo, R. Crabtree, and F. P. Bowles. 1999. Plant performance and soil nitrogen mineralization in response to simulated climate change in subarctic dwarf shrub heath. Oikos **86**:331-343.

Harvey, C. J., B. J. Peterson, W. B. Bowden, L. A. Deegan, J. C. Finlay, A. E. Hershey, and M. C. Miller. 1997. Organic Matter Dynamics in the Kuparuk River, a Tundra River in Alaska, Usa. Journal of the North American Benthological Society **16**:18-23.

Hedin, L. O., P. M. Vitousek, and P. A. Matson. 2003. Nutrient losses over four million years of tropical forest development. Ecology **84**:2231-2255.

Hessen, D. O., P. Blomqvist, G. Dahl-Hansen, S. Drakare, and E. S. Lindstrom. 2004. Production and food web interactions of Arctic freshwater plankton and responses to increased DOC. Archiv fur Hydrobiologie **159**:289-307.

Hinzman, L. D., N. D. Bettez, W. R. Bolton, F. S. Chapin, M. B. Dyurgerov, C. L. Fastie, B. Griffith, R. D. Hollister, A. Hope, H. P. Huntington, A. M. Jensen, G. J. Jia, T. Jorgenson, D. L. Kane, D. R. Klein, G. Kofinas, A. H. Lynch, A. H. Lloyd, A. D. McGuire, F. E. Nelson, W. C. Oechel, T. E. Osterkamp, C. H. Racine, V. E. Romanovsky, R. S. Stone, D. A. Stow, M. Sturm, C. E. Tweedie, G. L. Vourlitis, M. D. Walker, D. A. Walker, P. J. Webber, J. M. Welker, K. Winker, and K. Yoshikawa. 2005. Evidence and implications of recent climate change in northern Alaska and other arctic regions. Climatic Change **72**:251-298.

Hobbie, J. E. and E. A. Hobbie. 2006. 15N in symbiotic fungi and plants estimates nitrogen and carbon flux rates in arctic tundra. Ecology **87**:816-822.

Hobbie, S. E. 1996. Temperature and plant species control over litter decomposition in Alaskan tundra. Ecological Monographs **66**:503-522.

Hobbie, S. E. and L. Gough. 2002. Foliar and soil nutrients in tundra on glacial landscapes of contrasting ages in northern Alaska. Oecologia **131**:453-462.

Hobbie, S. E. and L. Gough. 2004. Litter Decomposition in Moist Acidic and Non-Acidic Tundra with Different Glacial Histories. Oecologia **140**:113-124.

Hobbie, S. E., L. Gough, and G. R. Shaver. 2005. Species compositional differences on different-aged glacial landscapes drive contrasting responses of tundra to nutrient addition. Journal of Ecology **93**:770-782.

Hobbie, S. E., T. A. Miley, and M. S. Weiss. 2002. Carbon and nitrogen cycling in soils from acidic and nonacidic tundra with different glacial histories in Northern Alaska. Ecosystems **5**:761-774.

Hobbie, S. E., M. Ogdahl, J. Chorover, O. A. Chadwick, J. Oleksyn, R. Zytkowiak, and P. B. Reich. 2007. Tree species effects on soil organic matter dynamics: the role of soil cation composition. Ecosystems **10**:999-1018.

Holmes, R. M., J. W. McClelland, P. A. Raymond, B. B. Frazer, B. J. Peterson, and M. Stieglitz. 2008. Lability of DOC transported by Alaskan rivers to the Arctic Ocean. Geophysical Research Letters **35**:L03402.

IPCC. 2007. Summary for Policymakers. *in* S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K. B. Averyt, M. Tignor, and H. L. Miller, editors. Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Jenny, H. 1941. Factors of soil formation: A system of quantitative pedology. Dover Publications, Inc., New York.

Jones, J. B., K. C. Petrone, J. C. Finlay, L. D. Hinzman, and W. R. Bolton. 2005. Nitrogen loss from watersheds of interior Alaska underlain with discontinuous permafrost. Geophysical Research Letters **32**.

Judd, K. E., B. C. Crump, and G. W. Kling. 2006. Variation in dissolved organic matter controls bacterial production and community composition. Ecology **87**:2068-2079.

Judd, K. E., B. C. Crump, and G. W. Kling. 2007. Bacterial responses in activity and community composition to photo-oxidation of dissolved organic matter from soil and surface waters. Aquatic Sciences **69**:96-107.

Judd, K. E. and G. W. Kling. 2002. Production and export of dissolved C in arctic tundra mesocosms: the roles of vegetation and water flow. Biogeochemistry **60**:213-234.

Kaiser, K. 1998. Fractionation of dissolved organic matter affected by polyvalent metal cations. Organic Geochemistry **28**:849-854.

Kaiser, K., and G. Guggenberger. 2000. The role of DOM sorption to mineral surfaces in the preservation of organic matter in soils. Organic Geochemistry **31**:711-725.

Kaiser, K., and G. Guggenberger. 2003. Mineral surfaces and soil organic matter. European Journal of Soil Science **54**:219-236.

Kaiser, K. and G. Guggenberger. 2005. Storm flow flushing in a structured soil changes the composition of dissolved organic matter leached into the subsoil. Geoderma **127**:177-187.

Kaiser, K., G. Guggenberger, L. Haumaier, and W. Zech. 2002. The composition of dissolved organic matter in forest soil solutions: changes induced by seasons and passage through the mineral soil. Organic Geochemistry **33**:307-318.

Kalbitz, K., J. Schmerwitz, D. Schwesig, and E. Matzner. 2003. Biodegradation of soil-derived dissolved organic matter as related to its properties. Geoderma **113**:273-291.

Kalbitz, K., S. Solinger, J. H. Park, B. Michalzik, and E. Matzner. 2000. Controls on the dynamics of dissolved organic matter in soils: A review. Soil Science **165**:277-304.

Kaplan, L. A. and J. D. Newbold. 2000. Surface and Subsurface Dissolved Organic Carbon. Streams and Ground Waters.

Kaushal, S. S. and W. M. Lewis. 2003. Patterns in the chemical fractionation of organic nitrogen in Rocky Mountain streams. Ecosystems **6**:483-492.

Kaushal, S. S. and W. M. Lewis. 2005. Fate and transport of organic nitrogen in minimally disturbed montane streams of Colorado, USA. Biogeochemistry **74**:303-321.

Kawahigashi, M., K. Kaiser, K. Kalbitz, A. Rodionov, and G. Guggenberger. 2004. Dissolved organic matter in small streams along a gradient from discontinuous to continuous permafrost. Global Change Biology **10**:1576-1586.

Kawahigashi, M., K. Kaiser, A. Rodionov, and G. Guggenberger. 2006. Sorption of dissolved organic matter by mineral soils of the Siberian forest tundra. Global Change Biology **12**:1868-1877.

Keller, K., J. D. Blum, and G. W. Kling. 2007. Geochemistry of soils and streams on surfaces of varying ages in arctic Alaska. Arctic, Antarctic, and Alpine Research **39**:84-98.

Kielland, K. 1994. Amino acid absorption by arctic plants: implications for plant nutrition and nitrogen cycling. Ecology **75**:2373-2383.

Kimball, J. S., M. Zhao, A. D. McGuire, F. A. Heinsch, J. Clein, M. Calef, W. M. Jolly, S. Kang, S. E. Euskirchen, K. C. McDonald, and S. W. Running. 2007. Recent climate-driven increases in vegetation productivity for the western Arctic: Evidence of an acceleration of the northern terrestrial carbon cycle. Earth Interactions **11**:30.

Kipton, H., J. Powell, and R. M. Town. 1992. Solubility and fractionation of humic acid: effect of pH and ionic medium. Analytica Chimica Acta **267**:47-54.

Kling, G. W. 1995. Land-water Interactions: the influence of terrestrial diversity on aquatic systems. Pages 297-310 *in* F. S. Chapin and C. Korner, editors. The role of biodiversity in arctic and alpine tundra ecosystems. Springer-Verlag, Berlin.

Kling, G. W., G.W. Kipphut, and M.C. Miller. 1991. Arctic lakes and streams as gas conduits to the atmosphere: implications for tundra carbon budgets. Science **251**:298-301.

Kling, G. W., G.W. Kipphut, and M.C. Miller. 1992. The flux of CO_2 and CH_4 from lakes and rivers in arctic Alaska. Hydrobiologia **240**:23-36.

Kling, G. W., W. J. O'Brien, M. C. Miller, and A. E. Hershey. 1992. The biogeochemistry and zoogeography of lakes and rivers in arctic Alaska. Hydrobiologia **240**:1-14.

Lara, R. J., V. Rachold, G. Kattner, H. W. Hubberten, G. Guggenberger, A. Skoog, and D. N. Thomas. 1998. Dissolved organic matter and nutrients in the Lena River, Siberian Arctic: Characteristics and distribution. Marine Chemistry **59**:301-309.

Larsen, K. S., S. Jonasson, and A. Michelsen. 2002. Repeated freeze-thaw cycles and thier effects on biological processes in two arctic ecosystem types. Applied Soil Ecology **21**:187-195.

Lawrence, D. M. and A. G. Slater. 2005. A projection of sever near-surface permafrost degradation during the 21st century. Geophysical Research Letters **32**.

Lilienfein, J., R. G. Qualls, S. M. Uselman, and S. D. Bridgham. 2003. Soil formation and organic matter accretion in a young andesitic chronosequence at Mt. Shasta, California. Geoderma **116**:249-264.

Lilienfein, J., R. G. Qualls, S. M. Uselman, and S. D. Bridgham. 2004. Adsorption of dissolved organic carbon and nitrogen in soils of a weathering chronosequence. Soil Science Society of America Journal **68**:292-305.

Lipson, D. and T. Nasholm. 2001. The unexpected versatility of plants: organic nitrogen use and availability in terrestrial ecosystems. Oecologia **128**:305-316.

Lovett, G. M., K. C. Weathers, and M. A. Arthur. 2002. Control of nitrogen loss from forested watersheds by soil carbon: Nitrogen ratio and tree species composition. Ecosystems **5**:712-718.

Lovett, G. M., K. C. Weathers, M. A. Arthur, and J. C. Schultz. 2004. Nitrogen cycling in a northern hardwood forest: Do species matter? Biogeochemistry **67**:289-308.

Mack, M. C., E. A. G. Schuur, M. S. Bret-Harte, G. R. Shaver, and F. S. Chapin. 2004. Ecosystem carbon storage in arctic tundra reduced by long-term nutrient fertilization. Nature **431**.

Malmer, N., T. Johansson, M. Olsrud, and T. R. Christensen. 2005. Vegetation, climatic changes and net carbon sequestration in a North-Scandinavian subarctic mire over 30 years. Global Change Biology **11**:1895-1909.

Marschner, B. and K. Kalbitz. 2003. Controls of bioavailability and biodegradability of dissolved organic matter in soils. Geoderma **113**:211-235.

McClelland, J. W., M. Stieglitz, F. Pan, R. M. Holmes, and B. J. Peterson. 2007. Recent changes in nitrate and dissolved organic carbon export from the upper Kuparuk River, North Slope, Alaska. Journal of Geophysical Research-Biogeosciences **112**.

McDowell, W. H. 2003. Dissolved organic matter in soils - future directions and unanswered questions. Geoderma **113**:179-186.

McDowell, W. H. and G. E. Likens 1988. Origin, composition, and flux of dissolved organic carbon in the Hubbard Brook Valley. Ecological Monographs **58**:177-195.

McDowell, W. H., A. Zsolnay, J. A. Aitkenhead-Peterson, E. G. Gregorich, D. L. Jones, D. Jodemann, K. Kalbitz, B. Marschner, and D. Schwesig. 2006. A comparison of methods to determine the biodegradable dissolved organic carbon from different terrestrial sources. Soil Biology & Biochemistry **38**:1933-1942.

McGuire, A. D., J. S. Clein, J. M. Melillo, D. W. Kicklighter, R. A. Meier, C. J. Vorosmarty, and M. C. Serreze. 2000. Modeling carbon responses of tundra ecosystems to historical and projected climate: sensitivity of pan-Arctic carbon

storage to temporal and spatial variation in climate. Global Change Biology **6**:141-159.

McKnight, D. M., E. W. Boyer, P. K. Westerhoff, P. T. Doran, T. Kulbe, and D. T. Andersen. 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. Limnology and Oceanography **46**:38-48.

Meier, M., Y.-P. Chin, and P. A. Maurice. 2004. Variations in the composition and adsorption behavior of dissolved organic matter at a small, forested watershed. Biogeochemistry ; **67**:39-56.

Michaelson, G. J., C. L. Ping, G. W. Kling, and J. E. Hobbie. 1998. The character and bioactivity of dissolved organic matter at thaw and in the spring runoff waters of the arctic tundra North Slope, Alaska. Journal of Geophysical Research.D.Atmospheres **103**:28,939-928,946.

Michalzik, B., K. Kalbitz, J. H. Park, S. Solinger, and E. Matzner. 2001. Fluxes and concentrations of dissolved organic carbon and nitrogen - a synthesis for temperate forests. Biogeochemistry **52**:173-205.

Monroe, J. S., and J. G. Bockheim. 2001. Soil development in low-arctic tundra of the Northern Brooks Range, Alaska, U.S.A. Arctic, Antarctic, and Alpine Research **33**:78-87.

Moore, T. R., and J. Turunen. 2004. Carbon accumulation and storage in mineral subsoil beneath peat. Soil Science Society of America Journal **68**:690-696.

Nadelhoffer, K. J., A. E. Giblin, G. R. Shaver, and J. A. Laundre. 1991. Effects of temperature and substrate quality on element mineralization in six Arctic soils. Ecology **72**:242-253.

Naiman, R.J., and H. Decamps. 1997. The ecology of interfaces: Riparian zones. Annu. Rev. Ecol. Syst. **28:** 621-658.

Neff, J. C., F. S. Chapin, and P. M. Vitousek. 2003. Breaks in the cycle: dissolved organic nitrogen in terrestrial ecosystems. Frontiers in Ecology **1**:205-211.

Nilsson, S. I., S. Andersson, I. Valeur, T. Persson, J. Bergholm, and A. Wiren. 2001. Influence of dolomite lime on leaching and storage of C, N, and S in a Spodosol under Norway spruce (Picea abies (L.) Karst.). Forest Ecology and Management **146**:55-73.

Nordin, A., I. K. Schmidt, and G. R. Shaver. 2004. Nitrogen uptake by arctic soil microbes and plants in relation to soil nitrogen supply. Ecology **85**:955-962.

Oades, J. M. 1988. The retention of organic matter in soils. Biogeochemistry **5**:35-70.

Oechel, W. C., G. L. Vourlitis, J. Verfaillie, T. Crawford, S. Brooks, E. Dumas, A. Hope, D. Stow, B. Boynton, V. Nosov, and R. Zulueta. 2000. A scaling approach for quantifying the net CO_2 flux of the Kuparuk River Basin, Alaska. Global Change Biology **6**:160-173.

Opsahl, S., R. Benner, and R. M. W. Amon. 1999. Major flux of terrigenous dissolved organic matter through the Arctic Ocean. Limnology and Oceanography **44**:2017-2023.

Oste, L. A., E. J. M. Temminghoff, and W. H. Van Riemsdijk. 2002. Solid-solution partitioning of organic matter in soils as influenced by an increase in pH or Ca concentration. Environmental Science and Technology **36**:208-214.

Osterkamp, T. E., M. T. Jorgenson, E. A. G. Schuur, Y. L. Shur, M. Z. Kanevskiy, J. G. Vogel, and V. E. Tumskoy. 2009. Physical and ecological changes associated with warming permafrost and thermokarst in interior Alaska. Permafrost & Periglacial Processes **20**:235-256.

Overpeck, J., K. Hughen, D. Hardy, R. Bradley, R. Case, M. Douglas, B. Finney, K. Gajewski, G. Jacoby, A. Jennings, S. Lamoureux, A. Lasca, G. MacDonald, J. Moore, M. Retelle, S. Smith, A. Wolfe, and G. Zielinski. 1997. Arctic environmental change of the last four centuries. Science **278**:1251-1256.

Perakis, S. S. 2002. Nutrient limitation, hydrology and watershed nitrogen loss. Hydrological Processes **16**:3507-3511.

Perakis, S. S. and L. O. Hedin. 2002. Nitrogen loss from unpolluted South American forests mainly via dissolved organic compounds. Nature **415**:416-419.

Perakis, S. S. and L. O. Hedin. 2007. State factor relationships of dissolved organic carbon and nitrogen losses from unpolluted temperate forest watersheds. Journal of Geophysical Research-Biogeosciences **112**.

Peterson, B. J., J. E. Hobbie, and T. L. Corliss. 1986. Carbon flow in a tundra stream ecosystem. Canadian Journal of Fisheries and Aquatic Sciences **43**:1259-1270.

Peterson, B. J., T. L. Corliss, K. Kriet, and J. E. Hobbie. 1992. Nitrogen and phosphorus concentration and export for the Upper Kuparuk River on the North Slope of Alaska in 1980. Hydrobiologia **240**:61-69.

Ping, C. L., J. G. Bockheim, J. M. Kimble, G. J. Michaelson, and D. A. Walker. 1998. Characteristics of cryogenic soils along a latitudinal transect in Arctic Alaska. Journal of Geophysical Research **103**:28917-28928.

Qualls, R. G. 2000. Comparison of the behavior of soluble organic and inorganic nutrients in forest soils. Forest Ecology and Management **138**:29-50.

Qualls, R. G. and B. L. Haines. 1992. Biodegradability of dissolved organic-matter in forest throughfall, soil solution, and stream water. Soil Science Society of America Journal **56**:578-586.

Qualls, R. G., B. L. Haines, and W. T. Swank. 1991. Fluxes of dissolved organic nutrients and humic substances in a deciduous forest. Ecology **72**:254-266.

Qualls, R. G., B. L. Haines, W. T. Swank, and S. W. Tyler. 2000. Soluble organic and inorganic nutrient fluxes in clearcut and mature deciduous forests. Soil Science Society of America Journal **64**:1068-1077.

Qualls, R. G., B. L. Haines, W. T. Swank, and S. W. Tyler. 2002. Retention of soluble organic nutrients by a forested ecosystem. Biogeochemistry **61**:135-171.

Rastetter, E. B., B. L. Kwiatkowski, S. L. Dizes, and a. J. E. Hobbie. 2004. The role of down-slope water and nutrient fluxes in the response of Arctic hill slopes to climate change. Biogeochemistry **69**:37-62.

Raymond, P. A., J. W. McClelland, R. M. Holmes, A. V. Zhulidov, K. Mull, B. J. Peterson, R. G. Streigl, G. R. Aiken, and T. Y. Gurtovaya. 2007. Flux and age of dissolved organic carbon exported to the Arctic Ocean: A carbon isotopic study of the five larget arctic rivers. Global Biogeochemical Cycles **21**:GB4011.

Richardson, S. J., D. A. Peltzer, R. B. Allen, M. S. McGlone, and R. L. Parfitt. 2004. Rapid development of phosphorus limitation in temperate rainforest along the Franz Josef soil chronosequence. Oecologia **139**:267-276.

Roehm, C. L., R. Giesler, and J. Karlsson. 2009. Bioavailability of terrestrial organic carbon to lake bacteria: The case of a degrading subarctic permafrost mire complex. Journal of Geophysical Research **114**:G03006.

Schimel, J. P. and J. S. Clein. 1996. Microbial response to freeze-thaw cycles in tundra and taiga soils. Soil Biol. Biochem. **28**:1061-1066.

Selmants, P. C., and S. C. Hart. 2008. Substrate age and tree islands influence carbon and nitrogen dynamics across a retrogressive semiarid chronosequence. Global Biogeochemical Cycles **22**.

Shaver, G., and F. S. Chapin. 1991. Production : biomass relationships and element cycling in contrasting arctic vegetation types. Ecological Monographs **61**:1-31.

Shaver, G. R., W. D. Billings, F. S. Chapin, III, A. E. Giblin, K. J. Nadelhoffer, W. C. Oechel, and E. B. Rastetter. 1992. Global change and the carbon balance of arctic ecosystems. Bioscience **42**:433-441.

Shaver, G. R., S. M. Bret-Harte, M. H. Jones, J. Johnstone, L. Gough, J. Laundre, and F. S. Chapin. 2001. Species composition interacts with fertilizer to control long-term change in tundra productivity. Ecology **82**:3163-3181.

Shaver, G. R., A. E. Giblin, K. J. Nadelhoffer, K. K. Thieler, M. R. Downs, J. A. Laundre, and E. B. Rastetter. 2006. Carbon turnover in Alaskan tundra soils: effects of organic matter quality, temperature, moisture and fertilizer. Journal of Ecology **94**:740-753.

Shaver, G. R., J. A. Laundre, A. E. Giblin, and K. J. Nadelhoffer. 1996. Changes in Live Plant Biomass, Primary Production and Species Composition along a Riverside Toposequence in Arctic Alaska, Usa. Arctic & Alpine Research **28**:363-379.

Shaver, G. R., and S. Jonasson. 1999. Response of Arctic ecosystems to climate change: results of long-term field experiments in Sweden and Alaska. Polar Research **18**:245-252.

Shen, Y.-H. 1999a. Sorption of natural dissolved organic matter on soil. Chemosphere **38**:1505-1515.

Shen, Y. H. 1999b. Sorption of humic acid to soil: The role of soil mineral composition. Chemosphere **38**:2489-2499.

Sjogersten, S., and P. A. Wookey. 2005. The role of soil organic matter quality and physical environment for nitrogen mineralization at the forest-tundra ecotone in Fennoscandia. Arctic Antarctic and Alpine Research **37**:118-126.

Solórzano, L. 1969. Determination of ammonia in natural waters by the phenolhypochlorite method. Limnology and Oceanography **14**:799-801.

Stepanauskas, R., H. Laudon, and N. O. G. Jorgensen. 2000. High DON bioavailability in boreal streams during a spring flood. Limnology and Oceanography **45**:1298-1307.

Stieglitz, M., J. Hobbie, A. Giblin, and G. Kling. 1999. Hydrologic modeling of an arctic tundra watershed: Toward Pan-Arctic predictions. Journal of Geophysical Research-Atmospheres **104:**27507-27518.

Stieglitz, M., J. Shaman, J. McNamara, V. Engel, J. Shanley, and G. W. Kling. 2003. An approach to understanding hydrologic connectivity on the hillslope and the implications for nutrient transport. Global Biogeochemical Cycles **17**:1105.

Streigl, R. G., G. R. Aiken, M. M. Dornblaser, P. A. Raymond, and K. P. Wickland. 2005. A decrease in discharge-normalized DOC export by the Yukon River during summer through autumn. Geophysical Research Letters **32**.

Swift, R. S. 2001. Sequestration of carbon by soil. Soil Science **166**:858-871.

Trulleyova, S. and M. Rulik. 2004. Determination of biodegradable dissolved organic carbon in waters: comparison of batch methods. Science of the Total Environment **332**:253-260.

van Wijk, M. T., K. E. Clemmensen, G. R. Shaver, M. Williams, T. V. Callaghan, F. S. Chapin, J. H. C. Cornelissen, L. Gough, S. E. Hobbie, S. Jonasson, J. A. Lee, A. Michelsen, M. C. Press, S. J. Richardson, and H. Rueth. 2003. Long-term ecosystem level experiments at Toolik Lake, Alaska, and at Abisko, Northern Sweden: generalizations and differences in ecosystem and plant type responses to global change. Global Change Biology **10**:105-123.

Valderrama. 1981. The simultaneous analysis of total nitrogen and total phosphorus in natural waters. Marine Chemistry **10**:109-122.

Waelbroeck, C., P. Monfray, W. C. Oechel, S. Hastings, and G. Vourlitis. 1997. The Impact of Permafrost Thawing on the Carbon Dynamics of Tundra. Geophysical Research Letters **24**:229-232.

Wagner, D., A. Lipski, A. Embacher, and A. Gattinger. 2005. Methane fluxes in permafrost habitats of the Lena Delta: effects of microbial community structure and organic matter quality. Environmental Microbiology **7**:1582-1592.

Walker, D. A. 2000. Hierarchical subdivision of Arctic tundra based on vegetation response to climate, parent material and topography. Global Change Biology **6**:19-34.

Walker, D. A., N. A. Auerbach, J. G. Bockheim, F. S. Chapin, W. Eugster, J. Y. King, J. P. Mcfadden, G. J. Michaelson, F. E. Nelson, W. C. Oechel, C. L. Ping, W. S. Reeburg, S. Regli, N. I. Shiklomanov, and G. L. Vourlitis. 1998. Energy and trace-gas fluxes across a soil Ph boundary in the Arctic. Nature **394**:469-472.

Walker, D. A., N. A. Auerbach, and M. M. Shippert. 1995. NDVI, biomass, and landscape evolution of glaciated terrain in northern Alaska. Polar Record **31**:169-178.

Walker, M. D., D. A. Walker, and N. A. Auerbach. 1994. Plant communities of a tussock tundra landscape in the Brooks Range Foothills, Alaska. Journal of Vegetation Science **5:**843-866.

Walker, D. A., W. A. Gould, H. A. Maier, and M. K. Raynolds. 2002. The Circumpolar Arctic Vegetation Map: AVARR-derived base maps, environmental controls, and integrated mapping procedures. International Journal of Remote Sensing **23**:4551-4570.

Walter, K. M., S. A. Zimov, J. P. Chanton, D. Verbyla, and F. S. Chapin. 2006. Methane bubbling from Siberian thaw lakes as a positive feedback to climate warming. Science **443**.

Walvoord, M. A., and R. G. Striegl. 2007. Increased groundwater to stream discharge from permafrost thawing in the Yukon River basin: Potential impacts on lateral export of carbon and nitrogen. Geophysical Research Letters **34**.

Webster, J. R., P. J. Mulholland, J. L. Tank, H. M. Valett, W. K. Dodds, B. J. Peterson, W. B. Bowden, C. N. Dahm, S. Findlay, S. V. Gregory, N. B. Grimm, S. K. Hamilton, S. L. Johnson, E. Marti, W. H. McDowell, J. L. Meyer, D. D. Morrall, S. A. Thomas, and W. M. Wollheim. 2003. Factors affecting ammonium uptake in streams - an inter-biome perspective. Freshwater Biology **48**:1329-1352.

Weintraub, M. N. and J. P. Schimel. 2005a. Nitrogen cycling and the spread of shrubs control changes in the carbon balance of arctic tundra ecosystems. Bioscience **55**:408-415.

Weintraub, M. N. and J. P. Schimel. 2005b. The seasonal dynamics of amino acids and other nutrients in Alaskan Arctic tundra soils. Biogeochemistry **73**:259-280.

Weishaar, J. L., G. R. Aiken, B. A. Bergamaschi, M. S. Fram, R. Fujii, and K. Mopper. 2003. Evaluation of specific Ultraviolet absorbance as an Indicator of the

chemical composition and reactivity of dissolved organic carbon. Environmental Science & Technology **37**:4702-4708.

Wood, E. D., F. A. J. Armstrong, and F. A. Richards. 1967. Determination of nitrate in seawater by cadmium-copper reduction to nitrite. Journal of the Marine Biological Association of the United Kingdom **47**:23-31.

Worrall, F., T. P. Burt, and J. Adamson. 2006. The rate of and controls upon DOC loss in a peat catchment. Journal of Hydrology **321**:311-325.

You, S.-J., Y. Yin, and H. E. Allen. 1999. Partitioning of organic matter in soils: Effects of pH and water/soil ratio. The Science of the Total Environment **227**:155-160.

Yu, Z., E. C. T. Kraus, R. A. Dahlgren, W. A. Horwath, and R. J. Zasoski. 2003. Mineral and Dissolved Organic Nitrogen Dynamics along a Soil Acidity-Fertility Gradient. Soil Sci. Soc. Am. J. **67**:878-888.

Zak, D. R. and G. W. Kling. 2006. Microbial community composition and function across an arctic tundra landscape. Ecology **87**:1659-1670.

Appendix 1: Soil water sampling

Methods:

To examine availability of dissolved carbon and nitrogen in soil water, we samples small surface pools and soil water across the chronosequence. We collected water from three to five surface pools 0.5m to 1m in diameter from two to four sites on each of the three younger landscape ages. In addition to water samples collected for organic carbon and nutrient analysis, we collected a bubble-free water sample by filling a 20mL serum vial with bubble-free pond water using a syringe, fixing the sample using 0.2mL of mercuric chloride, and capping the serum vial with a aluminum cap and Teflon septa. We also sampled soil water from three to four sites on each of three landscape ages (Itkillik II, Itkillik I, and Sagavanirktok) for twenty four hours using tension lysimeters. Tension lysimeters were made from a syringe (to collect the sample) and a 10cm ceramic lysimeter tube placed in the organic soil to 10cm depth.

Collected soil and pond water samples were filtered through a Whatman GF/F glass fiber filter and analyzed for dissolved organic carbon, total dissolved nitrogen, nitrate and ammonia. We analyzed water samples for dissolved organic carbon and total nitrogen using a total organic carbon and total nitrogen analyzer (TOC-V CSH and TNM-1, Shimadzu, Columbia, MD). We used an auto analyzer (Alpkem, O.I. Analytical, College Station, TX) to measure nitrate plus nitrite (NO_3^- and NO_2^-) (cadmium reduction, (Wood et al. 1967)) and ammonium (NH_4^+) (phenol hypochlorite, (Solórzano 1969)) in soil and pond water samples. Dissolved organic nitrogen export was calculated as TDN less the sum of NO_3^- and NH_4^+ in each water sample. We measured dissolved inorganic

carbon concentrations in bubble free water samples by acidifying 10mL of sample with 5mL of 2N HCl and shaking for one hour with 20mL of nitrogen gas. We analyzed the resulting gas headspace for CO_2 and methane concentrations as measured on a gas chromatograph with a thermal conductivity detector, flame ionization detector, and poropak N column (GC-14A, Shimadzu, Columbia, MD).

Results:

The pH of surface pools was significantly different among landscape ages and was significantly lower in pools on the Sagavanirktok glacial drift than in pools from the two younger glacial drifts (ANOVA: $p=0.004$, $F_{2,10}=19.83$; Tukey's HSD: $\alpha=0.05$). Although the temperature of surface pools on the youngest glacial drift was higher than the temperature of pools on the two older glacial drifts; there were no significant differences in water temperature among landscape ages (ANOVA: $p=0.058$, $F_{2,10}=5.27$). There were significant differences among landscape ages in surface pool concentrations of dissolved inorganic carbon with the highest concentrations on the youngest landscape age (ANOVA: $p=0.041$, $F_{2,9}=5.71$; Tukey's HSD: $\alpha=0.05$). We found no significant differences in concentrations of dissolved organic carbon (ANOVA: $p=0.12$, $F_{2,10}=2.67$), DON (ANOVA: $p=0.51$, $F_{2,10}=0.71$), nitrate (ANOVA: $p=0.60$, $F_{2,10}=0.55$), or ammonium (ANOVA: $p=0.51$, $F_{2,10}=0.76$) in surface pools among landscape ages. There were also no significant differences among landscape age in soil water DON concentrations (ANOVA: $p=0.37$, $F_{2,7}=1.16$), nitrate concentrations (ANOVA: $p=0.30$, $F_{2,8}=1.46$), ammonium concentrations (ANOVA: $p=0.69$, $F_{2,8}=0.38$), or dissolved organic carbon concentrations (ANOVA: $p=0.36$, $F_{2,8}=1.17$) (Table 5). The percent of total

dissolved nitrogen in soil water which was organic nitrogen ranged from 55 to 95% and there were no significant differences in percent of organic nitrogen among landscape ages (ANOVA: $p=0.66$, $F_{2,7}=0.44$).

Appendix 2: Microbial biomass after five months of incubation

There was a significant calcium by pH interaction for microbial biomass carbon and nitrogen and their ratio at the end of the experiment when normalized per gram of soil (ANOVA: carbon: $p<0.001$, $F_{1,111}=17.05$; nitrogen: $p=0.005$, $F_{1,111}=8.22$; Figure 2.6) and per gram of soil carbon (ANOVA: carbon: $p=0.013$, $F_{1,111}=6.34$; nitrogen: $p=0.031$, $F_{1,111}=4.76$; C:N ratio: ANOVA: $p=0.014$, $F_{1,111}=6.21$; Figure 2.6). At acidic pH, soils in high calcium treatments had higher microbial biomass carbon and nitrogen and higher microbial carbon to nitrogen ratios than soils from low calcium treatments (Figure 2.6). However, at circumneutral pH, soils in high calcium treatments had lower microbial biomass carbon and nitrogen and lower microbial carbon to nitrogen ratios than low calcium treatments (Figure 2.6). At the end of the experiment, microbial biomass carbon and nitrogen and microbial carbon to nitrogen ratios were higher in acidic pH soils than circumneutral pH soils at high concentrations of calcium (Figure 2.6). However, at low concentrations of calcium, microbial biomass carbon and nitrogen were higher in circumneutral pH soils than acidic pH soils, while microbial biomass carbon to nitrogen ratios were similar between low and circumneutral pH soils (Figure 2.6). At the end of the experiment there were no significant age effects on microbial biomass carbon or nitrogen when normalized per gram of soil (ANOVA: carbon: $p=0.051$, $F_{3,168}=3.84$; nitrogen: $p=0.062$, $F_{3,168}=3.52$; Figure 2.6) or when normalized per gram of soil carbon (ANOVA: carbon: $p=0.085$, $F_{3,168}=3.04$; nitrogen: $p=0.059$, $F_{3,168}=3.60$; Figure 2.6). Microbial biomass carbon to nitrogen ratios were also not significantly different among landscape ages at the end of the experiment (ANOVA: $p=0.08$, $F_{3,168}=3.14$, Figure 2.6).

Appendix 3: Nutrient data

Methods

We also measured changes in the relative abundance of dissolved inorganic and organic nutrients during the incubation by comparing concentrations of these nutrients in water samples at the end of the experiment to those in initial soil extracts. We analyzed sub-samples of water from the end of the experiment for DON, DOP, TDN, TDP, PO_4^-, NO_3^-, and NH_4^+ concentration as described for initial soil extracts.

Results: Soil and Stream Water

There were no significant age by hillslope position interactions nor significant differences among hillslope positions for DON concentrations in soil water (ANOVA hillslope positions: p=0.084, $F_{2,87}$=3.78; age x hillslope position: p=0.095, $F_{6,85}$=1.88; Figure 4.9). There were no significant differences in soil water NO_3^- or NH_4^+ concentrations among landscape ages (ANOVA: NH_4: p=0.20, $F_{3,93}$=1.95; NO_3: p=0.50, $F_{3,92}$=0.86; Figure 4.9) nor among hillslope positions (ANOVA: NH_4: p=0.17, $F_{2,87}$=2.38; NO_3: p=0.22, $F_{2,87}$=1.95; Figure 4.9). There were no significant differences among either landscape ages or hillslope positions in the percent of TDN in soil water which is in the organic form (ANOVA: age: p=0.13, $F_{3,93}$=2.95; hillslope position: p=0.077, $F_{2,87}$=3.33; Figure 4.9).

There were no significant differences among hillslope positions or landscape ages in soil water TDP concentrations (ANOVA: age: p=0.47, $F_{3,87}$=0.92; hillslope position: p=0.65, $F_{2,79}$=0.46; Figure 4.10). Neither DOP concentrations nor PO_4^- concentrations in

soil water differed significantly among hillslope positions (ANOVA: DOP: p=0.61, $F_{2,81}$=1.08; PO_4: p=0.90, $F_{2,81}$=0.11; Figure 4.10). Soil water concentrations of PO_4^- were significantly different among landscape ages (ANOVA: p=0.01, $F_{3,87}$=6.85; Figure 4.11); however, there were no landscape age differences in DOP concentrations in soil water (ANOVA: p=1.09, $F_{3,87}$=0.41; Figure 4.10). The percent of TDP in soil water in the organic form did not differ significantly among either landscape ages or hillslope positions (ANOVA: age: p=0.30, $F_{3,87}$=1.44; hillslope position: p=0.89, $F_{2,81}$=0.13; Figure 4.10).

Stream water concentrations of DOC and NO_3^- were not significantly different among landscape ages (ANOVA: DOC: p=0.12, $F_{3,24}$=2.61; NO_3^-: p=0.44, $F_{3,24}$=1.00; Figure 4.9). However concentrations of DON and NH_4^+ in stream water did differ significantly among landscape ages (ANOVA: DON: p=0.029, $F_{3,24}$=5.08; NH_4^+: p=0.031, $F_{3,24}$=4.96; Figure 4.9). Concentrations of DON were significantly lower in streams on the oldest (i.e. Sagavanirktok) surface compared to those on the youngest (Itkillik I) site, while NH_4^+ concentrations were significantly higher in streams on the Itkillik III surface than the Itkillik II and Sagavanirktok surfaces (ANOVA; Tukey's HSD α=0.05; Figure 4.9). The percent of TDN present as DON was significantly higher in streams on the three younger landscape ages than on the oldest (Sagavanirktok) landscape (ANOVA: p=0.008, $F_{3,24}$=8.12; Tukey's HSD α=0.05; Figure 4.9). There were no significant differences in stream water concentrations of PO_4^- or DOP among landscape ages (ANOVA: PO_4^-: p=0.065, $F_{3,24}$=3.61; DOP: p=0.88, $F_{3,24}$=0.22; Figure 4.10). However, the percent of TDP made up of DOP was significantly higher in streams on the

Itkillik III surface than on the oldest (Sagavanirktok) surface (ANOVA: p=0.042, $F_{3,24}$=4.34, Tukey's HSD α=0.05; Figure 4.10).

Results: Soil Extracts and Incubation

There were no significant differences in initial concentrations of NH_4^+ or NO_3^- in soil extracts among either landscape ages (ANOVA: NH_4^+: p=0.60, $F_{3,93}$=0.67; NO_3^-: p=0.70, $F_{3,93}$=0.49; Figure 4.11) or among hillslope positions (ANOVA: NH_4^+: p=0.33, $F_{2,95}$=1.11; NO_3^-: p=0.39, $F_{2,95}$=0.96; Figure 4.11). There were no significant differences among either landscape ages nor among hillslope positions in initial concentrations of DON (ANOVA: age: p=0.39, $F_{3,95}$=1.13; hillslope position: p=0.25, $F_{2,93}$=1.42; Figure 4.11). At the end of the incubation there were no significant differences among landscape ages in DON, NH_4^+, or NO_3^- concentrations (ANOVA: DON: p=0.28, $F_{3,95}$=1.59; NH_4^+: p=0.51, $F_{3,95}$=0.84; NO_3^-: p=0.77, $F_{3,95}$=0.39; Figure 4.12). Nor were there significant differences in concentrations of DON, NH_4^+, or NO_3^- among hillslope positions at the end of the experiment (ANOVA: DON: p=0.49, $F_{2,95}$=0.87; NH_4^+: p=0.41, $F_{2,95}$=1.02; NO_3^-: p=0.22, $F_{2,95}$=1.42; Figure 4.12). There were no significant differences in the proportion of TDN made up of DON among either landscape ages or hillslope positions at the beginning (ANOVA: age: p=0.50, $F_{3,95}$=0.86; hillslope position: p=0.16, $F_{2,93}$=1.88; Figure 4.11) or end (ANOVA: age: p=0.79, $F_{3,95}$=0.35; hillslope position: p=0.71, $F_{2,93}$=0.36; Figure 4.12) of the 10 month experiment. There were corresponding significant increases in DON and NO_3^- concentrations, but a significant decrease in NH_4^+ concentrations during the course of the experiment (Paired t-test: DON: p<0.001, t_{116}=1.03; NO_3^-: p<0.001, t_{115}=6.45; NH_4^+: p<0.001, t_{118}=-5.43; Figure 4.11 and 4.12).

However there were no significant changes in the percent of TDN composed of DON (Paired t-test: $p=0.31$, $t_{116}=1.03$; Figure 4.11 and 4.12). There were no significant differences among landscape ages or hillslope positions in the ratio of DOC:DON in soil extracts at the end of the experiment (ANOVA: age: $p=0.75$, $F_{3,95}=0.40$, hillslope positions: $p=0.39$, $F_{2,93}=0.96$).

Concentrations of DOP in initial soil extracts did not differ significantly among hillslope positions (ANOVA: $p=0.69$, $F_{2,93}=0.37$; Figure 4.13); however, DOP was significantly different among landscapes, with significantly higher DOP in extracts from the Itkillik III surface than in extracts from soils on the Itkillik II surface (ANOVA: $p=0.021$, $F_{2,93}=7.88$; Tukey's HSD $\alpha=0.05$; Figure 4.13). Neither the concentration of PO_4^- nor the percent of TDP as DOP was significantly different among either landscape ages or among hillslope positions in initial soil extracts (ANOVA: PO_4^-: age: $p=0.33$, $F_{3,95}=1.35$; hillslope position: $p=1.00$, $F_{2,93}=0.003$; %organic P: age: $p=0.25$, $F_{3,95}=1.77$; hillslope position: $p=0.91$, $F_{2,93}=0.088$; Figure 4.13). There were no significant differences in DOP or PO_4^- among hillslope positions or landscape ages at the end of the 10 month incubation (ANOVA: DOP: age: $p=0.23$, $F_{3,95}=1.76$; hillslope position: $p=0.61$, $F_{2,93}=0.49$; PO_4^-: age: $p=0.32$, $F_{3,95}=1.38$; hillslope position: $p=0.067$, $F_{2,93}=2.79$; Figure 4.13). The percent of TDP as DOP at the end of the experiment was significantly different among landscape ages with a significantly higher percentage of DOP in extracts from the Sagavanirktok surface than in extracts from the three younger surfaces (ANOVA: $p=0.002$, $F_{3,95}=13.67$; Tukey's HSD $\alpha=0.05$; Figure 4.13), but not among hillslope positions (ANOVA: $p=0.062$, $F_{2,93}=2.87$; Figure 4.13). There were significantly

higher concentrations of PO_4^- and significantly lower concentrations of DOP at the end of the incubation than there were in the beginning (Paired t-test: DOP: $p<0.001$, $t_{78}=-16.15$; PO_4^-: $p<0.001$, $t_{107}=21.97$; Figure 4.13). As a result the proportion of TDP in extracts which was DOP decreased significantly throughout the incubation (Paired t-test: $p<0.001$, $t_{78}=-26.30$; Figure 4.13).