

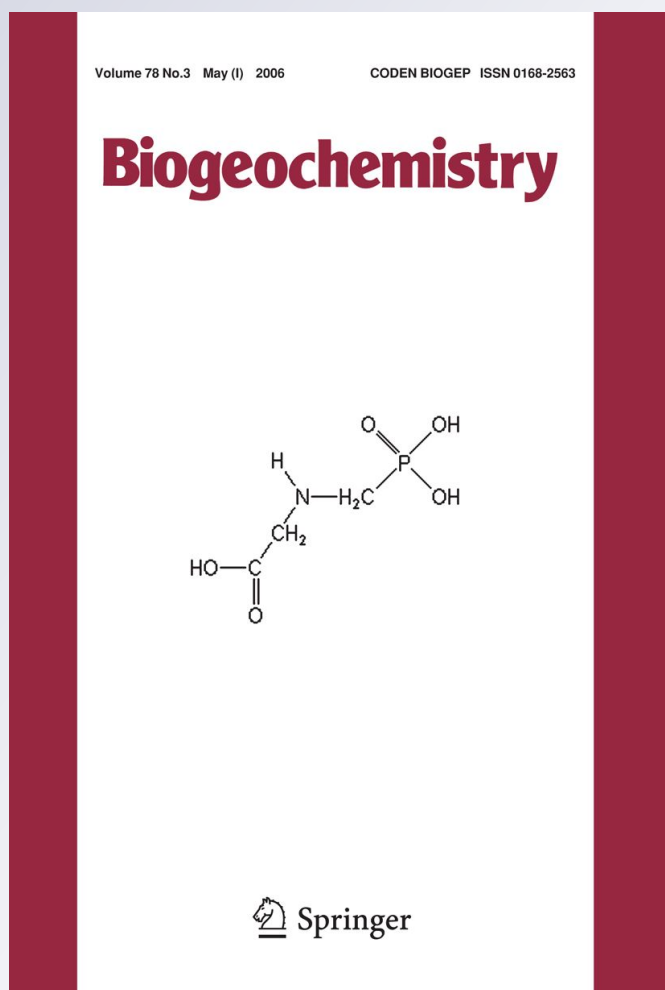
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Seon-young Kim & Carla Koretsky

Biogeochemistry
An International Journal

ISSN 0168-2563

Biogeochemistry
DOI 10.1007/s10533-012-9728-x



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Effects of road salt deicers on sediment biogeochemistry

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Received: 27 June 2011 / Accepted: 10 March 2012
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Abstract Road salt deicers, especially NaCl and CaCl_2 , are increasingly applied to paved areas throughout the world. The goal of this study is to investigate the influence of high concentrations of these salts on wetland biogeochemistry. Sediment cores were collected in fall and spring from a freshwater wetland fringing an urban kettle lake (Asylum Lake, Kalamazoo, MI, USA), and incubated for 100 days in deionized water (control) or with treatments of 1 or 5 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ or 5 g/L NaCl to simulate addition of road salt deicers. At monthly intervals, cores were sliced into three depths (0–5, 5–10, 10–15 cm) and pore waters extracted for analysis of pH, total alkalinity and dissolved Mn(II), Fe(II), PO_4^{3-} , NH_3 , H_2S , SO_4^{2-} , Na, K, Mg, and Ca. Changes in solid phase geochemistry were assessed by measuring the percent organic matter and the distribution of Fe and Mn among four

operationally defined sediment fractions (exchangeable, carbonate, reducible, oxidizable) in the control and treatment cores. Addition of NaCl, and especially CaCl_2 , stimulated significant growth of microbial mats at the core sediment–water interface and led to decreased pH and increased concentrations of Mn(II), Fe(II) and exchangeable cations (Ca, Mg, K, Na) in the sediment pore waters. This study demonstrates that the influx of road salt deicers is likely to have a significant impact on biogeochemical cycling in wetland sediments.

Keywords Road salt · Deicer · Redox · Wetland · Anaerobic · Sediment

Introduction

Globally, the use of road salt deicers, typically NaCl and CaCl_2 , has increased dramatically with urbanization and expansion of paved areas. For example, in the United States, ~164,000 tons of salt per year was used for deicing purposes in 1940 compared to >15,000,000 tons in the early 2000's (Salt Institute 2011). In Canada, an estimated 4,749,847 tons of NaCl was applied as a deicer in 1997–1998 with levels of use in most provinces the same or increasing over the period from 1980 to 2000 (Environment Canada 2001). Road salt is also commonly used in Europe (e.g. Kjensmo 1997; Thunqvist 2003; Rodrigues et al. 2010; Galuszka et al. 2011) and Asia (e.g. Kayama et al. 2003; Kim et al. 2004).

Electronic supplementary material The online version of this article (doi:10.1007/s10533-012-9728-x) contains supplementary material, which is available to authorized users.

S. Kim · C. Koretsky (✉)
Department of Geosciences, Western Michigan
University, Kalamazoo, MI, USA
e-mail: carla.koretsky@wmich.edu

Present Address:
S. Kim
Wonju Regional Environmental Office,
Ministry of Environment, Wonju, Korea
e-mail: ecosun0@korea.kr

Many adverse environmental impacts associated with road salt use have been reported. For example, investigators have demonstrated using both field and laboratory studies that road salt additions may result in decreased aquatic biodiversity (Tuchman et al. 1984; Bridgeman et al. 2000; Ramakrishna and Viraraghavan 2005), detrimental effects on amphibians (Sanzo and Hecnar 2006; Karraker et al. 2008) and changes in microbial community structure (Hale and Groffman 2006; Tiquia et al. 2007). Road salt additions also alter the chemistry and density structure of lakes, with important ecosystem consequences (e.g. Bubeck et al. 1971; Bubeck and Burton 1989; Kjensmo 1997; Bridgeman et al. 2000; Judd et al. 2005; Novotny et al. 2008; Koretsky et al. 2011), and there is increasing concern regarding the potential contamination of potable water supplies by deicers (e.g. Williams et al. 1999; Kaushal et al. 2005; Bester et al. 2006; Findlay and Kelly 2011).

Relatively little is known regarding changes in sediment biogeochemistry resulting from the enormous seasonal influx of NaCl, CaCl₂ and other deicing agents to wetland soils (e.g., Environment Canada 2001; Kelly et al. 2008). Both field and laboratory studies show that deicer additions may lead to increased concentrations of calcium, potassium and magnesium in wetland pore waters (e.g. Bauske and Goetz 1993; Norrstrom and Jacks 1998; Lofgren 2001; Norrstrom and Bergstedt 2001; Backstrom et al. 2004), and decreases in pore water pH (Lofgren 2001; Backstrom et al. 2004), presumably due to ion exchange processes. Backstrom et al. (2004) attributed seasonal decreases in the dissolved organic carbon concentrations of soil pore waters to the combined effects of coagulation and sorption of DOC resulting from decreases in pH and increases in dissolved Ca levels caused by influxes of road salt. Several studies have also suggested that addition of road salt deicers may increase trace metal mobility and bioavailability in soils and sediments. For example, increases in dissolved cadmium are attributed to release via ion exchange and to enhanced solubility due to the formation of aqueous cadmium-chloro complexes (Amrhein et al. 1992; Bauske and Goetz 1993; Lofgren 2001; Backstrom et al. 2004; Mayer et al. 2008; Nelson et al. 2009). Increases in dissolved Zn, Cu, Cr, Ni and Pb have also been documented in field and laboratory studies of soils and sediments impacted by road salt deicers (Amrhein et al. 1992; Bauske and Goetz 1993; Norrstrom and Jacks 1998; Lofgren 2001;

Backstrom et al. 2004; Nelson et al. 2009). Considerably less is known regarding changes in organic matter degradation pathways or cycling of redox-sensitive elements such as manganese, iron and sulfur in wetlands impacted by deicers. Mayer et al. (2008) collected pore waters from Rouge River Pond bottom sediments (maximum water depth ~4 m) with large concentrations of Na (~2,000 ppm) and Cl (~3,000 ppm) at the sediment–water interface due to road salt deicer runoff, and found elevated concentrations of Fe (up to 100 ppm) and Mn (up to 4 ppm) in the upper 40 cm of the sediments, suggesting that road salt could influence redox processes in wetland sediments and soils.

The objective of this study is to investigate changes in sediment pore water and solid phase geochemistry, especially major (Na, Ca, Mg, K) and redox-sensitive (Fe, Mn, S) elements, resulting from the application of NaCl and CaCl₂ deicers to wetland sediments. Sediments cores were incubated in deionized water, NaCl or CaCl₂ solutions to mimic the effect of runoff with high levels of road salt deicers. The evolution of the pore water chemistry (pH, total alkalinity, Fe(II), Mn(II), sulfate, sulfide, phosphate, ammonia, calcium, magnesium, potassium, and sodium) was monitored as a function of deicer and incubation time. Changes in solid phase organic matter content were measured using loss-on-ignition, and a sequential extraction scheme was used to assess changes in solid-phase metal-association with four operationally defined fractions (readily exchangeable metals, carbonate, reducible and oxidizable). These measurements were intended to provide insights into changes in sediment geochemistry resulting from the widespread application of NaCl and CaCl₂ deicers.

Methods

Experiments were conducted using sediments from a fringe wetland on the west side of Asylum Lake, a ~19.8 ha kettle lake located in Kalamazoo, MI. The lake is surrounded by light residential development together with forests and meadows in a nature preserve. The wetland sediments have been influenced by both surface water runoff and groundwater input contaminated by road salt, primarily originating from US-131, located to the west of the lake (Fig. 1). Sauck

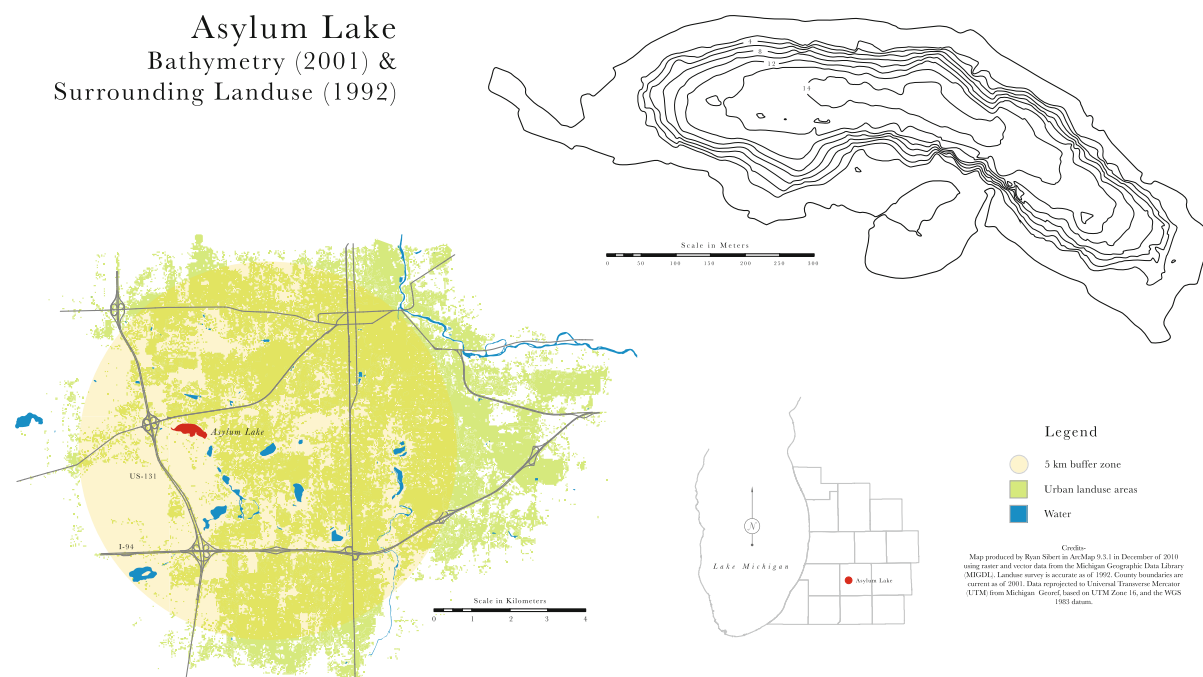


Fig. 1 Maps of study site showing urban land use in 5 km buffer zone and bathymetric map of Asylum Lake (based on data collected by Western Michigan University Facilities Management, personal communication)

and Barcelona (1992) measured dissolved Na and Cl concentrations of up to 248 and 480 mg/L, respectively, in shallow ground waters to the west of Asylum Lake and east of US-131 in June 1992. Sodium and Cl levels were nearly two orders of magnitude lower in ground waters located just to the west (up gradient) of US-131 (Sauck and Barcelona 1992). Koretsky et al. (2011) reported ~90 mg/L Na and ~160 mg/L Cl in Asylum Lake surface waters increasing to >100 mg/L Na and >200 mg/L Cl in lake bottom waters (~16 m depth) collected in July 2010. Prior studies demonstrated that sediment pore waters from the south shore of Asylum Lake were strongly redox-stratified with both iron- and sulfate-reduction suggested to be important organic matter degradation pathways (Koretsky et al. 2006).

In this study, sediments were collected in fall 2009 and spring 2010 using cylindrical PVC cores (diameter 5 cm, length 15 cm). The experiments were replicated in spring and fall because microbial community structure in wetland sediments often shows strong seasonal variations (e.g., Koretsky et al. 2003, 2005, 2006). Thirty cores were collected in fall and 39 were collected in spring. In each season, three cores were used to measure the initial

conditions. The remaining cores were incubated in sets of nine, with each set placed in a vat containing deionized water (control), 5 g/L NaCl (0.086 M NaCl = 2.0 mg/L Na = 3.0 mg/L Cl), 5 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (0.034 M CaCl_2 = 1.4 mg/L Ca = 2.4 mg/L Cl) or 1 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (0.0068 M CaCl_2 = 0.27 mg/L Ca = 0.48 mg/L Cl).

The concentrations of salt used in the incubations were based on reported levels of NaCl in surface waters and soils in areas of road salt deicer application. Environment Canada (2001) reports up to 5 g/L NaCl in urban lakes and ponds, up to 4 g/L NaCl in ponds and wetlands and >18 mg/L NaCl in road runoff impacted by deicers. High levels of chloride have also been reported in roadside soils in Sweden (>1.74 g/L Cl; Backstrom et al. 2004) and in the upper portion of retention pond sediments in Michigan (>3 g/L Cl; Mayer et al. 2008). Ohne (1990) found up to 9.1 g/L Na and 13.5 g/L Cl in wetland surface waters adjacent to salt storage facilities in Maine. Fall cores were incubated in 5 g/L NaCl or 5 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. Because a large effect on the pore water biogeochemistry was observed with the CaCl_2 treatment, spring

cores were also incubated in a lower concentration of CaCl_2 (1 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$).

Water levels were maintained at 8 cm above the sediment–water interface by adding small quantities of deionized water to each vat periodically as needed. Every 30 days, for 3 months, three cores were sacrificed from each treatment vat and sliced into three vertical subsections (0–5, 5–10, 10–15 cm depths) in a Coy anaerobic chamber ($\sim 95\%$ N_2 and 5% H_2 atmosphere). Pore waters were removed from each depth interval using suction under N_2 followed by syringe-filtration ($0.45\ \mu\text{m}$). Redox-sensitive species (total alkalinity, ammonia, sulfide, ferrous iron) and pH were measured immediately. UV–Vis spectrophotometric methods were used to measure total alkalinity (bromophenol blue; Sarazin et al. 1998), ammonium (indophenol blue, Grasshoff et al. 1982), phosphate (molybdate blue; Greenberg et al. 1992), sulfide (methylene blue; Grasshoff et al. 1982), sulfate (barium gelatin turbidity, Tabatabai 1974), and ferrous iron (ferrozine, Stookey 1970). Samples analyzed by ICP-OES for major elements (Ca, Na, Mg, K) were preserved in trace-metal grade nitric acid and were spiked with internal standards (1,000 ppb Y) prior to analysis. ICP-OES measurements were made with matrix-matched calibration standards (DI, NaCl or CaCl_2).

To assess the organic carbon content of the soils, loss-on-ignition was measured. Sediments were first air dried to constant weight, sieved (2 mm) and then ~ 5 g subsamples were weighed and heated at $550\ ^\circ\text{C}$ for 5 h and reweighed (Heiri et al. 2001). A sequential extraction scheme (Tessier et al. 1979, 1982, 1996) was used to assess Fe and Mn associations with four operationally defined fractions (readily exchangeable, carbonates, reducible and oxidizable). Approximately 1–2 g of fresh sediment (weighed exactly) was extracted using the reactants and procedures shown in Table 1. After addition of each extractant, the slurry

was centrifuged and the supernatant removed, syringe-filtered, and preserved for ICP-OES analyses with trace metal grade nitric acid. The remaining sediment was washed by adding deionized water to the wet sediment, mixing the slurry by hand, centrifuging and discarding the supernatant, after which the next extracting agent was added. The filtered, acidified supernatants were spiked with internal standards (1,000 ppb Y) and analyzed for total Fe and Mn using ICP-OES with matrix-matched calibration standards.

Speciation calculations were completed with the software JCHESS (Van der Lee and De Windt 2000) to calculate saturation indices for a suite of carbonates including calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$) and rhodochrosite (MnCO_3). The default thermodynamic database (based on the EQ3 database) was used for the calculations, together with the entire suite of data measured for the pore waters as a function of treatment and time. For these calculations, the measured total alkalinity was assumed to be equal to the total dissolved carbonate (e.g. Koretsky et al. 2007).

All statistical analyses were performed using PASW statistics software (version 18.0, SPSS Inc., Chicago, IL). Comparisons of treatments (i.e., control, 5 g/L NaCl and 1 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ or 5 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) were performed by one-way ANOVA at each sampling time. Repeated measures ANOVA was employed to analyze for treatment and time effects on measurements.

Results

Pore waters

Average concentrations of dissolved solutes from three replicate cores extracted at three depths (0–5, 5–10, 10–15 cm) as a function of incubation time are shown in Fig. 2. The full suite of depth-dependent data is available in the supplementary data. pH remains

Table 1 Sequential extraction methodology adapted from Tessier et al. (1979, 1982)

Target fraction	Reagent	Time	Temperature
Exchangeable	8 mL 1 M MgCl_2 adjusted to pH 7.0	1 h	Room temp
Carbonate	8 mL 1 M sodium acetate, adjusted to pH 5.0 with acetic acid	5 h	Room temp
Reducible	20 mL 0.04 M hydroxyl amine HCl in 25 % (v/v) acetic acid	6 h	95 $^\circ\text{C}$
Oxidizable	3 mL 0.02 M HNO_3 and 5 mL 30 % H_2O_2 (adjusted to pH 2)	2 h	95 $^\circ\text{C}$
	5 mL 3.2 N ammonium acetate in 20 % (v/v) HNO_3 , + DI to total volume of 20 mL	30 min	Room Temp

relatively constant with time at ~ 7.5 – 8 in both the spring and fall controls, declining with time in all treatment cores (Fig. 2a; Table 2). pH values are similar in the fall and spring treatments, with values declining to pH ~ 7 by 100 days in cores amended with 5 g/L NaCl or 1 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and to ~ 6 – 6.5 in cores amended with 5 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Fig. 2a; Table 3). Alkalinity levels are greater in the initial cores collected in spring (~ 8.5 mM) compared to those from fall (~ 2.5 mM; Fig. 2b; $F = 27.2$, $P < 0.01$). In fall, alkalinity increases with time in all cores, except for a low value in the control core at 100 days. In contrast, in spring, alkalinity generally decreases with time in all cores. Alkalinity levels tend to be greatest in the cores incubated in 5 g/L NaCl and lowest in the control cores and those incubated with 1 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Fig. 2b; Tables 2, 3).

Dissolved Mn(II) concentrations are very low (~ 50 μM) in the control core pore waters, changing little with incubation time (Fig. 2c; Table 2). In contrast, Mn(II) levels increase with time in all of the treatment cores. The most dramatic changes occur in cores treated with 5 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$; in these, dissolved Mn(II) concentrations increase about tenfold, reaching ~ 600 μM after 100 days of incubation. Mn(II) levels also increase in the 5 g/L NaCl and 1 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ treatment cores, although more slowly, reaching ~ 200 μM after 100 days (Fig. 2c; Table 3).

Like dissolved Mn(II), dissolved Fe(II) concentrations are low (< 1 μM) throughout the incubations of the control cores, while concentrations increase dramatically with time in the 5 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ treatments, reaching up to 1,980 μM Fe(II) after 100 days (Fig. 2d; Table 2). Dissolved Fe(II) concentrations also increase with time in the 5 g/L NaCl and 1 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ treatments, but more slowly than dissolved Mn(II), with maximum dissolved Fe(II) concentrations of ~ 15 – 110 μM after 100 days of incubation (Fig. 2d; Table 2).

Dissolved sulfate and sulfide were measured on the fall cores only. Sulfate concentrations decrease precipitously with time in both the control and the treatment cores from initial levels of ~ 250 to < 50 μM after 100 days of incubation (Fig. 2e). Sulfide concentrations increase with time, from an initial concentration of < 20 μM , reaching levels as high as ~ 65 μM after 65 days (Fig. 2f).

Phosphate concentrations are close to detection limits in the initial fall cores (Fig. 2g), increasing with

time in the control and treatment cores. The largest accumulation of phosphate occurs in the 5 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ treatments, reaching ~ 35 μM at 100 days, with the lowest accumulation of phosphate in the control cores. Phosphate concentrations were not measured in spring. Average ammonia concentrations as a function of time and treatment are quite variable (Fig. 2h; Table 2), although depth-averaging of the data obscures some trends. Depth-dependent data (see supplementary materials) reveal that more ammonia typically accumulates with time in the deeper sections of 1 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ cores ($P < 0.05$). Initial levels of ammonia are greater in spring (~ 100 μM) compared to fall (near detection limits). In fall, ammonia levels increase with time in all cores, except that a low value is observed in the control at 100 days. In spring, ammonia levels increase more rapidly with time in the deeper sections of the 5 g/L NaCl or $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ cores (supplementary material; Table 2), with increased ammonia levels occurring at 100 days in the deeper portions of the control and 1 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ cores (Fig. 2h).

Solid phase

Organic matter concentrations calculated from loss-on-ignition (Heiri et al. 2001) are greatest in the upper 5 cm of the core, decreasing with depth for all treatments (Fig. 3). No significant differences in percent organic matter are observed between the treatments and controls, nor does organic matter percentage change significantly with time (Table 2). Due to these small changes in bulk organic matter, analyses were not completed for the sediments from the spring incubations.

A sequential extraction technique was used to assess partitioning of Fe and Mn among four operationally defined sediment fractions: exchangeables, carbonates, reducibles and oxidizables (Tessier et al. 1979, 1982, 1996). Few consistent trends emerge with respect to the average concentrations of Fe or Mn extracted with the exchangeable, carbonate or reducible fractions as a function of time or treatment (Fig. 4; Table 2). In the fall cores, the quantity of oxidizable-associated Fe and Mn increases as a function of time in all cores, including the controls (Fig. 4g, h).

Most of the Fe is extracted in the upper portion of the cores and is associated with the reducible and oxidizable fractions (Fig. 5a–f). After 100 days of incubation, the quantity of reducible- and oxidizable-associated Fe in the fall cores is somewhat lower

in the treatments compared to the control cores (Fig. 5a–c). However, in spring, the levels of both reducible- and oxidizable-associated Fe are significantly greater in the upper portion of the treated cores compared to the control (Fig. 5d–f). As for Fe, few consistent trends in extractable Mn are observed as a function of either treatment or incubation time (Fig. 5g–i). In contrast to Fe, Mn is much more evenly distributed among the four fractions and among the three depths of the core (Fig. 5g–i). Most of the Mn is typically extracted with the carbonate and reducible fractions of the sediment. After 100 days of incubation, carbonate- and reducible-associated Mn is somewhat greater in the upper 0–5 cm of the NaCl treatments compared to the controls, but few other differences between controls and treatments are apparent.

Discussion

Stimulation of anaerobic respiration

The reductive dissolution of Mn(IV) and Fe(III) oxides results in accumulation of dissolved Mn and Fe in suboxic pore waters (e.g. Davison 1993). Mn(IV) and Fe(III) reduction is often microbially mediated and coupled to oxidation of organic matter, but can also occur chemically or microbially via reaction with more reduced solutes, such as ferrous iron (for Mn(IV) reduction) or sulfide (e.g., Burdige and Nealson 1986; Burdige 1993; Yao and Millero 1996; Boudreau 1999). Mn(IV) is a more energetically favorable electron acceptor compared to Fe(III), therefore, Fe(II) typically accumulates after readily reducible Mn(IV) is exhausted.

Dissolved Mn(II) and Fe(II) increased significantly with time in cores treated with NaCl, and especially in cores amended with 5 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, but not in the control cores (Fig. 2c, d; Table 3). Mn(II) production rates were ~ 5.5 , 1.3–1.6 and 1.1 $\mu\text{M}/\text{day}$ after 100 days of incubation in the 5 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 5 g/L NaCl and 1 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ experiments, respectively. Dissolved Fe(II) accumulated more slowly: ~ 15 , 0.34 and 1.0 $\mu\text{M}/\text{day}$ after 100 days of incubation in the 5 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 5 g/L NaCl and 1 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ experiments, respectively. The significant accumulation of Mn(II), followed by Fe(II), in the treated cores suggests that the addition

Fig. 2 Average **a** pH, **b** alkalinity, **c** dissolved Mn(II), **d** dissolved Fe(II), **e** sulfate, **f** sulfide, **g** phosphate, **h** ammonia, **i** magnesium, **j** calcium, **k** sodium and **l** potassium as a function of time and treatment. Error bars indicate standard deviations of measurements completed at three depths (0–5, 5–10, 10–15 cm) on triplicate cores. Na was not measured in cores with added Na, and Ca was not measured in cores with added Ca and sulfide was not measured for 100 days incubation

of NaCl or CaCl_2 stimulates anaerobic respiration with consequent reductive dissolution of Fe(III) and Mn(IV) oxides.

The rates of Mn(II) production observed here are similar to those measured by Thomsen et al. (2004) in anoxic incubations of sediments from the bottom of Lake Michigan ($\sim 3 \mu\text{M}/\text{day}$ in 1–2 cm portion of sediment core incubated for 20 days). Thomsen et al. (2004) also measured production of ΣCO_2 , Fe^{+2} , NH_4^+ and sulfate reduction rates. With these data, they demonstrated that although a significant quantity of dissolved Mn(II) accumulated, most of it was produced by reoxidation of more reduced solutes, with relatively little contributing to organic matter mineralization. This may also be the case for incubations in this study, particularly given that significant ferrous iron production occurred in spring and fall (up to 15 $\mu\text{M}/\text{day}$), whereas Fe(II) production rates reported by Thomsen et al. (2004) were generally quite low. Sulfate consumption rates in the fall cores from this study are lower ($\sim 2.5 \mu\text{M}/\text{day}$) compared to those reported by Thomsen et al. (2004), but without sulfate reduction rates and ΣCO_2 data, the contributions of each anaerobic respiration pathway to organic matter mineralization cannot be determined. Nonetheless, the large accumulation of Fe(II) and Mn(II), especially in the 5 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ treatments, suggests that anaerobic respiration is stimulated by the addition of the deicing salts.

Primary productivity was not measured in this study. However, visual evidence of enhanced primary productivity was apparent at the top of cores incubated in NaCl or CaCl_2 . Thick, orange-red fungal or microbial mats developed at the top of these cores, but not on control cores incubated in DI water (Fig. 3). Furthermore, the mats were thicker, brighter and formed more quickly on the cores incubated in 5 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ compared to those incubated in 5 g/L NaCl. Thus, we hypothesize that degradation of the organic matter produced in these mats resulted in the significant accumulation of dissolved Mn(II) and

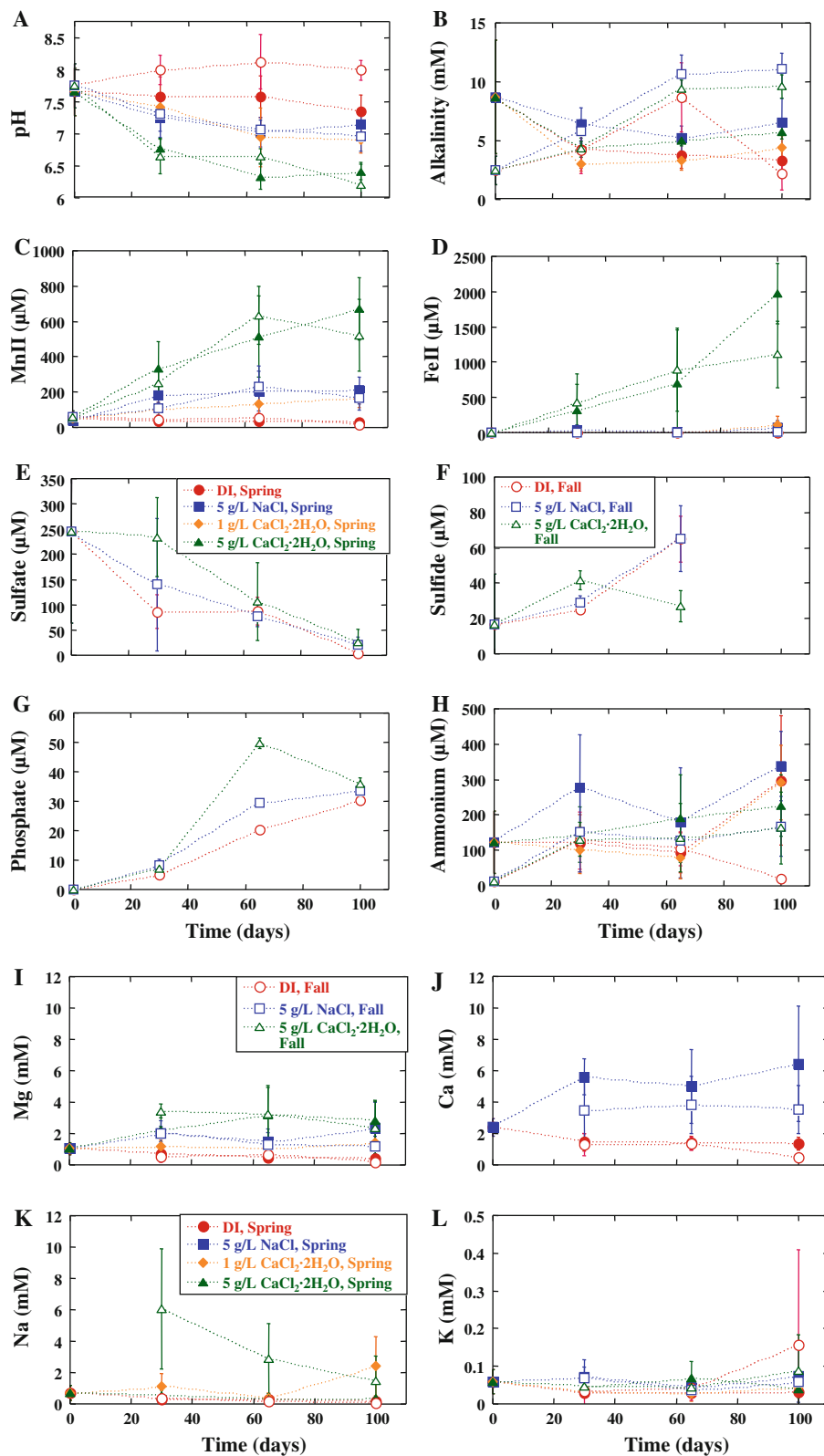


Table 2 The *F* statistic and degree of freedom for the treatment and time effects and their interactions on measurements as results of repeated measures ANOVAs

GLM repeated measures				
Measurements	Season	Treatment	Time	Treatment \times Time
pH	Fall	$F = 319.7$ ($df = 2$)***	$F = 36.3$ ($df = 3$)***	$F = 23.7$ ($df = 6$)***
	Spring	$F = 16.9$ ($df = 3$)*****	$F = 21.8$ ($df = 3$)***	$F = 2.2$ ($df = 9$)
Alkalinity	Fall	$F = 1.2$ ($df = 2$)	$F = 1.18$ ($df = 3$)	$F = 78.3$ ($df = 6$)***
	Spring	$F = 9.0$ ($df = 3$)**	$F = 28.7$ ($df = 3$)***	$F = 1.5$ ($df = 9$)
Dissolved Mn(II)	Fall	$F = 43.8$ ($df = 2$)***	$F = 20.0$ ($df = 3$)***	$F = 10.4$ ($df = 6$)***
	Spring	$F = 100.5$ ($df = 3$)***	$F = 20.1$ ($df = 3$)***	$F = 22.5$ ($df = 9$)***
Dissolved Fe(II)	Fall	$F = 43.8$ ($df = 2$)***	$F = 20.0$ ($df = 3$)***	$F = 10.4$ ($df = 6$)***
	Spring	$F = 100.5$ ($df = 3$)***	$F = 20.1$ ($df = 3$)***	$F = 22.5$ ($df = 9$)***
Ammonium	Fall	$F = 1.6$ ($df = 2$)	$F = 6.8$ ($df = 3$)**	$F = 1.0$ ($df = 6$)
	Spring	$F = 1.9$ ($df = 3$)	$F = 7.6$ ($df = 3$)**	$F = 0.7$ ($df = 9$)
Organic matter content	Fall	NA	NA	NA
	Spring	$F = 0.4$ ($df = 3$)	$F = 2.8$ ($df = 2$)	$F = 0.5$ ($df = 6$)
Exchangeable Fe	Fall	$F = 3.2$ ($df = 2$)	$F = 4.9$ ($df = 3$)*	$F = 5.6$ ($df = 6$)**
	Spring	$F = 1.2$ ($df = 3$)	$F = 0.8$ ($df = 3$)	$F = 0.9$ ($df = 9$)
Exchangeable Mn	Fall	$F = 1.1$ ($df = 2$)	$F = 4.0$ ($df = 3$)*	$F = 0.4$ ($df = 6$)
	Spring	$F = 1.1$ ($df = 3$)	$F = 4.5$ ($df = 3$)*	$F = 1.1$ ($df = 9$)
Carbonate Fe	Fall	$F = 1.3$ ($df = 2$)	$F = 4.6$ ($df = 3$)*	$F = 2.8$ ($df = 6$)*
	Spring	$F = 0.9$ ($df = 3$)	$F = 2.0$ ($df = 3$)	$F = 1.4$ ($df = 9$)
Carbonate Mn	Fall	$F = 2.6$ ($df = 2$)	$F = 4.9$ ($df = 3$)*	$F = 0.3$ ($df = 6$)
	Spring	$F = 0.02$ ($df = 3$)	$F = 2.5$ ($df = 3$)	$F = 0.3$ ($df = 9$)
Reducible Fe	Fall	$F = 0.8$ ($df = 2$)	$F = 3.6$ ($df = 3$)*	$F = 2.2$ ($df = 6$)
	Spring	$F = 0.2$ ($df = 3$)	$F = 0.8$ ($df = 3$)	$F = 0.6$ ($df = 9$)
Reducible Mn	Fall	$F = 1.5$ ($df = 2$)	$F = 2.4$ ($df = 3$)	$F = 0.7$ ($df = 6$)
	Spring	$F = 0.6$ ($df = 3$)	$F = 0.1$ ($df = 3$)	$F = 0.5$ ($df = 9$)
Oxidizable Fe	Fall	$F = 1.1$ ($df = 2$)	$F = 2.3$ ($df = 3$)	$F = 0.9$ ($df = 6$)
	Spring	$F = 0.01$ ($df = 3$)	$F = 1.2$ ($df = 3$)	$F = 0.8$ ($df = 9$)
Oxidizable Mn	Fall	$F = 1.6$ ($df = 2$)	$F = 0.7$ ($df = 3$)	$F = 1.0$ ($df = 6$)
	Spring	$F = 2.5$ ($df = 3$)	$F = 1.8$ ($df = 3$)	$F = 1.6$ ($df = 9$)

Asterisks indicate statistically significant differences (* $P \leq 0.05$, ** $P \leq 0.01$, and *** $P \leq 0.001$)

Fe(II) which was particularly apparent in the 5 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ treatments.

Anaerobic respiration should result not only in increased levels of Mn(IV) and Fe(II), but also in mineralization of nitrogen and phosphorous. The similar release of phosphate in treated and control cores (Fig. 2g) is somewhat surprising. Possibly, trends in phosphate concentrations released by organic matter mineralization are obscured by multiple geochemical processes occurring in the cores; phosphate levels are also effected by adsorption on Fe(III) oxides or clays, precipitation of sparingly soluble P-bearing

aluminosilicates and by uptake of phosphate by biota (Jahnke 1992). Thus, enhanced release of phosphorous in the treatment cores relative to the controls due to increased organic matter mineralization might be difficult to detect based on pore water data alone. Ammonia can be contributed to the pore waters via ammonification. The more rapid increase of ammonia at depth in the spring trials for the 5 g/L NaCl and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ cores (supplementary data) is consistent with more rapid onset and greater magnitude of anaerobic respiration in these treatments. However, no significant differences in total ammonia accumulation

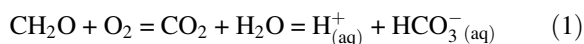
Table 3 The *F* statistic and degree of freedom for the treatment effects on measurements as results of One-way ANOVAs

One-way ANOVA				
Measurement	Season	Incubation days		
		30	60	100
pH	Fall (<i>df</i> = 2)	<i>F</i> = 42.8***	<i>F</i> = 55.0***	<i>F</i> = 254.6***
	Spring (<i>df</i> = 3)	<i>F</i> = 14.6**	<i>F</i> = 14.5**	<i>F</i> = 20.0***
Alkalinity	Fall (<i>df</i> = 2)	<i>F</i> = 1.2	<i>F</i> = 1.2	<i>F</i> = 78.3***
	Spring (<i>df</i> = 3)	<i>F</i> = 6.8*	<i>F</i> = 3.9	<i>F</i> = 16.6**
Dissolved Mn(II)	Fall (<i>df</i> = 2)	<i>F</i> = 42.4***	<i>F</i> = 65.1***	<i>F</i> = 11.2**
	Spring (<i>df</i> = 3)	<i>F</i> = 33.4***	<i>F</i> = 77.3***	<i>F</i> = 51.2***
Dissolved Fe(II)	Fall (<i>df</i> = 2)	<i>F</i> = 12368.6***	<i>F</i> = 9.5*	<i>F</i> = 14.3**
	Spring (<i>df</i> = 3)	<i>F</i> = 12.2**	<i>F</i> = 17.8**	<i>F</i> = 80.9***
Ammonium	Fall (<i>df</i> = 2)	<i>F</i> = 0.1	<i>F</i> = 0.2	<i>F</i> = 3.3
	Spring (<i>df</i> = 3)	<i>F</i> = 2.8	<i>F</i> = 0.9	<i>F</i> = 0.5
Mg	Fall (<i>df</i> = 2)	<i>F</i> = 20.3**	<i>F</i> = 20.9**	<i>F</i> = 3.8
	Spring (<i>df</i> = 3)	<i>F</i> = 30.0***	<i>F</i> = 10.8**	<i>F</i> = 11.1**
K	Fall (<i>df</i> = 2)	<i>F</i> = 0.7	<i>F</i> = 0.1	<i>F</i> = 0.4
	Spring (<i>df</i> = 3)	<i>F</i> = 4.7*	<i>F</i> = 1.4	<i>F</i> = 1.2
Na	Fall (<i>df</i> = 1)	<i>F</i> = 4.2	<i>F</i> = 8.7*	<i>F</i> = 1.4
	Spring (<i>df</i> = 2)	<i>F</i> = 3.6	<i>F</i> = 0.3	<i>F</i> = 3.6
Ca	Fall (<i>df</i> = 1)	<i>F</i> = 5.5	<i>F</i> = 8.6*	<i>F</i> = 13.9*
	Spring (<i>df</i> = 1)	<i>F</i> = 57.2**	<i>F</i> = 188.9***	<i>F</i> = 13.8*

Asterisks indicate statistically significant differences (**P* ≤ 0.05, ***P* ≤ 0.01, and ****P* ≤ 0.001)

are observed between the two treatments and little difference is apparent between the control and treatments in fall (Fig. 2h; Table 3). As for phosphorous, nitrogen mineralization may be masked by other processes, including uptake or release of ammonia by clay minerals and oxidation of ammonia by less reduced solutes.

Respiration processes also influence pore water pH (e.g. Van Cappellen and Wang 1996; Boudreau 1999). Aerobic respiration produces acidity, according to:



where “CH₂O” represents organic matter; conversely, anaerobic respiration consumes acidity. Pore water pH is also affected by chemical reactions: acidity is produced both by the oxidation of reduced solutes by oxygen and also by precipitation of carbonates, via,



Thermodynamic speciation calculations (see Methods) indicate that calcite, dolomite and rhodochrosite

are all supersaturated in both the NaCl and the CaCl₂ treatments. The significant decrease in pH in these treatments (Fig. 2a) is consistent with carbonate precipitation. Acidity may also have been contributed by photosynthetic production of oxygen in the mats, which was subsequently consumed in the suboxic underlying sediments together with ion exchange processes (see below).

Solid phase geochemistry can also be examined to evaluate organic matter mineralization pathways. For example, increased organic matter productivity might be reflected in greater quantities of organic matter, especially in the upper portion of the cores. However, solid-phase organic matter does not change significantly with time or treatment (Fig. 3; Table 2). This may be because loss-on-ignition is a bulk technique that cannot distinguish pools of organic matter (e.g. labile vs. refractory). Furthermore, in these organic-rich sediments, relatively small changes in organic matter content occurring over the course of the incubation experiment may be indistinguishable from the high background levels of organic carbon in the

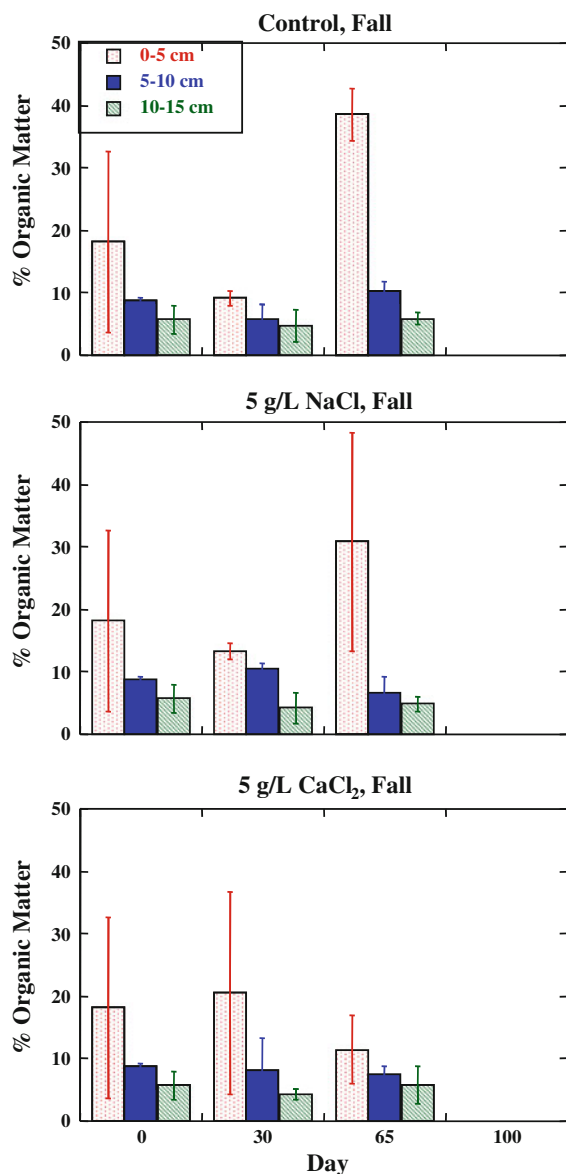


Fig. 3 Average and standard deviations of percent organic matter in triplicate cores as a function of depth and time for fall **a** control, **b** 5 g/L NaCl, and **c** 5 g/L CaCl₂·2H₂O

initial sediment cores. Thus, changes in the labile fraction of the organic matter produced by enhanced primary production may not be detectable using the loss-on-ignition technique.

Reductive dissolution of Fe(III) and Mn(IV) oxides should reduce the level of Fe and Mn associated with operationally defined reducible fractions of the sediment and increase the levels associated with other

operationally defined fractions, particularly carbonate- or oxidizable-phases. However, these pools do not change significantly with time (Fig. 4e, f; Table 2). Previous studies have shown that some Fe oxides may be only impartially removed by the Tessier sequential extraction step targeting the reducible fraction, and that this step may also partially remove Fe associated with Fe monosulfides (e.g. Filgueiras et al. 2002; Koretsky et al. 2006). Sediment preservation, especially drying or freeze-drying, can also mobilize metals, changing their distribution among various fractions (e.g., Rapin et al. 1986; Kersten and Forstner 1986; Hjorth 2004). Although other studies have shown that sequential extraction data, when used to compare similar sediments, and particularly when examined in conjunction with detailed pore water data, may yield useful insights into sediment geochemistry (e.g. Koretsky et al. 2006, 2007), the lack of correspondence observed here between increased dissolved Fe(II) and Mn(II) and Fe and Mn distribution among the extracted fractions (Figs. 2c, d, 5) is likely due to the inherent limitations of these operationally defined techniques.

Ion exchange

Addition of 5 g/L CaCl₂·2H₂O stimulates fungal or microbial mat growth and subsequent accumulation of reduced Fe(II) and Mn(II) in the core pore waters (Figs. 2c, d, 6). Calcium is a critical macronutrient for higher plants (e.g. Likens et al. 1998), but it is not essential for the growth of many microorganisms (Madigan et al. 2003). Furthermore, addition of 5 g/L NaCl also enhanced microbial mat formation and anaerobic respiration in treated cores, albeit to a lesser degree than the CaCl₂. Thus, while addition of the macronutrient Ca may be partially responsible for the observed mat growth, another mechanism must also be at work. One such process might be the release of key nutrients (e.g. Mg, K, NH₄⁺, trace nutrients) from organic matter and clays via ion exchange processes.

Previous studies have demonstrated that NaCl or CaCl₂ additions to soils and sediments stimulate ion exchange, releasing both major and trace cations to pore waters. For example, Norrstrom and Bergstedt (2001) used column studies to demonstrate that Na⁺ displaces Ca, K and Mg from cation exchange sites in soils collected from several sites in Sweden. Similarly,

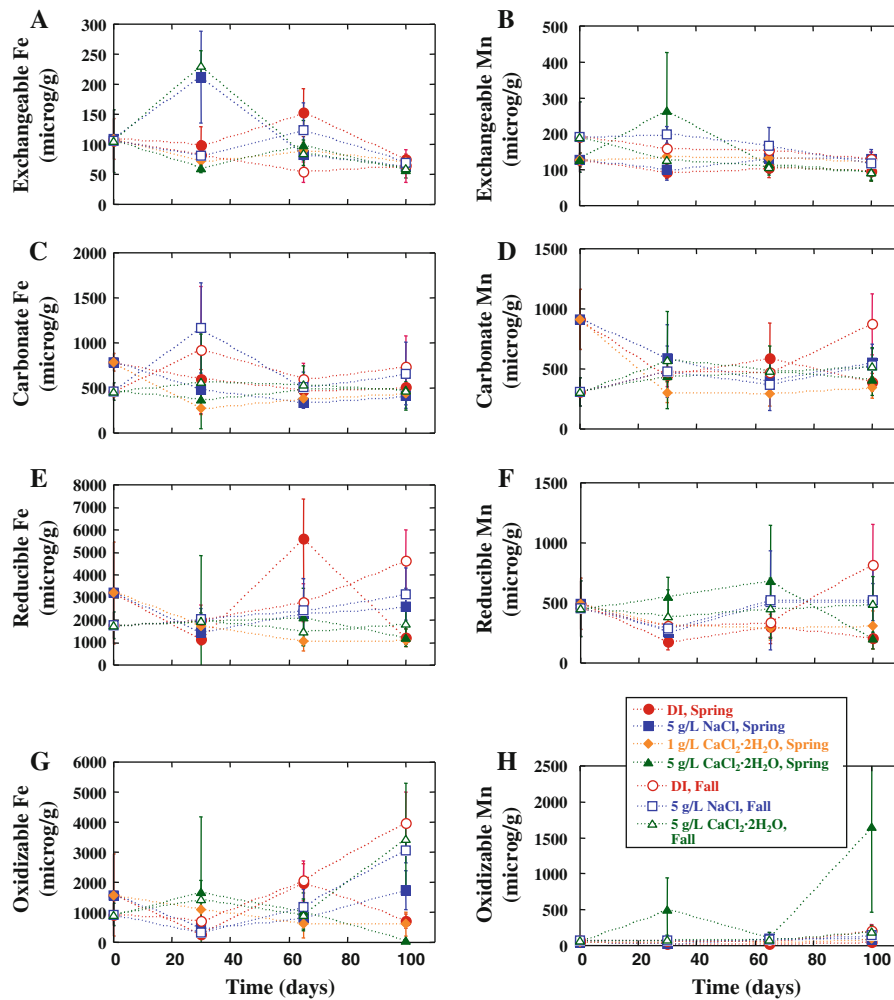


Fig. 4 Concentrations of **a** Fe or **b** Mn extracted with the exchangeable fraction, **c** Fe or **d** Mn extracted with the carbonate fraction, **e** Fe or **f** Mn extracted with the reducible fraction and **g** Fe or **h** Mn extracted with the oxidizable fraction

of the cores as a function of time and treatment. Error bars indicate standard deviations of measurements completed at three depths (0–5, 5–10, 10–15 cm) on triplicate cores

Lofgren (2001) showed that NaCl additions mobilize Zn, Cd, Ca and Mg in streams and soils of a forested catchment. Backstrom et al. (2004) observed increased Cd, Zn and Ca levels, and decreased pH, in soils near a road treated with NaCl. They attributed these changes to ion exchange processes, together with the formation of Cd-chloro aqueous complexes. Amrhein et al. (1992) used leaching experiments to demonstrate that NaCl mobilizes Cr, Pb, Ni, Fe and Cu, which they attributed to the combined effects of increased dispersion of organic matter, together with ligand and ion exchange processes. Nelson et al.

(2009) similarly found that infiltration of soils with NaCl or MgCl₂ mobilizes Pb, Cu and Cd through a combination of organic matter dispersion, ion exchange and the formation of aqueous metal-chloro complexes. Bauske and Goetz (1993) used a combination of field studies and laboratory leaching experiments with NaCl and CaCl₂ to demonstrate the potential mobilization of Zn and Cd via ion exchange and the formation of aqueous metal-chloro complexes.

In this study, incubation in either NaCl or CaCl₂ resulted in increased levels of dissolved Mg, K, Na

(for Ca additions) and Ca (for sodium additions) compared to controls and decreased pH (Fig. 2i–l; Table 3), consistent with findings from prior studies. The equivalent positive charge added to the core pore waters in this study varies between 18 mM for the 1 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ treatments and 86 mM for the 5 g/L NaCl treatments, with an intermediate equivalent charge (68 mM) for treatments with 5 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. Thus, ion exchange should result in the greatest release of cations in the 5 g/L NaCl treatments, with the least release in the 1 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ experiments. This trend is confirmed by the experimental data: with respect to the major elements, additions of the three solutions liberated similar proportions of positive charge relative to the added equivalents of charge. The sum of the charge equivalents associated with K + Mg + Ca (for sodium additions) + Na (for calcium additions) is approximately 14, 13 and 3 for the 5 g/L NaCl, 5 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 1 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ experiments, respectively, which is equivalent to 16, 19 and 22 % of the total positive charge added with the NaCl or CaCl_2 .

Ion exchange reactions are non-specific; addition of NaCl and CaCl_2 will release NH_4^+ and trace nutrients to the soil solutions, in addition to major ions. Enhanced nutrient release could promote the observed mat formation and subsequent accumulation of anaerobic respiration products [dissolved Fe(II) and Mn(II)] in the treatment experiments. The quantities of the nutrients, like the major ions, released by each treatment should be directly related to the added equivalent charge. Thus, the 5 g/L NaCl addition would be expected to release the largest quantities of nutrients and stimulate the greatest amount of productivity. However, this is not the case. Instead, there is a greater mat growth and more production of Mn(II) and Fe(II) in the 5 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ compared to the 5 g/L NaCl experiments in spite of the higher charge equivalents added with the NaCl treatments (86 mM compared to 68 mM). Thus, ion exchange processes alone cannot fully explain the incubation data. The mechanism for the apparent stimulation of productivity and increased Mn(IV) and Fe(III) reduction must involve at least some Ca-specific effects. Determining this mechanism will require further study, but possibilities include direct stimulation of mat growth (i.e. Ca behaving as a limiting nutrient) or mineral precipitation effects (e.g. enhanced calcite precipitation).

Fig. 5 Average Fe and Mn concentrations extracted with the exchangeable, carbonate, reducible and oxidizable fractions as a function depth at the termination of the experiments (100 days), for **a** Fe in fall control, **b** Fe in fall 5 g/L NaCl, **c** Fe in fall 5 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, **d** Fe in spring control, **e** Fe in spring 5 g/L NaCl, **f** Fe in 5 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, **g** Mn in fall control, **h** Mn in fall 5 g/L NaCl, **i** Mn in fall 5 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, **j** Mn in spring control, **k** Mn in spring 5 g/L NaCl, and **l** Mn in 5 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. Error bars indicate standard deviations of measurements completed on triplicate cores

Conclusions

Addition of the two commonly used road salt deicers, NaCl and CaCl_2 , to wetland sediments results in significant biogeochemical changes. The salt additions, particularly CaCl_2 , stimulate growth of a microbial or fungal mat, and enhanced production of dissolved Mn(II) and Fe(II). Pore water pH decreases dramatically, likely due to a combination of carbonate precipitation, oxidation and ion exchange reactions. Supply of Ca from CaCl_2 , together with the addition of macro- and micronutrients to pore waters via ion exchange reactions, is hypothesized to stimulate increased primary productivity and anaerobic respiration. However, further study is required to determine the mechanism of this stimulation and to quantify primary productivity and organic matter mineralization pathways.

The use of road salt deicer is widespread and continues to increase in much of Asia, North America and northern Europe. This study demonstrates that additions of NaCl and CaCl_2 to wetland sediments may greatly influence sediment biogeochemistry, even in the absence of macrofauna and macrophytes. Prior work has focused mostly on enhancement of ion exchange reactions, organic matter dispersion and aqueous complexation as mechanisms to enhance trace metal levels. Another potentially important mechanism is release of metals from reductively dissolving Mn(IV) and Fe(III) oxides. The apparent stimulation of anaerobic respiration observed in this study could have important consequences for trace metal cycling. Trace element bioavailability and mobility is closely related to metal speciation (e.g. Allen et al. 1980; Campbell 1995). Reduction of Mn(IV) and Fe(III) oxides is expected to release adsorbed trace metals into solution, potentially enhancing their bioavailability and mobility. Such processes could be quite important, particularly in road side sediments, which not only receive the

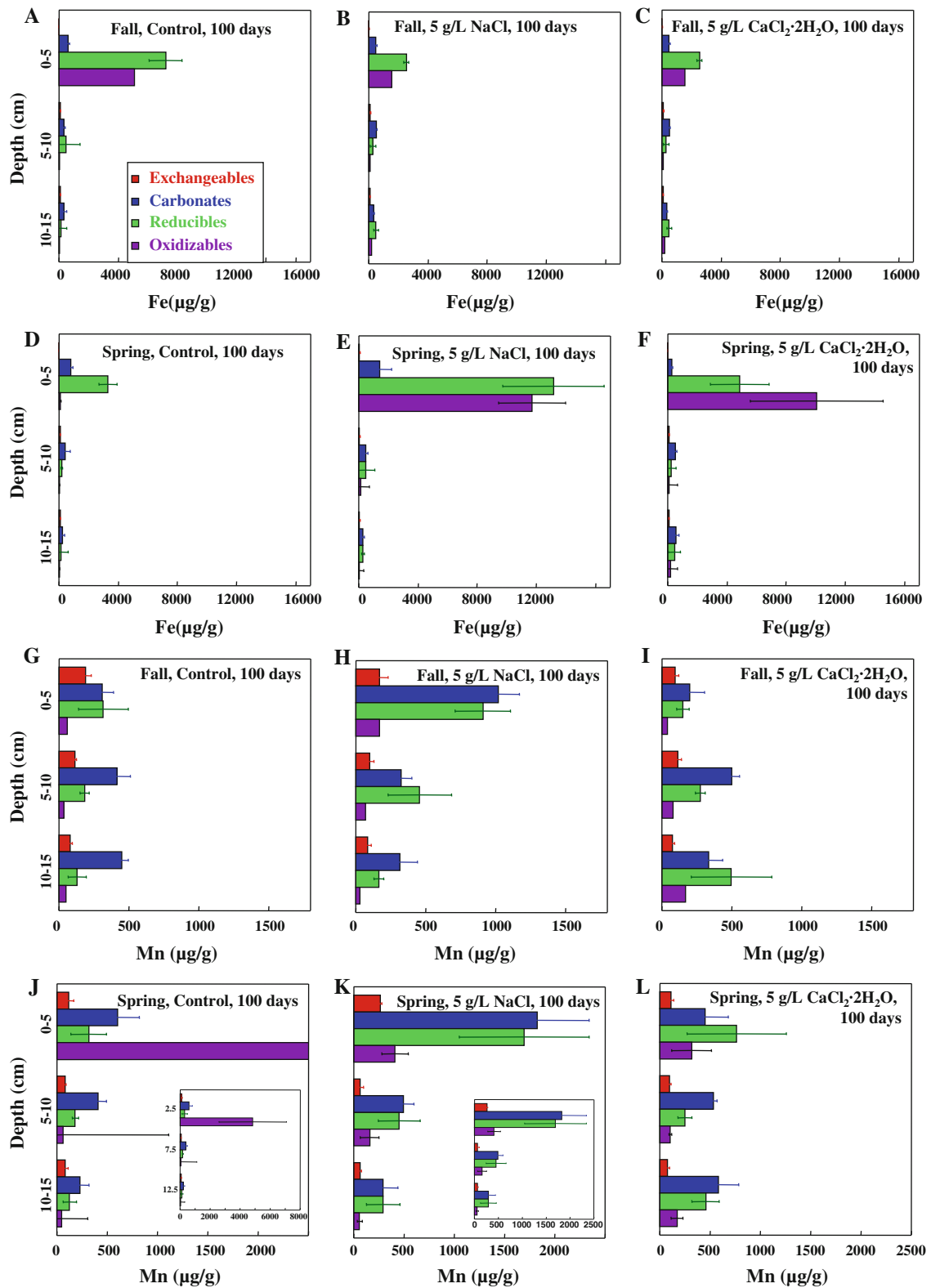




Fig. 6 Photographs of cores incubated in **a** DI water, **b** 5 g/L NaCl and **c** 5 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ after 60 days of incubation in fall

highest road salt loadings, but which often have a legacy of Pb contamination from leaded gasoline and which may have high levels of other trace metals, such as Cu, Zn, Cd and Cu (e.g., Amrhein et al. 1992; Nelson et al. 2009). Changes in trace metal speciation resulting from road salt deicers have largely been attributed to ion exchange, organic matter dispersion and aqueous complexation reactions (Amrhein et al. 1992; Bauske and Goetz 1993; Norrstrom and Jacks 1998; Lofgren 2001; Backstrom et al. 2004; Nelson et al. 2009). This study suggests that the onset of suboxic conditions with reduction of Fe(III) and Mn(IV) oxides may also be a significant factor. Future investigations should consider this pathway, together with changes in redox and microbial community structure that may result from road salt influx to wetland soils and sediments.

Acknowledgments This work was supported by the National Research Foundation of Korea (NRF-2009-352-C00145), the National Science Foundation (NSF-EAR-038435) and the Yonsei University Research Fund of 2010. Ryan Sibert is thanked for providing maps of the study site.

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