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Relationships Among pH, Minerals, and Carbon in Soils from Tundra to Boreal Forest Across Alaska

Satoru Hobara,[1,2]* Keiji Kushida,[3] Yongwon Kim,[4] Keisuke Koba,[5] Bang-Yong Lee,[6] and Noriharu Ae[2]

[1]College of Agriculture, Food and Environment Sciences, Rakuno Gakuen University, Midorimachi 582, Bunkyodai, Ebetsu 069-8501, Japan; [2]Graduate School of Dairy Science, Rakuno Gakuen University, Ebetsu 069-8501, Japan; [3]College of Bioresource Sciences, Nihon University, Fujisawa 252-0880, Japan; [4]International Arctic Research Center, University of Alaska Fairbanks, Alaska 99775-7340, USA; [5]Institute of Agriculture, Tokyo University of Agriculture and Technology, Fuchu 183-8509, Japan; [6]Arctic Research Center, Korea Polar Research Institute, Incheon 406-840, Korea

ABSTRACT

Tundra and boreal forests in northern high latitudes contain significant amounts of carbon (C) in the soil, indicating the importance of clarifying controls on soil C dynamics in the region and their feedback effects on climate systems. In northern Alaska, variations in soil C processes are closely associated with variations in soil acidity within ecosystems; however, the reason for this association remains unclear. In this study, we demonstrate that it results from weathering and subsequent changes in soil geochemical characteristics, including minerals and adsorptive organic C. We sampled soils from 12 sites in Alaska along a 600-km transect from the Arctic Ocean to interior Alaska, spanning the biomes of tundra, tundra–boreal forest ecotone, and boreal forest. Mineral soil analyses revealed that soils with low pH have fewer base cations, more aluminum/iron minerals, and lower base saturation, indicating that weathering is a major function of these geochemical characteristics in the broad area over northern Alaska. Adsorbed organic C in soil presented strong correlations with Al and Fe minerals, soil pH, and soil total C and represented approximately 30–55% of total soil C, suggesting that soil C accumulation in the Alaskan ecosystems is strongly controlled by weathering-related changes in geochemical characteristics. An adsorption test supported these observations and illustrated a greater capacity for acidic soil to adsorb organic C. These findings demonstrate that variations in weathering-associated characteristics have a strong influence on the regional variation in C dynamics and biogeochemical consequences in the Alaskan ecosystems.

Key words: soil pH; soil organic carbon; weathering; adsorption; Alaska; extractable organic carbon.

INTRODUCTION

Arctic and subarctic ecosystems are extremely vulnerable to current and projected climate change (Anisimov and others 2007; Schuur and others 2013). The tundra and boreal forests in the northern high latitudes contain over 5 times more carbon (C) in the soil than in the plants (Schlesinger and Bernhardt 2013). Increased permafrost thaw

and wildfire are suggested to change the soil C cycle in the region and represent feedbacks to climate change (Schuur and others 2009; Mack and others 2011). Permafrost stores approximately twice the amount of soil organic C as the active layer does in the circumpolar ecosystems (Hugelius and others 2014). In northern Alaska, climate change is expected to increase the thawing of mineral permafrost soils (Lawrence and Slater 2005; Slater and Lawrence 2013). It is therefore crucial to elucidate the controls on soil C dynamics in the mineral soil layer to understand the impact of accelerated permafrost thaw.

In northern Alaska, the soil pH ranges from acidic to circumneutral (pH 4–7) and is closely linked with differences in C fluxes and organic C characteristics in soil. For example, as compared with neutral soils, acidic soils show greater respiration (Walker and others 1998), greater DOC leaching (Hobbie and others 2002), and lower DOC biodegradability (Abbott and others 2014). However, the reason behind the link in soil pH and soil C dynamics is not completely understood, probably because soil C pools and C dynamics are controlled by various factors such as temperature, moisture, vegetation, litter quality and quantity, microbial activity, and minerals in soil systems. Whittinghill and Hobbie (2012) tested the effects of soil pH and Ca on microbial respiration and DOC solubility by experimental pH treatments, which did not completely explain in situ patterns of the relationship between soil pH and the soil functions, and indicated the possibility of other landscape age-related controls.

Soil organic matter sorption, binding, and occlusion with mineral soils are substantial geochemical processes that retain C in mineral soils (Guggenberger and Kaiser 2003; Schmidt and others 2011). Moreover, these geochemical processes are closely associated with organic C leaching in northern ecosystems (Kawahigashi and others 2004, 2006). Hobara and others (2013) found a stronger correlation of soluble DOC with Al and Fe than with Ca in the Alaskan tundra organic layer; however, little is understood about the role of these geochemical characteristics in the linkage between soil pH and C dynamics. Reactive and/or non-crystalline minerals such as aluminum (Al) and iron (Fe) oxides/hydroxides can provide long-term preservation of soil organic matter (Torn and others 1997; Mikkuta and others 2009). Reactive soil minerals are related to soil acidity, such as the negative correlation between soil pH and $CuCl_2$-extractable Al, an index of reactive Al (Godsey and others 2007). In Arctic ecosystems, soils from carbonate-free parent material can be acidified through weathering, and acidic soils are likely to have fewer base cations but more Al and Fe amorphous minerals than neutral soils (Goryachkin and others 2004). Therefore, the variation in soil pH observed in Alaska may reflect the variety of mineral soil characteristics linked with the adsorption and accumulation of organic C.

Thus, we hypothesize that the extent of weathering of soil minerals affect not only soil pH but also soil C accumulation and C dynamics in Alaskan ecosystems, resulting in a close relationship between soil pH and C dynamics, rather than a direct effect of pH on C dynamics. We also hypothesize that the sorption of organic C to Al and Fe minerals is an important soil function, leading to a greater C accumulation and an increased microbial activity in well-weathered, acidic soil. To examine the hypotheses and its applicability, we analyzed soil characteristics of minerals and organic C using soils from a broad area of Alaska, including tundra and boreal forest. We also performed a repeated extraction experiment to measure the percentage of adsorbed organic C relative to total soil C and conducted an adsorption experiment to compare the adsorption potential among soils.

MATERIALS AND METHODS

The soil sampling sites were distributed along the Dalton Highway in north to central Alaska (Figure 1). The 12 sites cover approximately 600 km
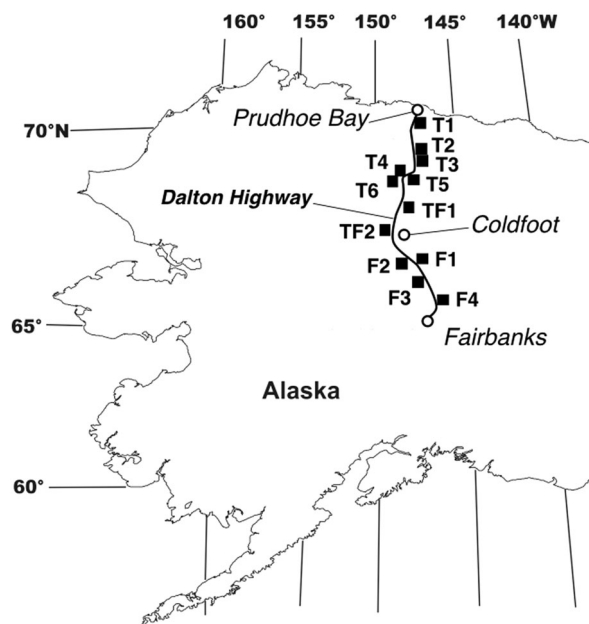

Figure 1. Locations of the study sites.

from the Arctic Ocean to Fairbanks and occur in biomes defined as tundra, tundra–forest ecotone, white spruce forest, and black spruce forest (Table 1). The six tundra sites (encoded as T1, T2, T3, T4, T5, and T6) were established in coastal tundra (T1), upland tundra (T2), tundra near Sagavanirktok River (T3), moist non-acidic tundra near Toolik Lake (T4), Imnavait Creek (T5), and moist acidic tundra near Toolik Lake (T6). The tundra–forest ecotone sites (encoded as TF1 and TF2) were in a transient zone between tundra and white spruce (TF1). The white spruce forest site was located in Gold Creek (TF2). The four black spruce forest sites (encoded as F1, F2, F3, and F4) were in Coldfoot (F1 and F2), Yukon River's upper side (F3), and Yukon River's lower side (F4). The upper mineral soils of most study sites are frozen in winter but they seasonally thaw. The substrates of northern Alaska are partly characterized by their glacial history. The T4 and T6 sites are located at the northern and western sides of Toolik Lake and experience similar climatic conditions but are on landscapes with different glacial histories: The T4 site occurs on Itkillik II glacial drift (approximately 25,000–11,500 years old) and T6 site occurs on Itkillik I glacial drift (50,000–120,000 years old) (Hamilton 2003). The parent materials at the T3 and T5 sites are known to be on loess of Itkillik II age (20,000 years old) and on loess of Sagavanirktok age (300,000 years old), respectively (Hamilton 2003). Detailed site information is shown in Table 1. For further site information, see Kim and others (2013) and Kim (2014) for the T1, T2, TF1, TF2, F1, F2, F3, and F4 sites; Giblin and others (1991) and Shaver and others (1996) for the T3 site; Hobbie and Gough (2002) for the T4 and T6 sites; and Hobara and others (2006) and Yano and others (2010) for the T5 site.

We sampled soils from the T3, T4, T5, and T6 sites in July and August 2002 and from the other sites in August 2012. We sampled soil from the hilltop heath ecosystem at the T3 site and from the heath and tussock tundra ecosystem at the T5 site, mainly because the mineral soils of the other ecosystems were frozen. The sampling points were at least 30 m apart to promote variability between the soil samples. Most sites were too small to have multiple sampling points; hence, we sampled from 1 point at the T2, TF1, TF2, F3, and F4 sites; from 2 points at the T1, F1, and F2 sites; from 3 points at the T3 site; from 6 points at the T5 site; and from 8 points at the T4 and T6 sites. All soil samples were taken from the upper 5-cm layer of mineral soil after removing the surface organic layer. The upper layer soils of all sites were not frozen in the sampling time (observed in the active layer), whereas in most sites, we found frozen ground a few dozen centimeters below the surface mineral soil at the samplings.

In the laboratory, plant roots, coarse woody debris, and rocks were removed from soil samples. Half of the soil sample was oven-dried (40°C) and stored for measuring soil pH, exchangeable base cations [calcium (Ca), magnesium (Mg), and potassium (K)], pyrophosphate-extractable Al (Al-p) and Fe (Fe-p), and oxalate-extractable Al (Al-o) and Fe (Fe-o). The remaining soil was stored at less than 5°C for measuring extractable organic C and for repeated soil extractions and batch extractions.

Soil pH was determined in a 0.01 M $CaCl_2$ slurry (dry soil:$CaCl_2$ = 1:1) with a pH meter (F-51, Horiba, Japan). Exchangeable Ca, Mg, and K were determined by extraction with 1 M ammonium acetate at pH 7.0 (0.4 g dry soil and 30 ml extractant) and measured using atomic adsorption spectrophotometry (AA800, PerkinElmer Japan). Cation exchange capacity (CEC) was measured after ammonium acetate extraction by measuring the ammonium adsorbed to the soil using 1 M KCl extraction. Base saturation was calculated as the percentage of base cations relative to CEC. Al and Fe associated with organic matter were determined by extraction with 0.1 M sodium pyrophosphate at pH 10.0 (0.4 g dry soil and 40 ml extractant) and 0.2 M ammonium oxalate at pH 3.0 (0.4 g dry soil and 40 ml extractant). Total C and N contents in the soil were determined with a CN analyzer (Sumigraph NC-900, Sumigraph, Japan).

To compare the amount of soluble organic C and organic C potentially associated with mineral soils at the sites, we extracted organic C using phosphate buffer (Matsumoto and others 2000; Matsumoto and Ae 2004; Hobara and others 2013). Firstly, approximately 5 g of wet soil was shaken with 40 ml of 1/15 M phosphate buffer ($Na_2HPO_4\cdot12$-H_2O and KH_2PO_4, pH 7) in 50-ml volume centrifuge tubes on a shaker for 1 h. The soil suspension was centrifuged at 3000 rpm for 10 min and filtered with ashed glass fiber filters (Whatman GF/F). The organic C in the extractants [phosphate buffer-extractable organic C (PEOC)] were measured using a total organic C (TOC) analyzer (Shimadzu TOC-V, Shimadzu, Japan) after acidification (pH < 3) with HCl. Organic C released from the soil by phosphate solutions is due to the higher affinity of phosphate than organic C for binding sites on mineral soils (Kaiser and Zech 1996). The phosphate buffer extractant can yield about 10 times more C than the KCl and water extractant, and the concentration of PEOC correlates with the

Table 1. Geography and Vegetation for Study Sites

Ecosystem	Site name	Site characteristics	Latitude (N)	Longitude (W)	Elevation (m a.s.l.)	Dominant species
Tundra						
	T1	Coastal tundra	69°50′26.8″	148°42′31.6″	35	*Eriophorum vaginatum, Salix pulchra, Carex lugens, Betula glandulosa*
	T2	Upland tundra	68°53′57.7″	148°52′02.5″	425	*Eriophorum vaginatum, Ledum palustre, Vaccinium vitis-idaea, Betula glandulosa*
	T3	Healthy tundra near Sagavanirktok River	68°46′40.7″	148°51′08.5″	470	*Eriophorum vaginatum, Carex bigelowii, Vaccinium uliginosum, Betula nana*
	T4	Moist non-acidic tundra near Toolik Lake	68°37′51.3″	149°37′19.7″	770	*Eriophorum vaginatum, Vaccinium vitis-idaea, Dryas integrifolia, Salix arctica*
	T5	Moist acidic tundra around Imnavait Creek	68°37′40.8″	149°18′08.6″	930	*Eriophorum vaginatum,Carex bigelowii, Vaccinium vitis-idaea, Cassiope tetragona*
	T6	Moist acidic tundra near Toolik Lake	68°37′32.8″	149°36′08.4″	770	*Eriophorum vaginatum, Vaccinium vitis-idaea, Betula nana, Ledum palustre*
Tundra–forest ecotone						
	TF1	Transient zone	67°59′27.5″	149°45′37.5″	690	*Picea glauca, Vaccinium uliginosum, Vaccinium vitis-idaea, Empetrum nigrum*
	TF2	Gold Creek	67°44′09.5″	149°45′23.1″	478	*Picea glauca, Betula glandulosa, Vaccinium uliginosum, Vaccinium vitis-idaea*
Black spruce forest						
	F1	Black spruce in Coldfoot1	67°10′47.6″	150°18′24.9″	349	*Picea mariana, Vaccinium vitis-idaea, Ledum palustre, Betula glandulosa*
	F2	Black spruce in Coldfoot2	67°10′59.7″	150°17′54.7″	245	*Picea mariana, Vaccinium vitis-idaea, Eriophorum vaginatum, Sphagnum spp.*
	F3	Yukon River upper	66°04′48.2″	150°09′56.3″	220	*Picea mariana, Vaccinium vitis-idaea, Vaccinium uliginosum, Betula glandulosa*
	F4	Yuron River lower	65°50′30.5″	149°38′44.2″	360	*Picea mariana, Ledum palustre, Vaccinium vitis-idaea, Vaccinium uliginosum*

extracted minerals (Al and Fe) (Hobara and others 2013).

To estimate the percentage of C adsorbed to mineral soils relative to total soil C, we conducted a repeated extraction experiment in the laboratory in the Toolik Field Station using 2 soils (Soil 1 and 2) from the T6 site. The T6 site was selected for this test because this site was most accessible for us from the laboratory and to minimize biochemical changes in soil before test. We removed exchangeable organic C and weakly bound organic C by extraction with 1 M KCl and Milli-Q water. In a 50-ml centrifuge tube, 3 g of wet T6 soil and 40 ml of 2 M KCl were shaken for 30 min and then centrifuged. The supernatant was filtered (Whatman GF/F) and analyzed for TOC to estimate KCl-extractable organic C. The soil was then rinsed with Milli-Q water, and the rinsed water was also analyzed for TOC. The rinsed soil was then subjected to repeated extractions with pyrophosphate buffer [0.1 M sodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$) and 0.1 M pyrophosphate acid, pH 7.0]. In total, 8 pyrophosphate extractions were performed and the solutions were analyzed for TOC. We used pyrophosphate buffer for the repeated extractions because it is a strong metal chelator compared with phosphate buffer, although both buffers are chelating agents. Thus, we assumed that pyrophosphate-extractable organic C is associated more tightly with metals, less leachable and less bioavailable than PEOC. In contrast, KCl and water-extractable organic C are used for indices of exchangeable organic C or organic C less interacted with soil.

To compare the potential of acidic and non-acidic soils to absorb organic C, we conducted a batch extraction to determine the equilibrium adsorption of organic C. We designed the experiment according to Jardine and others (1989) and Qualls (2000). Four solutions were prepared with different DOC concentrations from 1 extract solution as follows. Wet T6 organic layer soil (100 g) was extracted with 500 ml of deionized water, shaken for 24 h at 70 rpm, and filtered (0.45-μm cellulose acetate filter, Sartorius), and the solution was analyzed for TOC. The solution contained 30 mg l^{-1} of DOC, which was concentrated approximately 3- or 6-fold using rinsed gel filtration units (VIVA Spin, 3,000 MW cut-off, Sartorius), and 81 or 161 mg l^{-1} DOC solutions were prepared. A 0 mg l^{-1} DOC solution was prepared by mixing Milli-Q water with NaCl to achieve an ionic strength equivalent to the 30 mg l^{-1} DOC solution ($I = 0.05$ M). To minimize the effect of solution pH, the solutions were adjusted to pH 5.0 with 0.1 M HCl. Thus, we obtained 4 solutions with different concentrations (0, 30, 81, and 161 mg l^{-1} DOC). The two test soils from the T4 and T6 sites were selected for batch extractions as these sites are near each other and have similar climatic conditions but contrasting soil geochemical characteristics, representing the wide variations in soil pH observed in Alaskan ecosystems (Walker and others 1998; Hobbie and Gough 2002). T4 and T6 soils were mixed with each of the 4 solutions (1 g soil and 10 ml solution), shaken for 24 h at 120 rpm and 23°C to reach equilibrium, centrifuged at 3000 rpm for 10 min, and then filtered through 0.45-μm cellulose acetate filters. The supernatant was analyzed for DOC using the TOC analyzer. The experiment was duplicated for each sample.

RESULTS

Soil pH varied between the sites, ranging from acidic to neutral (pH 3.26–7.24) (Supplementary Table 1), similar to observations in other studies (Bockheim and others 1998; Ping and others 1998; Walker and others 1998). The pH range across the sites was greater than the range within each site. Soils from the T2, T3, T5, T6, TF2, F1, F2, and F4 sites had relatively low pH (pH < 5), whereas soils from the T1, T4, and F3 sites had circumneutral pH (approximately pH 5–7).

Exchangeable Ca also varied widely between the sites, ranging from 0.11 to 7.56 mg g^{-1}. This range was considerably greater than that for exchangeable Mg and K. Wide variations between the sites were also found for CEC and base saturation. Extractable Al and Fe, such as Al-p, Fe-p, Al-o, and Fe-o, also varied widely between the sites (Al-p: 0.16–3.14 mg g^{-1}, Fe-p: 0.36–7.22 mg g^{-1}, Al-o: 0.15–1.90 mg g^{-1}, Fe-o: 1.34–11.25 mg g^{-1}).

The values of indices for soil characteristics, such as soil pH, extractable Ca, and extractable Al, were mutually related, despite the wide variations in these values among sites. Base saturation was a function of soil pH with a significant correlation ($P < 0.001$, $R^2 = 0.739$) (Figure 2). Both soil pH and base saturation showed positive correlation with exchangeable Ca and negative correlation with extractable Al and Fe (Figure 3A, B).

Total soil C and PEOC varied between the sites, but their concentrations showed positive correlation ($P < 0.001$; Figure 4), and the PEOC comprised approximately 5% of total C. Base saturation and soil pH were strong functions of total C and PEOC; both total C and PEOC in soil were significantly correlated with base saturation and soil pH, though the correlation coefficient was considerably
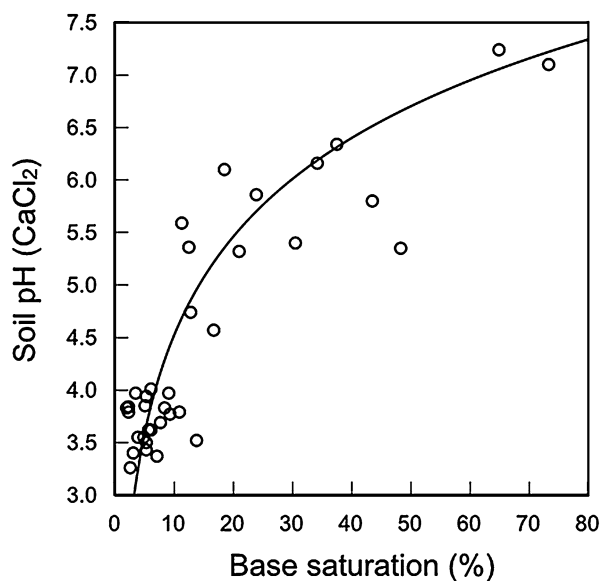
Figure 2. Relationship between base saturation and soil pH ($CaCl_2$) and of the study soils. The *solid line* indicates the regression curve ($y = 1.001 \log x + 2.210$, $R^2 = 0.739$, $P < 0.001$).

greater for PEOC than that for total C (Figure 5A–D). PEOC concentration was positively correlated with Al and Fe associated with organic matter, i.e., Al-p, Fe-p, Al-o, and Fe-o, ($P < 0.001$; Figure 6).

The repeated extraction experiment showed that a significant amount of C (30–55% of total soil C) was extracted from the test soils in a soluble form (Figure 7). The regression curves indicated that further extraction desorbed more C from the soils. Compared with the pyrophosphate-extractable organic C, KCl- and water-extractable organic C comprised less C ($<1\%$ of total C).

The adsorption experiment revealed that DOC adsorbed to soil increased with an increase in DOC concentration in the added solution (Figure 8). Significant correlations ($P < 0.001$) were observed between initial solution DOC and the amount of adsorbed DOC. The rates of increase for both correlation curves decreased with an increase in added DOC. Soil from the T6 site showed a greater rate of DOC adsorption with increasing added DOC than the soil from the T4 site, indicating greater potential for DOC sorption in the T6 soil than in the T4 soil. Addition of solutions containing 81 and 161 mg l^{-1} DOC resulted in positive values for adsorbed DOC (that is, a net decrease in DOC), and the T6 soil adsorbed about twice the amount of DOC than the T4 soil. Addition of solutions containing 0 and 24 mg l^{-1} DOC resulted in negative values for adsorbed DOC (that is, a net increase in DOC), and the T6 soil desorbed more DOC than the T4 soil.
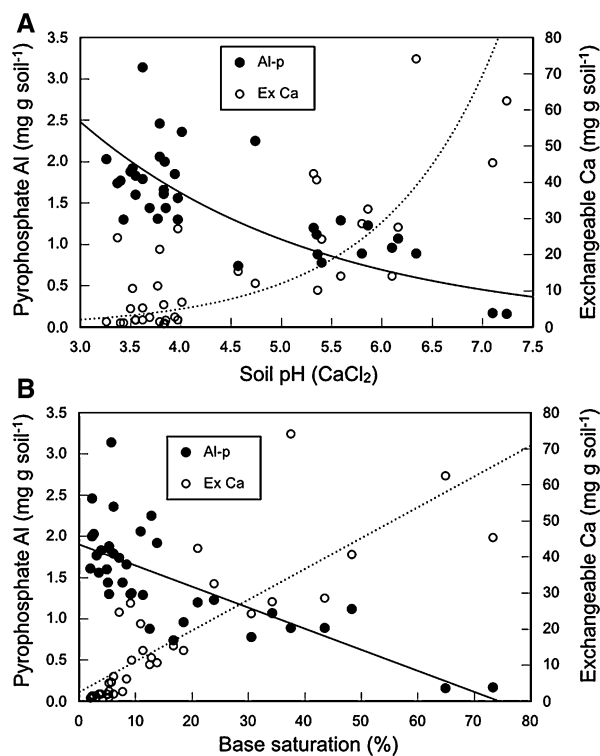

Figure 3. A Relationship of soil pH ($CaCl_2$) with pyrophosphate-extractable Al (*solid circles*) and exchangeable Ca (*open circles*). The *solid* ($y = 8.8872e^{-0.425x}$, $R^2 = 0.636$, $P < 0.001$) and *dashed* ($y = 0.1511e^{0.876x}$, $R^2 = 0.561$, $P < 0.001$) *lines* indicate the *regression curves* for extractable Al and exchangeable Ca, respectively. **B** Relationship of base saturation with pyrophosphate-extractable Al (*solid circles*) and exchangeable Ca (*open circles*). The *solid* ($y = -0.0255x + 1.9015$, $R^2 = 0.541$, $P < 0.001$) and *dashed* ($y = 0.8536x + 2.5534$, $R^2 = 0.686$, $P < 0.001$) *lines* indicate the regressions for extractable Al and exchangeable Ca, respectively.

DISCUSSION

The results of this study indicated that soil acidity represents a distinctive feature of the mineral characteristics of the Alaskan soils, which may differ due to variations in weathering. Close relationships were observed among base saturation, soil pH, Al and Fe minerals, and adsorptive organic C for soils from a broad area over northern Alaska, including tundra and boreal forest ecosystems. These observations clearly demonstrate that weathering-related geochemical changes in soil can lead to the strong relationship in the variations between soil pH and soil C dynamics in circum-Arctic ecosystems, and support the hypothesis that sorption of organic C to Al and Fe minerals is a key mechanism linking weathering with C dynamics in the soils.
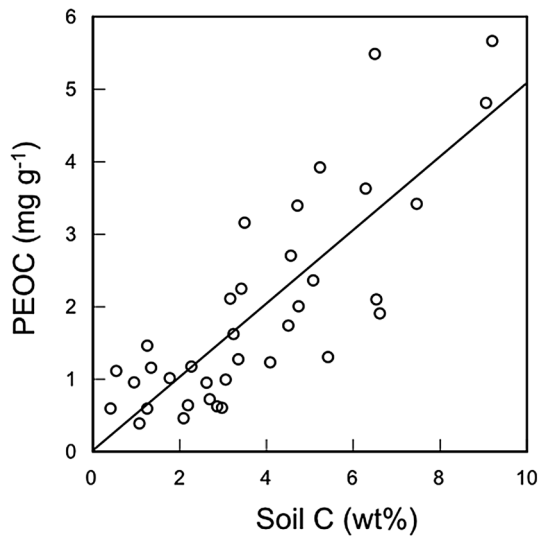
Figure 4. Relationship between concentrations of total soil C and PEOC. The *solid line* indicates regression line ($y = 0.5071x + 0.0155$, $R^2 = 0.668$, $P < 0.001$)
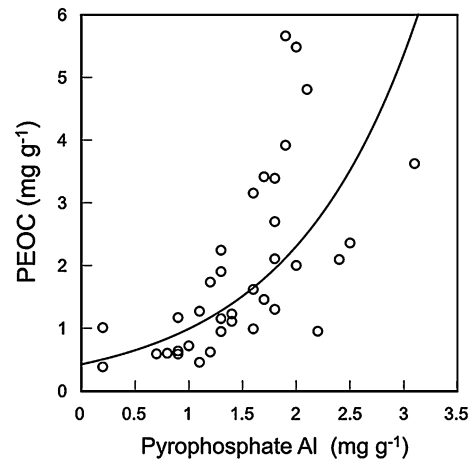

Fig. 6. Relationship between pyrophosphate-extractable Al and PEOC concentration. The *solid line* indicates the regression curve ($y = 0.4340e^{0.834x}$, $R^2 = 0.504$, $P < 0.001$).

In this study, a wide variety in mineral characteristics occurred between sites, and soil pH was a key indicator that correlated with many of these characteristics. Soils with a low pH showed low base saturation, low base cations, and high extractable Al and Fe. These relationships between soil pH and mineral characteristics concur with the results reported in other studies conducted in Alaska (Ping and others 1998; Hobbie and Gough 2002; Hobara and others 2013). In addition, these relationships suggest that mineral soil characteristics synchronously change as they are influenced by mineral weathering. For example, leaching of

base cations through mineral weathering results in decreased base saturation and increased protons in the soil (Ugolini and Dahlgren 2002). Thus, well-weathered soils have relatively low base cations, low base saturation, high proton concentrations, high reactivity of Al and Fe minerals remaining in the soil, and subsequently a low pH (Ugolini and Dahlgren 2002; Valentine and Binkley 1992; Ping and others 1998). Thus, the variations in mineral soil characteristics, including soil pH, observed in this study may result from differences in the extent of weathering. In northern Alaskan foothills, acidic soil is commonly observed in areas of relatively older substrates that are more weathered (Walker
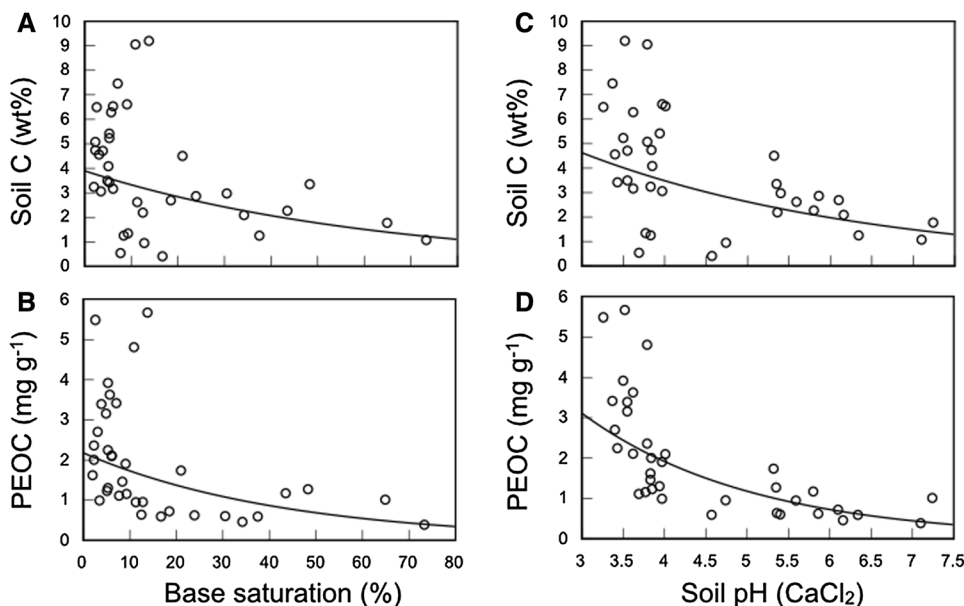

Figure 5. Relationships of base saturation with total soil C concentration (**A**) and PEOC concentration (**B**) and relationships of soil pH ($CaCl_2$) with total soil C concentration (**C**) and PEOC concentration (**D**). The *solid lines* indicate the regression curves (**A**: $y = 3.898e^{-0.016x}$, $R^2 = 0.141$, $P < 0.05$; **B**: $y = 2.179e^{-0.023x}$, $R^2 = 0.320$, $P < 0.001$; **C**: $y = 10.856e^{-0.284x}$, $R^2 = 0.190$, $P < 0.005$; and **D**: $y = 13.339e^{-0.485x}$, $R^2 = 0.593$, $P < 0.001$).
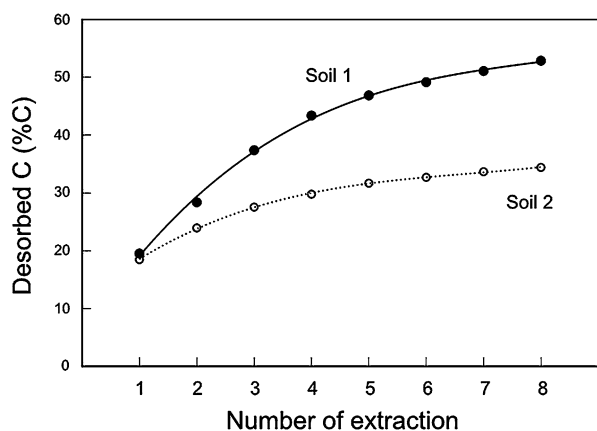
Figure 7. Percentage of C desorbed from Soil 1 (*solid circles*) and Soil 2 (*open circles*) relative to total soil C for the number of repeated extractions in the desorption experiment. The *solid* and *dotted lines* indicate the regression curves for Soil 1 ($y = 0.0537x^3 - 1.0836x^2 + 8.1084x + 11.4645$, $R^2 = 0.999$, $P < 0.001$) and Soil 2 ($y = 0.0686x^3 - 1.6696x^2 + 14.8159x + 5.8662$, $R^2 = 0.998$, $P < 0.001$), respectively.
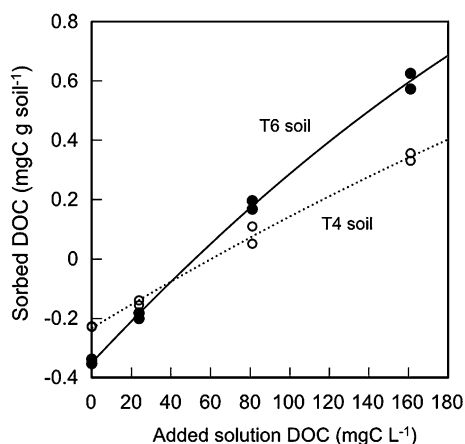

Figure 8. Relationship of DOC concentration in added solution with the amount of DOC sorbed to soil in the adsorption experiment. *Solid* and *open circles* indicate the soil samples from T4 and T6, respectively. The *solid* ($y = -0.000008x^2 + 0.0071x - 0.3499$, $R^2 = 0.998$, $P < 0.001$) and *dotted* ($y = -0.000003x^2 + 0.004x - 0.2334$, $R^2 = 0.994$, $P < 0.001$) *lines* indicate the regression curves.

and others 1998; Hobbie and others 2002; Hobara and others 2013). However, acidic soil can also be found in young substrates. T3 is on a relatively young substrate, and although most soils show circumneutral pH, acidic soils (approximately pH 4–5) occur in hilly sites such as heath and tussock tundra ecosystems (Giblin and others 1991; Valentine and Binkley 1992; Hobara and others

2013). The acidity may be due to greater weathering and good drainage.

The negative correlations between soil pH and Al-p/Fe-p indicate that the variations in mineral characteristics concur with the variations in minerals associated with soil organic matter. The positive correlations between PEOC and extractable Al/Fe suggest a strong control of Al and Fe minerals on C adsorption. Weathering would remove base cations and increase the relative abundance of Al and Fe minerals, which may increase the sorption of organic C. Reactive Al and Fe minerals in soil play an important role in long-term preservation of soil organic matter (Torn and others 1997; Kaiser and Guggenberger 2000). Thus, the trends for accumulation of organic matter in Alaskan soils, which varied between the sites, may be relatively stable and not temporal.

PEOC correlated with total C, and repeated extraction with pyrophosphate solution removed 50% of total soil C. Both phosphate buffer and pyrophosphate solution enable removal of metal-associated organic matter. Thus, the results indicate that organic C adsorption to mineral soils is a key mechanism for retaining and accumulating C in Arctic soils. The greater PEOC in low pH soils indicates that acidic soils have a relatively greater potential for organic matter adsorption, which concurs with the greater capacity for organic adsorption in acidic soil than neutral soil, as shown in the adsorption experiment. Pool size of PEOC in soil closely correlates with mineralization rate (Matsumoto and others 2000), suggesting an importance of this organic C fraction for soil C fluxes originating from biological activity. Therefore, our results suggest that acidic soils are a relatively greater sink for organic C compared with neutral soils and that soil geochemistry may critically influence site differences in C dynamics in Alaskan ecosystems.

In northern Alaska, the variations in soil pH are broadly linked with ecosystem characteristics related to dynamics of organic matter/C. The soil pH variations are closely associated with plant species composition (Shippert and others 1995; Gough and others 2000) and with significant differences in C dynamics in this region, such as CO_2 fluxes from soil (Walker and others 1998; Hobbie and others 2002) and mineralization characteristics (Hobbie and Gough 2002). In particular, respiration in Arctic soils is often greater at lower pH (Hobbie and others 2002), in contrast with the results of numerous studies demonstrating that circumneutral soil pH promotes greater litter decomposition than acidic soil pH (Andersson and others 1994;

Baath and Arnebrandt 1994; Webster and others 2000). Our results revealed that acidic soils contained greater organic matter adsorbed to mineral soils than the neutral soils, suggesting greater dissolution of organic C in acidic soils through chemical equilibrium between solid and liquid phases. This suggestion might be supported by the observation of greater DOC leaching from acidic soils than from neutral soils in northern Alaska (Hobbie and others 2002). Soil microbial activity can be strongly constrained by the precipitation of soil organic matter with minerals (Scheel and others 2008), and extractable and dissolved organic matter in the Arctic are known to be partly bioavailable (Shaver and others 2006; Abbott and others 2014; Larouche and others 2015). Therefore, dissolution of adsorbed organic matter and subsequent supply of organic matter to microorganisms, which could be greater in acidic soils, may lead to higher microbial activity. The stimulated microbial activity and higher primary production in acidic soils (Walker and others 1998) would lead to greater amounts of soluble C despite greater amounts of organic C adsorbed to minerals. These findings on the relationships between soil geochemical characteristics and ecosystem C processes are not necessarily related to permafrost and thus would be applicable to non-permafrost ecosystems.

In addition to the dynamics of C, the dynamics of other elements in Arctic soils would also be influenced by the geochemical characteristics associated with organic matter adsorption. For example, extractable and dissolved organic matter contains significant amounts of N and P, and their solubility affects the transport of metals such as Al and Fe (Kalbitz and others 2000; Chantigny 2003). Because these elements are linked with microbial activity through various pathways (Plante 2006), adsorption/desorption processes of soil organic matter and geochemical controls on these processes may lead to unexpected relationships with biological and biochemical processes by influencing the cycling of these elements as well as C.

An effect of minerals on C accumulation in soil by organic matter adsorption was also observed in organic layer soils at some of the study sites (Hobara and others 2013). Organic layer soil constitutes a major C reservoir and is an important source of nutrients and DOC in Arctic ecosystems (Judd and Kling 2002; Yano and others 2010). In addition, elemental cycles in the organic layer would be dynamic due to the activities of microorganisms and plant roots. As compared with organic soil, biological activities are small, but geochemical processes such as C adsorption are large in mineral

soil. The importance of C accumulation in mineral soil for ecosystem C cycling may be increased by warming and permafrost thawing because mineral soil comprises a major component of permafrost in Arctic ecosystems. In the North American Arctic, soil organic C accumulates approximately 20% in the organic enriched surface horizon, 43% in the subsurface horizons (to permafrost), and 37% in the upper permafrost to 1 m depth (Ping and others 2008) and some more in deeper soil (Hugelius and others 2014). Organic C loss from mineral soil might exceed that from organic soil through permafrost thaw processes (Abbott and Jones 2015; Abbott and others 2015), although there is a relatively large variability in soil organic C storage of organic soils across regions (Hugelius and others 2014). Our findings on the different capacities of DOC adsorption between acidic and non-acidic soils suggest that the role of the thawed mineral soil in C cycles varies with soil acidity; for example, DOC retention in thawed mineral soil could be greater in acidic sites. Permafrost is a distinctive component of circum-Arctic ecosystems and contains as much organic C as active mineral soil (Ping and others 2008). Numerical models have suggested a high risk of global-scale permafrost degradation due to warming (Lawrence and Slater 2005). Permafrost thaw and increased active layer thickness can also be promoted by increased number of wildfires in the circum-Arctic region, presumably associated with climate change (Hu and others 2010). Therefore, these consequences of climate change could result in an increase in the extent of geochemical control on C dynamics in Arctic soils. The relationships of weathering-related soil characteristics with soil C indicate that C cycle patterns in active soil layer can be switched via weathering in the circum-Arctic ecosystems. The clear differences in minerals and organic C in soil among sites with different glacial histories in this study suggest that temporal changes in these soil mineral characteristics lead to a dynamic shift in soil C as a consequence of permafrost thawing.

Arctic ecosystems may face further severe environmental changes this century (Anisimov and others 2007); therefore, consequences to the ecosystem from C cycle feedbacks increase our concern. Our research demonstrates that C retention in Arctic soils is closely associated with the mineral soil qualities characterized by the extent of weathering and varies widely among sites, indicating that mineral soil characteristics related to weathering explain differences in C dynamics, including C sinks, in Alaskan ecosystems. Particularly, soil pH may be a simple index that reflects soil

characteristics and would thus be useful for characterizing and scaling up ecosystem functions to broad areas with considerable site variability. Furthermore, although our study determined that organic C adsorption is an important process controlling C dynamics in the Alaskan ecosystems, this process can be influenced by environmental changes, such as temperature effects on adsorption (Davidson and Janssens 2006). Thus, further studies are required to consider how environmental changes will affect C processes in Arctic soils and to understand the fate of released organic matter in Arctic ecosystems.

ACKNOWLEDGMENTS

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