

# Rapid nutrient release from permafrost thaw in arctic aquatic ecosystems

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## Abstract

Few studies provide experimental data to support the role of permafrost thaw on changes in arctic freshwater chemistry. We designed an incubation experiment to look at rapid nutrient release from permafrost soils and active layer soils under different warming scenarios, changes in redox environment, and microbial activity. Permafrost soil tended to immediately release more nutrients than active layer soils, especially under warmer conditions; suggesting the active layer is depleted in nutrients and the water column may be re-supplied with these ions from thawing permafrost. The release of micronutrients (Ca, Fe, Mg, S, Si) from incubated permafrost soils responded strongly to increased temperature; however, temperature alone was not necessarily the primary driver of macronutrient (N, P) release from permafrost. Other physicochemical parameters influenced by temperature, such as oxidation-reduction potential (ORP), microbial activity, dissolved organic carbon (DOC), and Fe played an additional role in nutrient release from permafrost. These experiments suggest nutrient release via thaw of permafrost soils is able to contribute ample essential nutrients to arctic aquatic ecosystems, even within one day of warming. Further warming of the Arctic is likely to result in substantial changes to nutrient availability and cycling in these dominant habitats.

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## Introduction

Greater than one-half of the Arctic Coastal Plain in Alaska is covered by thaw lakes or drained thaw lake basins, which are often filled with ponds formed in ice-rich permafrost (Hinkel et al., 2003; Frohn et al., 2005). Other areas of the Arctic, including large expanses of permafrost-influenced areas in northern Canada and west Siberia, also have large concentrations of lakes (Smith et al., 2007). Despite this dominance of freshwater habitats, aquatic ecosystems of the Arctic tundra are poorly understood, especially how they will respond to future warming and permafrost degradation.

Arctic air temperatures are increasing at nearly twice the rate of lower latitudes (McBean et al., 2005) and substantial degradation of permafrost is predicted with further warming over the next 100 years (Lawrence and Slater, 2005). Permafrost degradation may lead to substantial increases in freshwater discharge to the ocean (Lawrence and Slater, 2005) and increased fluxes of carbon to the atmosphere (Christensen et al., 2004; Schuur et al., 2008; Belshe et al., 2013), and it may alter the availability of nutrients for plant growth (Yang et al., 2013). Several authors have suggested permafrost thaw and degradation is releasing stored soil nutrients into arctic freshwater environments (Hobbie et al., 1999; Frey and Smith, 2005; Schindler and Smol, 2006; Frey et al., 2007; Keller et al., 2007, 2010; McClelland et al., 2007; Lougheed et al., 2011; Lewis et al., 2012). For example, increased concentrations of macronutrients and dissolved organic carbon (DOC) observed in permafrost-free watersheds suggest that warming of permafrost zones will increase flux of these constituents to the Arctic Ocean (Frey and Smith, 2005; Frey et al., 2007). Keller et al. (2007) found that permafrost soils are more ion-rich than active layer soils, and in another study suggested elemental and isotopic changes through time in an arctic stream were indicative of a thickening active layer (Keller et al., 2010). Finally, thermokarst slumping into arctic aquatic ecosystems has also led to increased ionic concentrations

in these water bodies (Kokelj et al., 2005, 2009; Bowden et al., 2008; Dugan et al., 2012). However, most studies to date on nutrient release from permafrost in the Arctic have been observational. In a recent review, Frey and McClelland (2009) indicated that more studies comparing nutrient release from permafrost and active layer soils are required. In particular, an experimental study to identify differences in permafrost and active layer geochemistry during warming events could aid in interpretation of observational studies.

The biogeochemical response of permafrost to warming may be complicated as temperature changes alone are unlikely to be the only driver of nutrient release from soils. For example, permafrost soils can have a very active microbial community that may enhance decomposition and nutrient release at warmer temperatures (Keuper et al., 2012). Furthermore, release of nutrients may be driven by reducing conditions that may be linked to seasonal warming (Olivie-Lauquet et al., 2001). Finally, interactions among dissolved organic carbon (DOC) with nutrients and metals may be altered with climate warming (Porcal et al., 2009). Observational studies are unable to directly indicate thawing of permafrost leads to an increase in nutrient release from permafrost soils. However, experimental studies may provide stronger evidence to support the hypothesis of warming temperatures and permafrost thaw leading to nutrient enrichment of arctic freshwater environments.

Increased nutrient concentrations, coincident with warmer temperatures, would have important biological implications for arctic freshwaters. Experiments have shown that additions of phosphorus to arctic lakes and streams can lead to increases in algal biomass and insect abundance (Hobbie et al., 1999). Recent studies have indicated that nitrogen also plays an important role in algal growth in arctic freshwaters (Levine and Whalen, 2001; Hernandez, 2012). Increases in available nutrients, together with a warmer Arctic and longer growing seasons for algae, may lead to changes in algal community structure (Smol et al., 2005), increased algal primary production (Michelutti et al.,

2005), and consequences for the carbon budgets of high latitude ecosystems (Kling et al., 1992).

While active layer thickness (ALT) on the Alaskan coastal plain has remained stable over the past decade (Shiklomanov et al., 2010), elsewhere in the Arctic, Zhang et al. (2005) observed increased ALT through time in Russian river basins. One of the primary factors determining ALT is the number of accumulated degree days of thaw (Hinkel and Nelson, 2003; Shiklomanov et al., 2010), with other important drivers including snow cover (Zhang et al., 2005), the presence of standing water (Hinkel and Nelson, 2003; Shiklomanov et al., 2010), and vegetation cover (Walker et al., 2008). In particular, due to high thermal conductivity, thaw depth tends to be greatest in saturated soils and under shallow waters (Hinkel and Nelson, 2003; Streletskiy et al., 2008). ALT beneath tundra ponds has been neglected; however, deeper freshwater penetration with increasing ALT could result in the release of stored solutes from permafrost.

The arctic coastal tundra near Barrow, Alaska (U.S.A.) is characterized by drained-thaw lake basins (Hinkel et al., 2003) underlain by continuous permafrost with a thaw depth of 30–90 cm (Hinkel and Nelson, 2003). Tundra ponds in the region are frozen for approximately 9 months of the year (Miller et al., 1980), have a near to neutral pH, and are low in nutrients (Hobbie, 1980; Sheath, 1986). Recent studies revisited tundra ponds first sampled in the 1970s as part of the International Biological Program (IBP) and reported increases in water temperature, phosphorus, nitrate, ammonia, and algal biomass over the past 40 years (Lougheed et al., 2011). The source of these increased nutrients over time is unknown; possible hypotheses include anthropogenic inputs of nutrients (meteoric and run-off; e.g., Schindler and Smol, 2006), the effect of climate warming on biogeochemical cycles within aquatic ecosystems (e.g., Porcal et al., 2009), and nutrient release via permafrost degradation (e.g., Hobbie et al., 1999; Keller et al., 2010). In addition to these changes in nutrients, tundra pond margins have experienced large increases in macrophyte cover in recent decades (Lougheed et al., 2011; Lin et al., 2012; Villarreal et al., 2012), which may be related to nutrient increases (Lara, 2012). Understanding how warming may have influenced nutrient availability in these ponds is key to understanding these recent changes.

In order to determine the potential source and magnitude of increased nutrient concentrations in IBP ponds over the past 40 years, we designed several incubation experiments to examine the influence of temperature, reducing conditions, and microbial activity on rapid macro- and micronutrient release from thawed permafrost and active layer soils.

## Methods

### SOIL SAMPLING

Soil cores were collected in June 2010 ( $n = 20$ ) and 2011 ( $n = 9$ ) approximately 100 m from any nearby ponds at the International Biological Program (IBP) tundra ponds site near Barrow, Alaska (see Lougheed et al., 2011). The sample site (near 71.29620°N, 156.70395°W) was chosen in order to reflect what might happen upon warming and thaw in an ice-wedge polygon at the IBP site. Soil cores were drilled with a 3 inch diameter core barrel, extracted, sorted, and then stored in a freezer at  $-70^{\circ}\text{C}$  until use. Both permafrost and active layer soils were collected from the same core. Permafrost soils were identified as those below a visible freeze-thaw boundary; generally, this was deeper than 40 cm. While some cryoturbation below this depth may have occurred

through time, preliminary experiments indicated no difference in nutrient release among permafrost soils shallower or deeper than 60 cm. Active layer cores were from above this boundary, but below 10 cm in depth. Nutrient concentrations in samples closer to the surface could have recently been affected by waterfowl and/or lemmings, and our interest was in the nutrients that had been stored, not recently introduced.

### LABORATORY EXPERIMENTAL DESIGN AND SAMPLING

Three separate experiments were completed in this study. For all treatments described below, six replicate pre-weighed ( $139.3 \text{ g} \pm 22.5$  [standard deviation]) permafrost soil core segments were placed into separate, acid washed 600 mL beakers, covered with 500 mL of de-ionized water, and incubated in a cold room at temperatures specified below. For all treatments, replicate core segments came from multiple soil cores and depths depending on experiment type (active layer vs. permafrost). Water temperature was continually recorded in a control beaker during each experiment using a HOBO Pendant series temperature data logger. At the end of each experiment, pH in each beaker was measured with an Orion model 525 benchtop pH meter, while oxidation-reduction potential (ORP) was measured at 2 mm soil depth with a platinum electrode.

### EXPERIMENT 1: EFFECT OF TEMPERATURE ON NUTRIENT RELEASE FROM PERMAFROST SOILS

Cores were incubated at 7, 9, 11, 13, 15, or 17 °C for 24 hours. Temperatures were selected to represent the range of mean and maximum water temperatures in IBP ponds from the 1970s to present time (Lougheed et al., 2011). The experiment was limited to 24 hours in order to minimize the effect of algal growth and bacterial transformations, and to focus on the potential rapid nutrient release from even short-term permafrost thaw. We acknowledge that extended incubations would likely result in greater release of nutrients (Martinez et al., 2003; Kim et al., 2013).

### EXPERIMENT 2: EFFECT OF ORP, MICROBIAL ACTIVITY, AND TEMPERATURE ON NUTRIENT RELEASE FROM PERMAFROST SOILS

A second set of experiments was run at 7 and 17 °C, with separate treatments to examine the effects of (1) reduced water conditions (<0 mV) achieved by the addition of 0.1 M sodium dithionite, (2) water sterilized with addition of 50 mL of formalin to eliminate microbial activity, and (3) water containing both formalin and sodium dithionite. Treatments were corrected every 6 hr with additional aliquots of sodium dithionite, HCl, and NaOH to insure constant pH and ORP below 0 mV over the 24 hour incubation.

### EXPERIMENT 3: A COMPARISON OF NUTRIENT RELEASE FROM ACTIVE LAYER AND PERMAFROST SOILS

Active layer soil cores were incubated at 7 °C and 17 °C for 24 hours. Data were compared to permafrost core results from Experiment 1.

### CHEMICAL ANALYSES

At the end of the 24 hr period, we slowly sampled water from the middle of the beaker using a 60 mL acid-washed syringe and

collected samples into four separate acid washed bottles, processed as follows: (1) unfiltered water was collected for the analysis of total phosphorus (TP), nitrate-nitrogen ( $\text{NO}_3\text{-N}$ ), total ammonia (measured as  $\text{NH}_3\text{-N}$ ), and total nitrogen (TN); (2) water for total dissolved phosphorus (TDP) and soluble reactive phosphorus (SRP) was filtered through a Whatman 0.45  $\mu\text{m}$  syringe filter; (3) filtered water was stored without headspace in an amber glass bottle for determination of dissolved organic carbon (DOC); and (4) water for micronutrient analysis was filtered and acidified with concentrated nitric acid. Water samples were frozen immediately following collection and analyzed within a week. Macronutrients were analyzed spectrophotometrically using standard methods (American Public Health Association [APHA], 1998). TP and TDP were determined by ascorbic acid method following persulfate digestion; SRP by ascorbic acid method;  $\text{NO}_3\text{-N}$  by cadmium reduction; and  $\text{NH}_3\text{-N}$  by the salicylate method. DOC and total nitrogen (TN) were analyzed with a Lachat IL 550 TOC/TN Analyzer. Analysis of TN was not performed for Experiment 3 due to an analyzer malfunction. Micronutrients (Ca, Fe, K, Mg, Na, S, and Si) were measured with a Perkin Elmer Optima 7300 DV ICP-OES Spectrometer.

### STATISTICAL ANALYSES

For predictive models of the effect of temperature on nutrient release, least squares best fit simple regressions were performed in JMP (version 7.0, SAS Institute, Cary, North Carolina) and R-project (version 3.0.2) software. Since simple linear regressions with temperature were not always adequate to explain the complex causes of nutrient release from permafrost thaw, multiple regression models were also used to increase the explanatory power of the models. Explanatory variables in the multiple regressions included those that have the potential to impact nutrient concentrations through adsorption from complexes and oxidation-reduction reactions; this included sediment ORP, Fe, Ca, and DOC. Multivariate regressions used a stepwise regression to identify important independent variables, followed by a standard least squares best fit method. We used a three-way ANOVA to find effects of three treatment types on nutrient release: temperature (7 °C and 17 °C), redox conditions (reduced vs. oxidized), and microbial activity (samples with formalin and without). To compare differences among soil types (active layer and permafrost) and temperature (7 °C and 17 °C), a two-way ANOVA followed by a Tukey-Kramer honest significant difference (HSD) test was performed. Nutrient concentrations and redox potentials were log transformed as required to normalize their distributions prior to analysis.

## Results

### EXPERIMENT 1: TEMPERATURE EFFECTS ON NUTRIENT RELEASE

The immediate release of the majority of macronutrients from permafrost soils was not significantly related to temperature. One exception was TDP, which had a very strong positive linear relationship with warmer conditions (Fig. 1, part a;  $R^2 = 0.701$ ,  $p = 0.0187$ ). Mean TDP concentration of the highest temperature treatment (17 °C) was approximately three-fold higher than the lowest temperature treatment (7 °C). No significant relationships were observed between water temperature and SRP concentrations (Fig. 1, part b;  $p = 0.3592$ ) or TP (Fig. 1, part c;  $p = 0.506$ ). Both  $\text{NO}_3\text{-N}$  (Fig. 1, part e;  $p = 0.840$ ) and  $\text{NH}_3\text{-N}$  (Fig. 1, part d;  $p = 0.216$ ) release from sediment indicated no relationship with increasing

water temperature; however, TN concentrations were positively related to temperature (Fig. 1, part f;  $R^2 = 0.726$ ,  $p = 0.0149$ ). The relationship of water temperature and DIN was not significant (not shown;  $p = 0.194$ ). DOC concentrations ranged between 5.22 and 0.6  $\text{mg L}^{-1}$  but showed high variation among temperature treatments. Water temperature had no effect on DOC release from permafrost (Fig. 2, part a;  $p = 0.5437$ ).

Micronutrients tended to have stronger positive relationships with temperature. Increasing temperature greatly increased the release of Ca (Fig. 3, part a;  $R^2 = 0.860$ ,  $p = 0.0026$ ), Fe (Fig. 3, part b;  $R^2 = 0.768$ ,  $p < 0.0096$ ), Si (Fig. 3, part d;  $R^2 = 0.681$ ,  $p = 0.0222$ ), Mg (Fig. 3, part e;  $R^2 = 0.826$ ,  $p = 0.0046$ ), and S (Fig. 3, part g;  $R^2 = 0.773$ ,  $p = 0.0091$ ) from permafrost soils. A weaker, but marginally significant relationship was observed with temperature and Na (Fig. 3, part c;  $R^2 = 0.549$ ,  $p = 0.0566$ ). No relationship was observed between K release (Fig. 3, part f;  $p = 0.4708$ ) and temperature. Finally, as water temperature increased, water-saturated soil became less oxic (Fig. 4;  $R^2 = 0.739$ ,  $p = 0.0282$ ).

Multiple regression models explained substantially more variation in macronutrient release than temperature alone (Table 1). Individual replicates were kept separate in this analysis to account for the full range of observed variation. Temperature, DOC, Fe, and Ca were the largest contributors to the majority of the multivariate models. Interestingly, while the TDP multivariate model (Table 1;  $R^2 = 0.504$ ,  $p < 0.0001$ ,  $n = 35$ ) explained more variation than the univariate model, it did not include temperature, only Fe and ORP. Our multivariate models for phosphorus species were able to explain five-fold more variation in TP (Table 1;  $R^2 = 0.458$ ,  $p < 0.0001$ ,  $n = 36$ ) and two-fold more variation for SRP (Table 1;  $R^2 = 0.291$ ,  $p < 0.0001$ ,  $n = 42$ ) as compared to the simple regression model, by including variables such as DOC and Ca. There remained no significant model for nitrate release (Table 1;  $R^2 = 0.012$ ,  $n = 42$ ); however, the ammonia (Table 1;  $R^2 = 0.657$ ,  $p < 0.0001$ ,  $n = 42$ ) and TN (Table 1;  $R^2 = 0.654$ ,  $p < 0.0001$ ,  $n = 42$ ) multivariate models explained more variance than the simple model. Temperature was an important factor in each of these models, in addition to some combination of Ca, Fe, and DOC. Our DOC multivariate model greatly increased the significance and explained more variation than the simple regression model (Table 1;  $R^2 = 0.272$ ,  $p = 0.0005$ ,  $n = 36$ ). Our model indicated that the release of DOC was highly dependent on ORP, followed by Fe and temperature.

### EXPERIMENT 2: EFFECT OF ORP, MICROBIAL ACTIVITY, AND TEMPERATURE ON NUTRIENT RELEASE

The experiment examining the combined effects of temperature, ORP, and microbial activity confirmed temperature alone was not the only factor affecting macronutrient and micronutrient release from permafrost soils. In particular, ORP appeared to play a stronger role than temperature in both macronutrient and micronutrient release.  $\text{NH}_3\text{-N}$  and TN were the only macronutrients to significantly increase with temperature alone (Table 2, part a; Fig. 5;  $p < 0.05$ ). Reduced conditions resulted in significantly higher concentrations of SRP ( $p = 0.0087$ ), TDP ( $p = 0.0063$ ),  $\text{NO}_3\text{-N}$  ( $p < 0.0001$ ), and TN ( $p < 0.0001$ ). Conversely,  $\text{NH}_3\text{-N}$  concentrations were significantly lower in treatments containing sodium dithionite ( $p < 0.0001$ ). While ammonia release was related to temperature,  $\text{NH}_3\text{-N}$  was absent in the majority of anoxic experiments, suggesting nitrogen gas was released under these highly reduced and anoxic conditions. The addition of formalin significantly increased the concentrations of SRP ( $p = 0.0214$ ), whereas the concentration

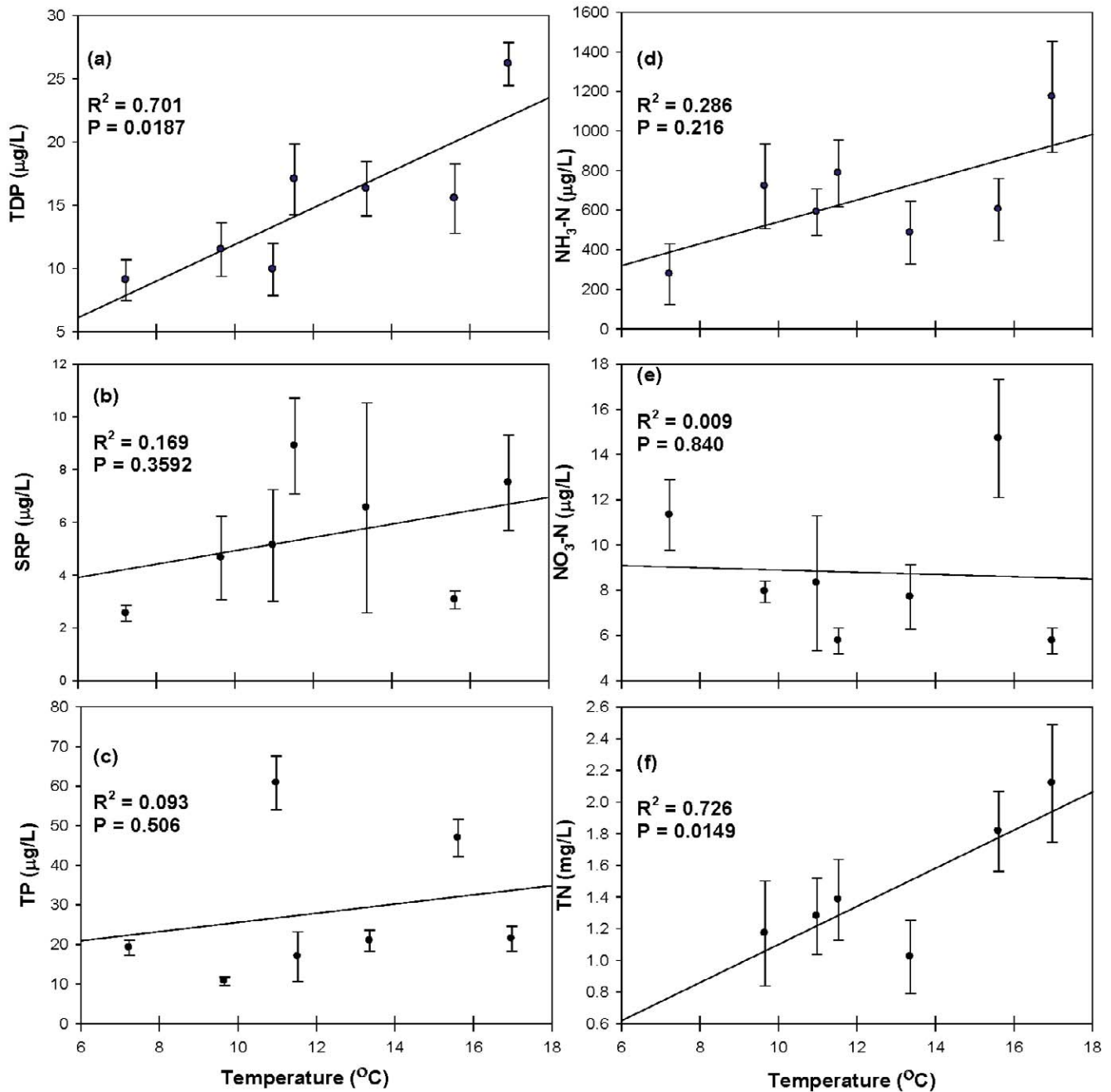


FIGURE 1. Macronutrient release (mean  $\pm$  standard error (SE)) from the permafrost incubation experiment as a function of temperature.

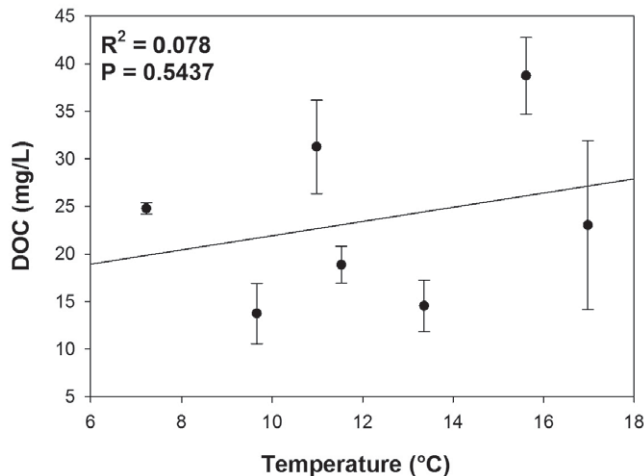
of  $\text{NH}_3\text{-N}$  decreased ( $p < 0.0001$ ). While TP was not significantly affected by any single treatment, the interaction among treatments led to changes in TP levels (Table 2, part a). The highest TP release was observed at warmer temperatures under anoxic conditions. There were also significant interaction effects between temperature and formalin for TDP and between ORP and formalin for  $\text{NH}_3\text{-N}$  and  $\text{NO}_3\text{-N}$ , likely because formalin decreased the reducing capability of sodium dithionite (Table 2, part a). Because formalin contains carbon, we did not measure the release of DOC in these experiments.

Both temperature and ORP significantly affected micronutrient release from permafrost soils (Table 2, part b; Fig. 6). Overall, all micronutrients measured were released in signifi-

cantly higher concentrations with reducing water conditions and warmer water temperatures (Table 2, part b). Interactions between temperature and formalin treatments were significant for K, and Fe concentrations indicated a significant interaction between reduced and formalin treatments. Because sodium dithionite contained S and Na, we did not measure S or Na in the treatments.

#### EXPERIMENT 3: COMPARISON OF NUTRIENT RELEASE BETWEEN ACTIVE LAYER AND PERMAFROST SOIL

For nearly one-half of our measured constituents, active layer released significantly fewer macronutrients and micronu-



**FIGURE 2.** Dissolved organic carbon (mean  $\pm$  SE) release from permafrost incubation experiment as a function of temperature.

trients as compared to permafrost soils at all temperatures (Figs. 7 and 8). For example, in the case of SRP and  $\text{NH}_3\text{-N}$ , significantly more macronutrients were released from the permafrost when compared to active layer, and also under warmer conditions (Fig. 7, parts a and d). While DOC was also released in greater amounts from permafrost, this difference was most pronounced at higher temperatures. In two instances (TDP and  $\text{NO}_3\text{-N}$ ) interactive effects were observed between temperature and soil type. Elevated temperature enhanced the release of TDP from permafrost (Fig. 7, part b; two-way ANOVA,  $p < 0.0001$ ,  $n = 22$ ), whereas  $\text{NO}_3\text{-N}$  release from active layer was elevated at higher temperatures. Observations of TP concentrations indicated no significant effects of temperature or soil type (Fig. 7, part c; two-way ANOVA,  $p > 0.05$ ).

All micronutrients showed an effect of temperature in this experiment; however, the effect of soil type varied (Fig. 8). Both Ca (Fig. 8, part a) and Mg (Fig. 8, part b) were released at significantly higher levels from permafrost and at 17 °C. Na concentrations were also significantly higher in the 17 °C treatment; however, this microelement was significantly higher in the active layer treatment. K (Fig. 8, part e), S (Fig. 8, part f), and Si (Fig. 8, part g) concentrations all showed no effect of soil type, but significant differences (two-way ANOVA,  $p < 0.0001$ ,  $n = 24$ ) among temperature treatments, with increased release at higher temperatures. Finally, Fe release from sediments indicated a significant interaction with temperature and soil.

Significant differences were also observed for physicochemical water parameters (pH and ORP) (Table 3; two-way ANOVA,  $p < 0.005$ ,  $n = 24$ ). Both pH and ORP showed a significant interaction with temperature and soil type; at 17 °C, permafrost incubations developed higher pH and lower ORP than active layer soils.

## Discussion

Permafrost soil tended to rapidly release more nutrients than active layer, especially with warming. Temperature alone,

however, was not necessarily the primary driver of macronutrient release from permafrost, while the release of micronutrients from incubated permafrost soils responded strongly to increased temperature. Several authors have observed or implied an effect of warming on nutrient release from thawing permafrost (Hobbie et al., 1999; Frey and Smith, 2005; Frey et al., 2007; Keller et al., 2007; Lougheed et al., 2011); however, none has evaluated the mechanism of this release. Our study indicates other physicochemical parameters influenced by temperature, such as ORP and microbial activity, may likely impact nutrient release from permafrost soils, by equal if not greater magnitude, when compared to temperature alone.

Several lines of evidence suggested increasing temperatures indirectly impacted rapid nutrient release by inducing less oxic conditions. We observed a decrease in soil ORP with increasing water temperature, and ORP was a significant component of our multivariate models explaining nutrient release in the temperature experiment. Furthermore, the release of most species of nitrogen and phosphorus, as well as micronutrients, increased when ORP was experimentally reduced. Redox potential is important in the biogeochemical cycling of many elements with more than one oxidation state, including N, S, and Fe. The increase in the concentrations of many micronutrients with only one oxidation state, such as Ca, K, Mg, and Si, under reducing conditions also suggests these elements were in complexes with redox sensitive elements. In addition, the mobility and cycling of P is easily controlled when P is combined with Fe in complexes. Conversely, while we expected total ammonia to increase under reducing conditions, it was largely absent from these incubations, suggesting dissolved  $\text{NH}_3\text{-N}$  was converted to a gaseous form under anaerobic conditions. Studies on wetland soils have indicated that reduced conditions can lead to release of nutrients (e.g., McLatchey and Reddy, 1998) and trace metals (e.g., Olivie-Lauquet et al., 2001); however, these relationships can also be mediated by the effect of microbial activity on ORP and DOC (Olivie-Lauquet et al., 2001). For example, organic matter bound to trace elements such as Fe can be released by microbial action under reducing conditions (Olivie-Lauquet et al., 2001; Grybos et al., 2009).

In the field, the redox condition of the active layer and recently thawed permafrost are likely to play a large role in the mobility of nutrients. In summer 2012, the ORP at the interface of the active layer and permafrost was  $112 \pm 9$  mV (Lougheed, unpub. data), which borders on anaerobic conditions, and could likely alter the mobility of previously frozen constituents in the soil. Conditions during our reducing experiment were much lower ( $< -180$  mV) than this value, and therefore may overestimate potential release; however, these are a better reflection than conditions during the temperature effects experiment, which were largely oxic ( $> 300$  mV).

Microbial mineralization of nutrients may be enhanced in warming permafrost (Keuper et al., 2012). Microbial communities in tundra ponds can respond quickly at thaw (Hobbie, 1980), with resultant rapid changes in microbial genes involved in carbon or nitrogen cycling (Mackelprang et al., 2011). In our experiments, the release of several forms of phosphorus increased with the prevention of microbial growth; SRP increased at both temperatures, while TDP and TP increased at 7 °C but not 17 °C. These data suggest that cold-adapted microbes are able to take up phosphorus even during a 24 hour experiment. However, at warmer temperatures, other factors may play a more important role in nutrient release. Conversely, there were no impacts of the formalin treatment on the release of any micronutrients; however, we did find that Fe

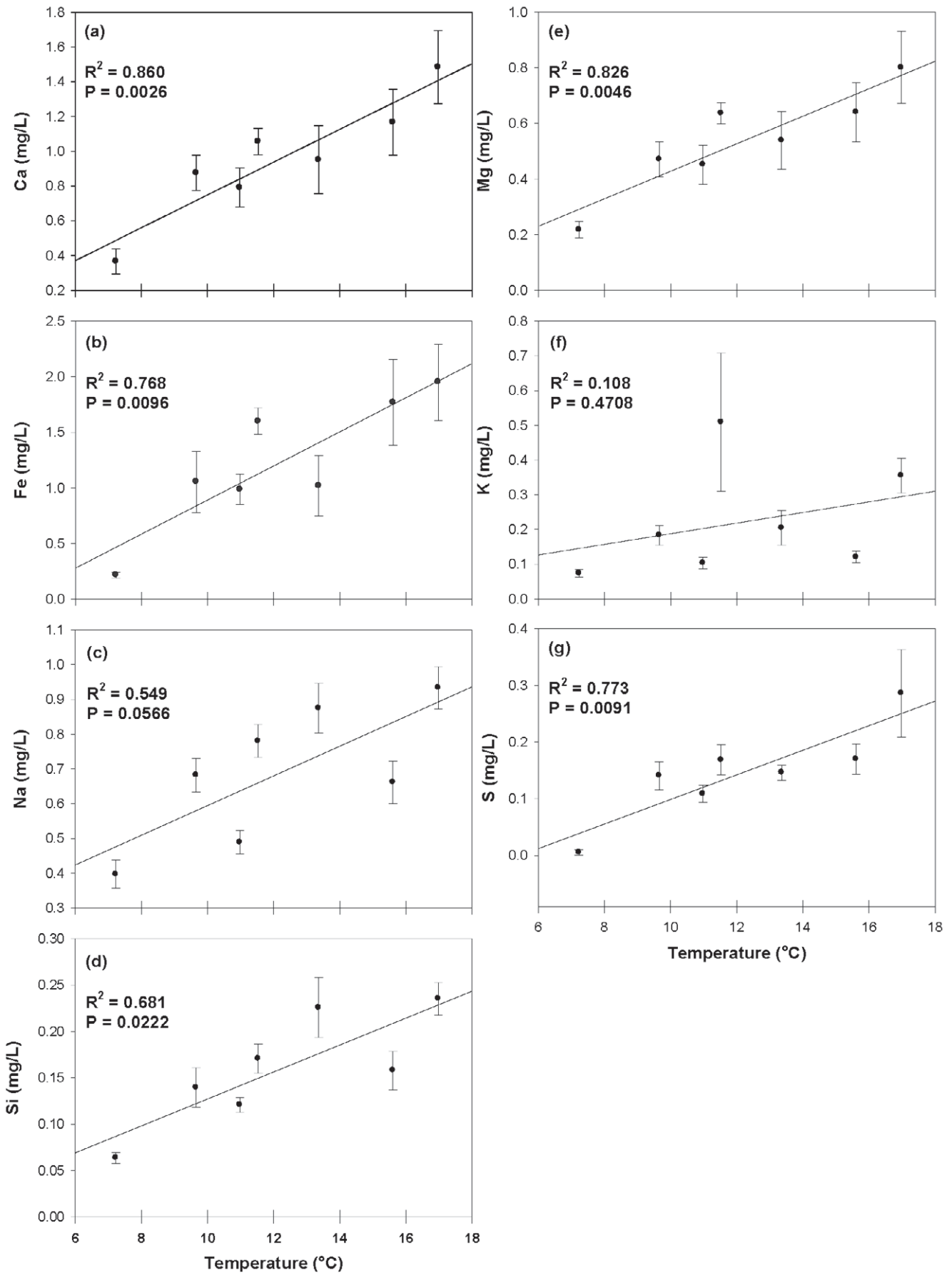
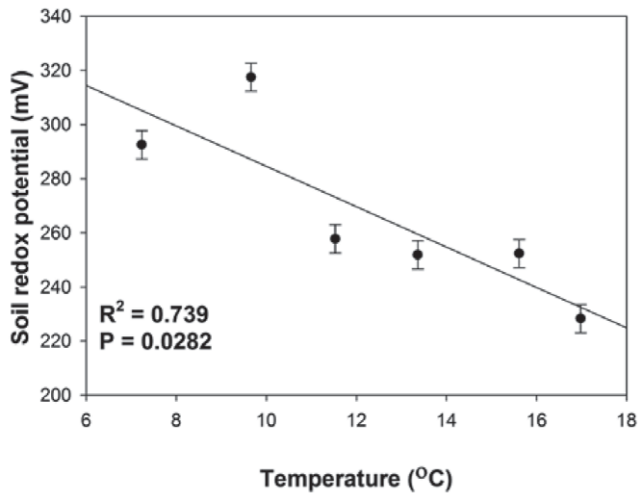


FIGURE 3. Micronutrient release (mean  $\pm$  SE) from permafrost incubation experiment as a function of temperature.



**FIGURE 4.** Oxidation-reduction potential (ORP) (mean  $\pm$  SE) of water column and soil (2 mm depth) as a function of temperature.

release was elevated in the absence of bacteria under ambient ORP only, indicating reduced bacterial uptake of Fe under oxidizing conditions.

Our experiments with altered ORP and microbial activity provide evidence that the primary mechanism of  $\text{NH}_3$  release in these systems was via microbial mineralization of organic matter under oxic conditions; minimal amounts of  $\text{NH}_3\text{-N}$  were recorded under low ORP levels or in the absence of microbial activity. While it is possible that no  $\text{NH}_3\text{-N}$  was released under anoxic conditions, it is more likely that volatilization or anaerobic oxidation resulted in the release of nitrogen gas. Conversely, TN was released from permafrost soil in the greatest amounts when both ORP was reduced and microbial activity was inhibited. A large proportion of released TN was likely organic, much like that observed in boreal forest soils (Brenner et al., 2006). The high TN observed under reducing conditions may have been due to the indirect and unintended effect of the experimental treatments on pH. To maintain a pH similar to the control, HCl was added to artificially reduced samples and could have affected nitrification rates. Furthermore, Persson et al. (1989) found that up to one-third of N mineralization could

be attributed to a reduction in soil organism biomass following acidification. Therefore, both microbial activity, microbial death, and leaching likely play a key role in total nitrogen release. Nitrate also remained high under reducing conditions. In our short-term experiments, nitrate was measured spectrophotometrically after reduction to  $\text{NO}_2\text{-N}$ , and observed concentrations may have largely reflected nitrite produced from degrading dissolved organic matter. Lastly, pH-related microbial death could have reduced the abundance of organisms that carry out dissimilatory nitrate reduction or denitrification, ultimately affecting N-speciation released during our reducing experiments.

Comparisons of nitrogen release from permafrost and active layer soils also suggested a predominance of microbial mineralization. Ammonia was released in relatively high amounts from permafrost soils at both low and high temperatures. Keuper et al. (2012) also found that an active microbial community was responsible for N mineralization in permafrost soil. While permafrost soils also released more nitrate at low temperatures, suggestive of elevated microbially mediated nitrification in permafrost soils, it is possible that nitrification in permafrost soils was inhibited at higher temperatures due to elevated levels ( $>1 \text{ mg L}^{-1}$ ) of ammonia. Although elevated ammonia has been shown to inhibit *Nitrobacter* activity (Reddy and DeLaune, 2008), pH concentrations (5.5–6) in this experiment may not have been high enough to promote this transformation.

Our multivariate models suggested that the release of macronutrients was related to increasing DOC release in our experiments. This is similar to findings of Frey et al. (2007), who found positive relationships between DOC and dissolved nitrogen and phosphorus concentrations in arctic streams and rivers. A similar soil incubation experiment on non-permafrost soil indicated that DOC release had a parallel relationship with metal release in warming experiments (Martinez et al., 2003). Organic-rich soils are influential in the speciation, fate, and transfer of elements, since DOC may control metal solubility (Martinez et al., 2003), and aromaticity of DOM influences the binding affinity of metals (Baken et al., 2011).

Although we saw no linear relationship between DOC and temperature alone, other physicochemical parameters combined with temperature may better explain DOC release from sediment (Porcal et al., 2009). Our results support the mechanism suggested by Olivie-Lauquet et al. (2001), whereby DOC re-

**TABLE 1**

**Results of multivariate models of carbon, phosphorus, and nitrogen release. All replicates were kept separate ( $n = 36\text{--}42$ ). The coefficient of determination for both the multivariate regression (Multiple  $r^2$ ) and simple linear regression with temperature (Simple  $r^2$ ) is included for comparison. Bold values indicate statistical significance of the model ( $p < 0.05$ ).**

Variable	Multivariate model	$r^2$	
		Multiple	Simple
log TDP	$5.793 - 0.0854 (\text{Fe}) - 1.959 (\text{log water-saturated soil ORP})$	<b>0.504</b>	<b>0.336</b>
log SRP	$0.423 + 0.1194 (\text{Fe}) - 0.0052 (\text{DOC}) + 0.1658 (\text{Ca})$	<b>0.291</b>	0.025
log TP	$0.7685 + 0.0296 (\text{temperature } (^\circ\text{C})) - 0.1898 (\text{Ca}) + 0.0171 (\text{DOC})$	<b>0.458</b>	0.068
log $\text{NO}_3$	$1.6086 + 0.4274 (\text{Ca}) - 0.0142 (\text{DOC})$	0.012	0.002
log $\text{NH}_3$	$2.5325 - 0.0505 (\text{temperature } (^\circ\text{C})) + 0.4987 (\text{Ca}) + 0.2374 (\text{Fe})$	<b>0.657</b>	0.069
log TN	$-0.5729 + 0.012 (\text{temperature } (^\circ\text{C})) + 0.0056 (\text{DOC}) + 0.1375 (\text{Fe}) + 0.1695 (\text{Ca})$	<b>0.654</b>	<b>0.131</b>
DOC	$54.386 - 0.245 (\text{temperature } (^\circ\text{C})) + 6.477 (\text{Fe}) - 15.383 (\text{log water-saturated soil ORP})$	<b>0.272</b>	0.046

TABLE 2a

Results of 3-way ANOVA with temperature (7 °C vs. 19 °C), ORP (oxic vs. anoxic), and formalin addition as the three factors. Bold values are significant ( $p < 0.05$ ).

	SRP	TDP	TP	NO <sub>3</sub> -N	NH <sub>3</sub> -N	TN
Temperature	0.1985	0.8802	0.0953	0.2438	<b>0.0231</b>	<b>0.0058</b>
ORP	<b>0.0087</b>	<b>0.0063</b>	0.0830	<b>&lt;0.0001</b>	<b>&lt;0.0001</b>	<b>&lt;0.0001</b>
Formalin	<b>0.0214</b>	0.7765	0.4245	0.0614	<b>&lt;0.0001</b>	<b>0.0020</b>
Temp*ORP	0.3643	0.0935	<b>0.0163</b>	0.0775	0.1237	0.6782
Temp* Formalin	0.8309	<b>0.0221</b>	<b>0.0027</b>	0.5851	0.8080	<b>0.0449</b>
ORP* Formalin	0.4365	0.9701	0.9928	<b>0.0054</b>	<b>&lt;0.0001</b>	<b>0.0449</b>
Temp*ORP*Formalin	0.1565	0.8070	<b>0.0273</b>	0.7877	0.3032	<b>0.0003</b>

TABLE 2b

Results of 3-way ANOVA with temperature (7 °C vs. 19 °C), ORP (oxic vs. anoxic), and formalin addition as the three factors. Bold values are significant ( $p < 0.05$ ).

	Ca	Fe	K	Mg	Si
Temperature	<b>0.0032</b>	<b>0.0021</b>	<b>0.0286</b>	<b>0.0083</b>	<b>0.0094</b>
ORP	<b>0.0001</b>	<b>&lt;0.0001</b>	<b>0.0007</b>	<b>&lt;0.0001</b>	<b>0.0001</b>
Formalin	0.4974	0.5732	0.4074	0.6366	0.9879
Temp*ORP	0.4365	0.7701	0.6660	0.4656	0.1133
Temp* Formalin	0.0911	0.4199	<b>0.0345</b>	0.1171	0.4322
ORP* Formalin	0.3222	<b>0.0040</b>	0.0932	0.2572	0.2757
Temp*ORP*Formalin	0.9760	0.2472	0.4871	0.9701	0.7018

lease is related to microbially mediated changes in ORP, as adding temperature, ORP, and Fe to our model of DOC release helped explain 50% of the variation in DOC release from our incubations.

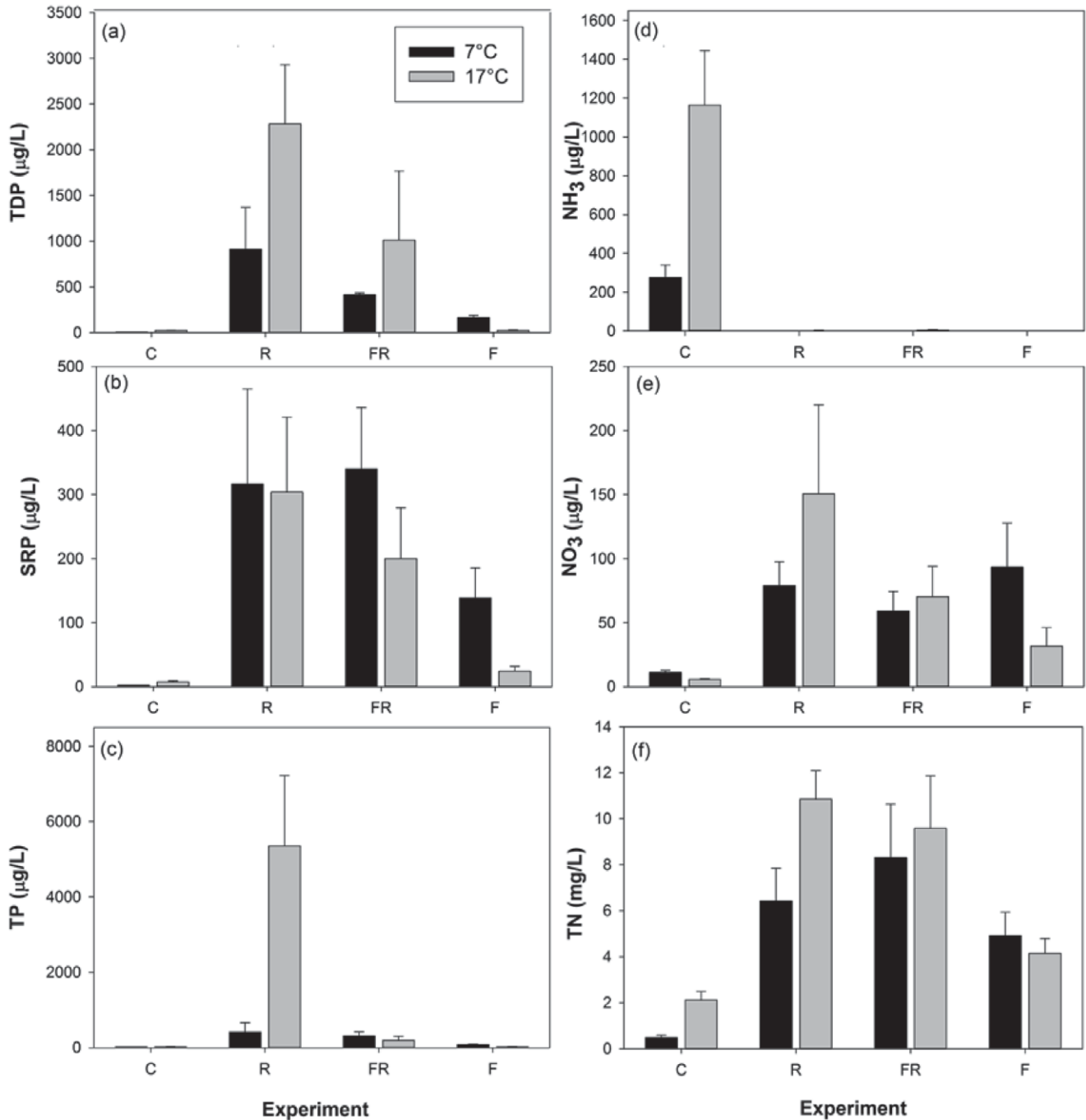
Several authors have suggested the release of both micro- and macronutrients differs among permafrost and active layer soils (e.g., Frey and Smith, 2005; Frey et al., 2007; Keller et al., 2007). Our experiments confirmed that permafrost is enriched in many constituents relative to the active layer. Both mineral weathering (Keller et al., 2007) and plant uptake (Keuper et al., 2012) have been suggested as possible mechanisms depleting nutrients in surface layers. Differences among the two soil types may also be related to decomposability and microbial abundances. In one study, permafrost was found to have more labile compounds but lower microbial numbers (Waldrop et al., 2010). Our results also lend support to the hypothesis that changing water chemistry in arctic tundra ponds (Lougheed et al., 2011) could be from increased release of nutrients via rapid and even short-term permafrost thaw. Besides a difference in available nutrients, a significantly lower redox potential and higher pH in permafrost incubations likely contributed to these differences. The significant interaction between soil type and temperature with ORP measurements, pH, TDP, NO<sub>3</sub>-N, and Fe suggest some constituents within permafrost and active layer soils can respond differently to changes in temperature. This phenomenon likely occurs because permafrost and active layer soils contain different proportions of easily weatherable materi-

als, including recalcitrant organic compounds (Waldrop et al., 2010), whose dissolution may be dependent on warmer temperatures and decreased ORP values.

With an increase in water temperature of 2 °C over the past 40 years (Lougheed et al., 2011), and increased number of degree days of thaw since the 1970s (Lougheed, unpub. data), we suggest that it is highly likely that increased nutrient concentrations in IBP arctic tundra ponds at Barrow, Alaska, are due to permafrost thaw and the coincident effects that temperature has on ORP at the active layer–permafrost boundary. Combined with elevated water temperatures, nutrient uptake from soil pore water could enhance primary productivity of macrophytes, much like lakes disturbed by retrogressive permafrost thaw have increased macrophyte biomass (Mesquita et al., 2010). Elevated nutrient levels in the water column could also lead to increased algal biomass in the tundra ponds, as suggested by Alexander et al. (1980) and as have been observed in the Barrow tundra ponds (Lougheed et al., 2011).

As with any experiment, there are limitations to how this can be applied to natural open systems. For example, our reducing experiment was considerably reduced compared to measured field IBP pond ORP values and thus may overestimate initial nutrient release. This most likely had an impact on volatilization of nitrogen gas and the proportion of dissolved nitrogen species. The use of the reducing agent sodium dithionite, with and without formalin, may have had non-target impacts on bacterial responses; however, this method has been successfully used in other studies (Ahlgren



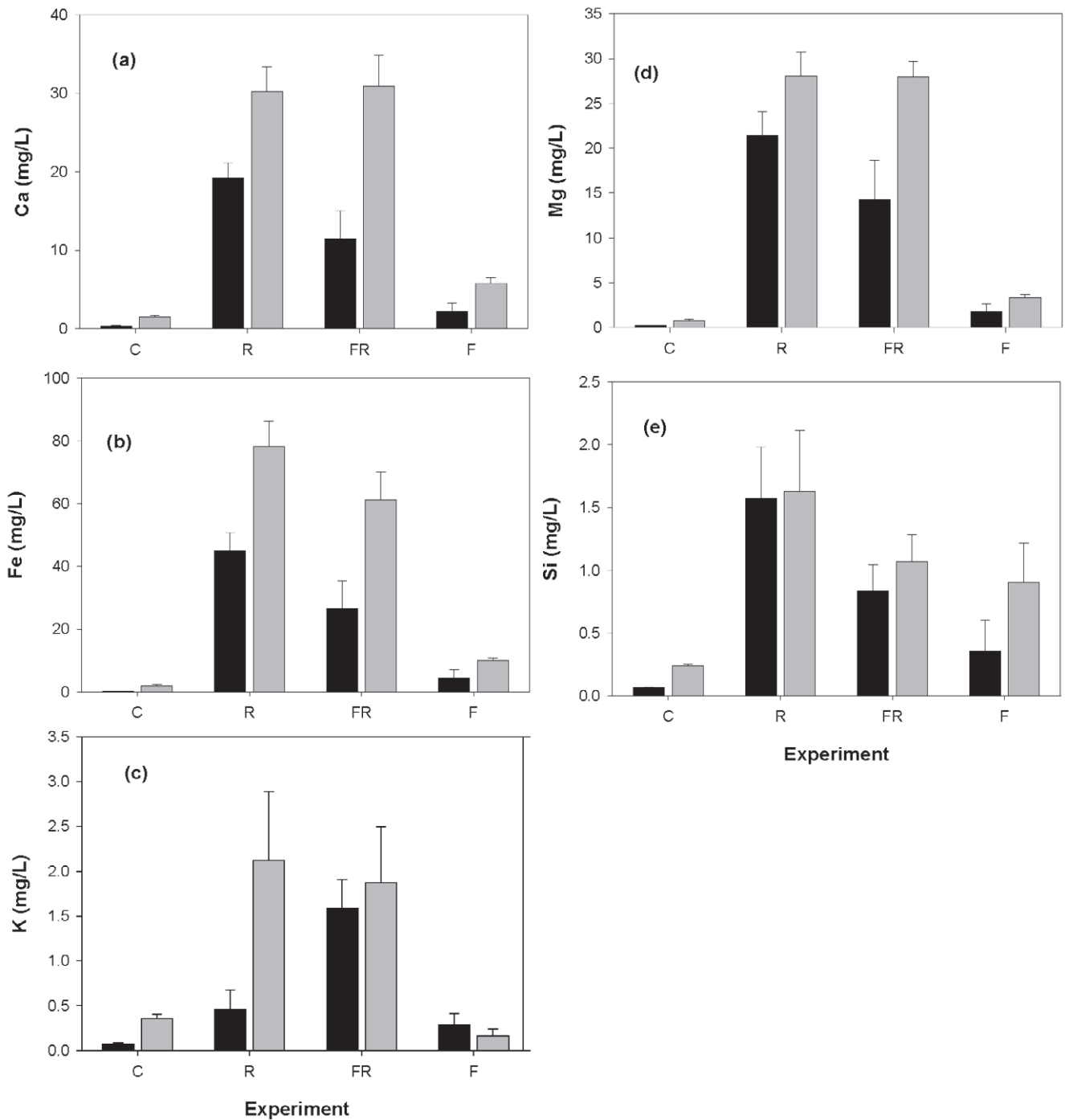


**FIGURE 5.** Macronutrient release (mean  $\pm$  SE) from chemical treatment experiments. C = control (no chemical additions), R = reduced experiment, FR = reduced and formalin experiment, and F = formalin experiment.

et al., 2011). Finally, while extended incubations would have resulted in greater release of nutrients (Martinez et al., 2003; Kim et al., 2013), the experiment was limited to 24 hours in order to minimize the effect of algal growth and bacterial transformations, and to focus on the potential rapid release from even short-term permafrost thaw.

While field conditions are obviously different from the laboratory, rough estimates of nutrient release into the IBP ponds were made based on the surface area ( $46 \text{ cm}^2$ ) and depth (2.5 cm) of the experimental cores, and known surface areas (Miller et al., 1980) and depths (Lougheed, unpub. data) of the IBP ponds. The

occurrence of  $17^\circ\text{C}$  conditions is relatively rare in IBP ponds, occurring less than 2% of the time during the summers of 2010–2013 (Lougheed, unpub. data). However, we estimate that if a 24 hour thawing event of  $17^\circ\text{C}$  occurred under reducing conditions and led to 1 cm of permafrost thaw, this could result in an average increase in SRP of  $0.9 \mu\text{g L}^{-1}$  and in TP of up to  $16.6 \mu\text{g L}^{-1}$ . These represent 27% and 66%, respectively, of modern SRP and TP concentrations observed in IBP ponds in a recent study (Lougheed et al., 2011) and thus could conceivably account for some of the chemical differences observed in IBP ponds over the past 40 years, over which time the ponds warmed by  $2^\circ\text{C}$

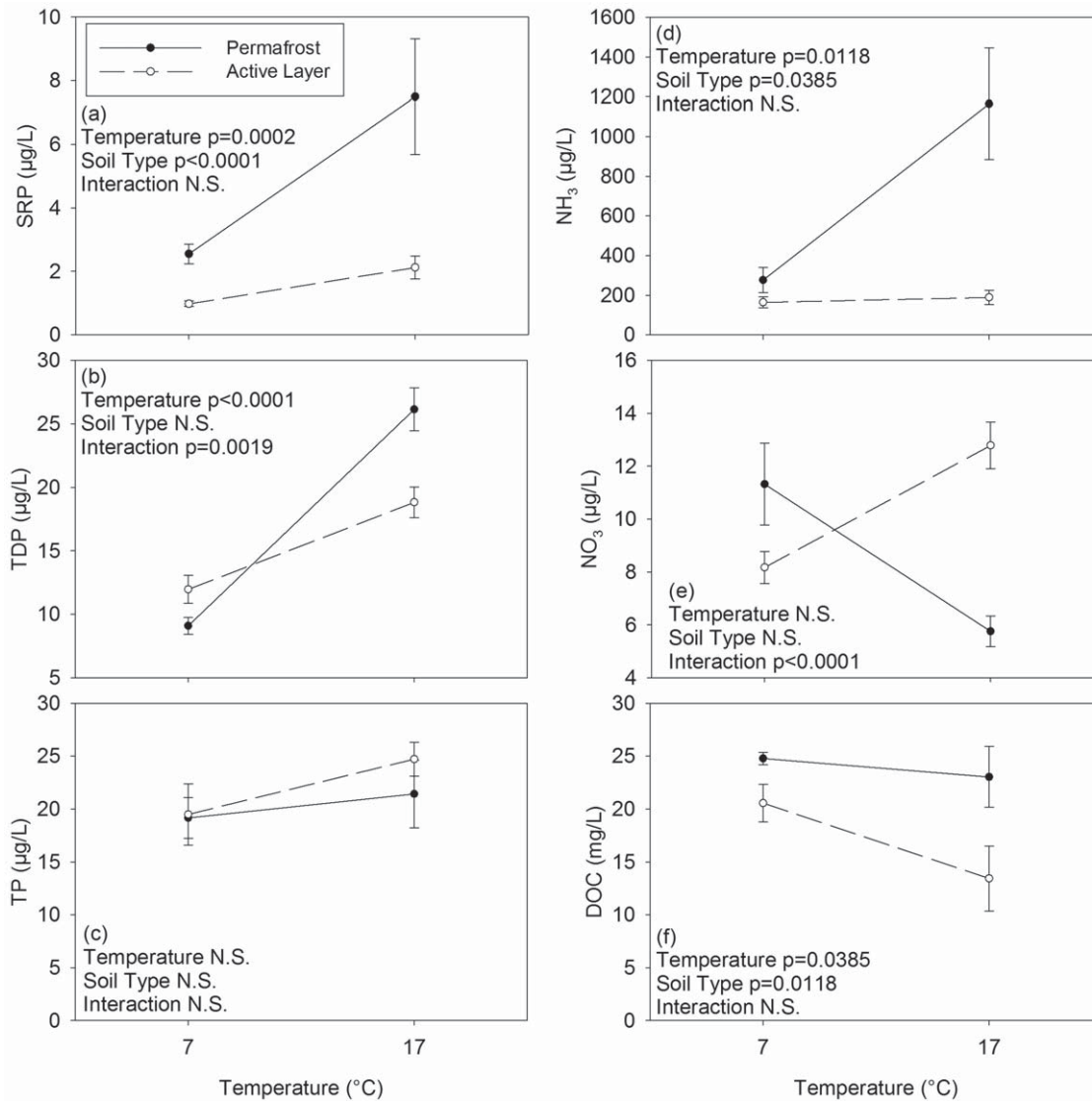


**FIGURE 6.** Micronutrient release (mean  $\pm$  SE) from chemical treatment experiments. C = control (no chemical additions), R = reduced experiment, FR = reduced and formalin experiment, and F = formalin experiment.

(Lougheed et al., 2011). On the other hand, estimated  $\text{NO}_3\text{-N}$  release under the same conditions ( $0.5 \mu\text{g L}^{-1}$ ) represents less than 5% of modern levels, and additional factors have likely contributed to the substantial increases in  $\text{NO}_3\text{-N}$  observed in IBP ponds in recent history. We emphasize that these are only estimates of the potential impacts of a short-term thaw event, longer-term experiments are required to determine the long-term rate of nutrient release from degrading permafrost.

Further studies on the geochemistry of these arctic water bodies are needed to fully understand how an increase in water

temperature will impact permafrost. While a few studies exist on stream geochemistry and mineral weathering influenced by permafrost (Keller et al., 2007, 2010), Arctic lakes and ponds have not been studied for their geochemistry, despite the fact that areas such as the Arctic Coastal Plain are dominated by lakes and pond-rich drained thaw lake basins (Hinkel et al., 2003). Although this study indicates rapid release of nutrients over a 24-hour thaw period, continuous, long-term thaw events would likely lead to substantial increases in nutrient release. These impacts could potentially differ with the depth of thaw. In



**FIGURE 7.** Interaction plots comparing macronutrient concentrations (mean ± SE) among permafrost and active layer soils incubated at low (7 °C) and high (17 °C) temperatures. N.S. indicates no significant effect.

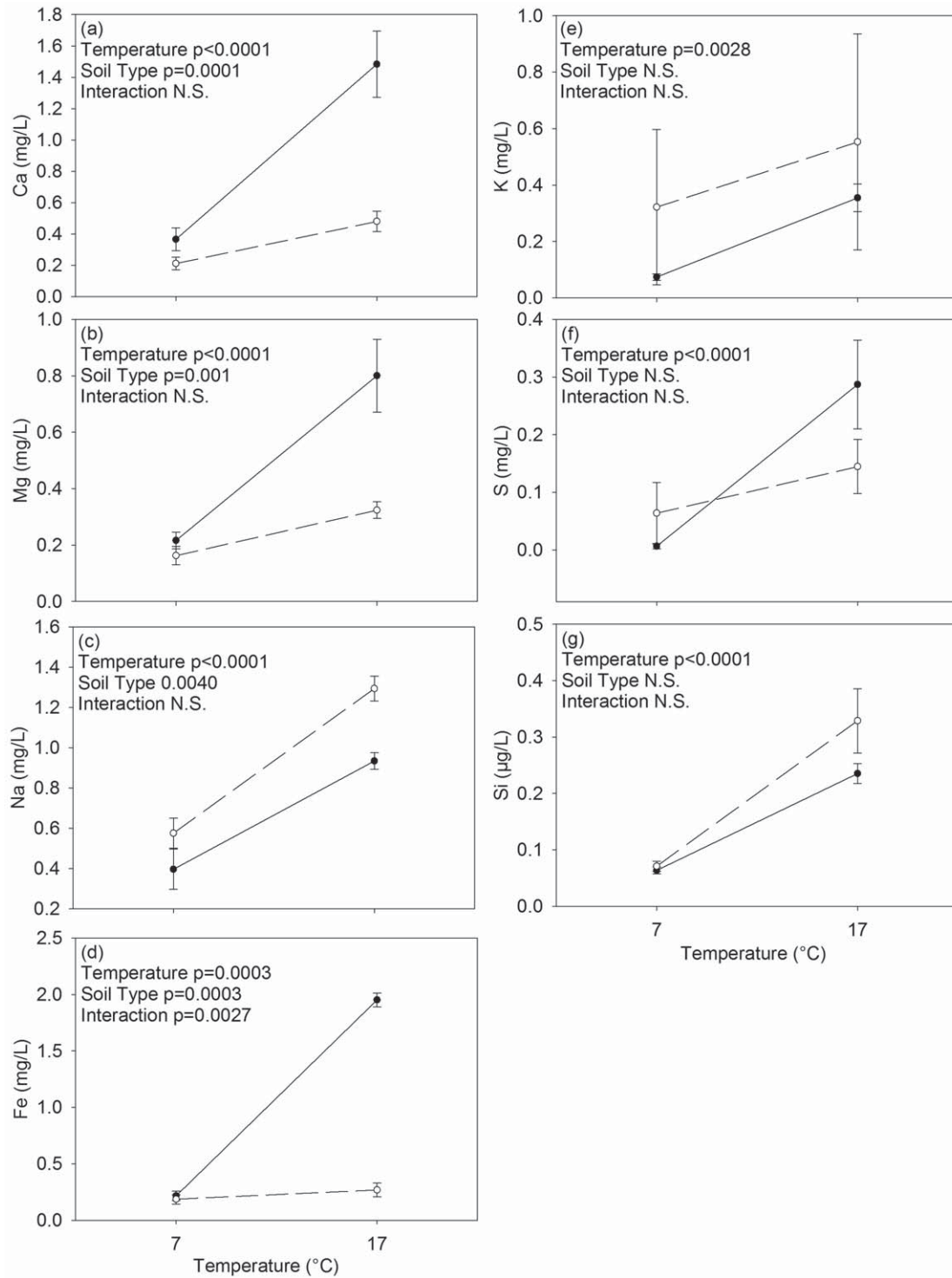
addition to ongoing studies at the historic IBP tundra ponds in Barrow (e.g., Lougheed et al., 2011), characterizing the differences between tundra ponds and thermokarst ponds, which have experienced accelerated rates of thaw, may help also elucidate the impact of permafrost thaw on pond geochemistry. In addition, distinguishing the relative contributions of evaporative and

thaw processes on pond geochemistry is a relatively new direction of study. Increased ion concentrations in Barrow IBP ponds may derive from evaporation (Prentki et al., 1980) and not solely from permafrost thaw; the use of stable isotopes could distinguish the relative contributions of these sources. Finally, with our direct evidence of solute release from permafrost, oth-

**TABLE 3**

**Physicochemical parameter results from two-way ANOVA with temperature (7 °C vs. 17 °C), and soil type (permafrost and active layer). Bold values are significant ( $p < 0.05$ ).**

	pH	Water Column ORP	Water-saturated sediment ORP
Soil type	<b>0.0017</b>	<b>&lt;0.0001</b>	<b>&lt;0.0001</b>
Temperature	<b>0.0002</b>	<b>&lt;0.0001</b>	<b>0.0022</b>
Soil type*Temp	0.0518	<b>&lt;0.0001</b>	<b>&lt;0.0001</b>



**FIGURE 8. Interaction plots comparing micronutrients (mean  $\pm$  SE) among permafrost and active layer soils incubated at low (7 °C) and high (17 °C) temperatures. See Figure 7 for legend (closed circles = permafrost; open circles = active layer). N.S. indicates no significant effect.**

er researchers can use these data to relate and identify potential fingerprints of permafrost thaw processes in aquatic ecosystems.

As the science community continues to model how the earth will respond to a changing climate, the Arctic will be a pivotal region where the integration of multiple physical, chemical, and biological

variables must be accounted for. Release of micro- and macronutrients from thawing permafrost has important implications for primary production, carbon cycling, and upper trophic levels (Hobbie et al., 1999) in both the numerous freshwaters of the Arctic Coastal Plain, as well as the nearshore Arctic Ocean environment (Frey et al., 2007;

Frey and McClelland, 2009). While recent evidence from Elberling et al. (2013) identifies connections between the carbon cycle, permafrost thaw, and hydrologic conditions, the contribution of biogeochemistry to the carbon cycle is greatly understudied, ultimately holding back the accuracy of future climate models.

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