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Influence of road salt deicers on anaerobic respiration and metal speciation in soils

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Abstract

Road salt deicers, especially NaCl and $CaCl_2$, are used throughout the world on paved areas during the winter. Previous studies suggest that road salt deicers can alter the biogeochemistry of sediment located near roadways and influence the mobility of heavy metals. The goal of this study is to investigate the influence of $CaCl_2$ on wetland soil biogeochemistry, especially trace metal speciation. Sediment cores were collected in the fall from a freshwater wetland near an urban kettle lake (Asylum Lake, Kalamazoo, MI) and incubated for 100 days in deionized water (control), 5 g/L of $CaCl_2$, or 5 g/L of $CaCl_2$ with approximately 1 ppm each of Cd, Cr(VI), and Pb. At 25 day intervals, two cores were sacrificed from each treatment and pore waters were extracted for analysis of pH, total alkalinity, and dissolved Mn(II), Fe(II), PO_4^{-3}, Na, K, Mg, Ca, Pb, Cr(VI), and Cd. The change in percent organic matter in the solid phase was also measured over time. Addition of $CaCl_2$ stimulated a significant growth of microbial mats on the surface of the cores and led to increased Mn(II) and Fe(II) in the pore waters due to anaerobic respiration of Fe(III) and Mn(IV). Siderite, rhodochrosite, calcite, and aragonite were supersaturated in the $CaCl_2$ and may have precipitated, decreasing the alkalinity and pH. This study demonstrates that the use of road salt deicers may have a significant impact on biogeochemical cycling in wetland sediments.

Introduction:

Sodium chloride (NaCl) and calcium chloride ($CaCl_2$) are widely used throughout the world as deicers on urban paved areas. The use of road salt deicers has increased as cities and paved areas have expanded. In 1940, ~164,000 tons of salt per year was used in the United States (Salt Institute 2013), while today the U.S. uses more than 22 million tons each year (Stromberg 2014). In Michigan, the Michigan Department of Transportation (MDOT) spreads about 500,000 tons of salt per year (Salt Institute 2013). Road salt is also commonly used in Europe (e.g. Löfgren 2001; Norrström and Jacks 1998) and other parts of the world, with the amount used also increasing over time. For example, the European Salt Company reported that there was a 50% increase in the use of deicing salt on German roads from 2002 to 2005.

Chemical deicers prevent ice formation or melt snow by lowering the freezing point of water. When deicers are spread on roads they dissolve and melt the ice or snow to produce brine. NaCl is the most widely used deicer in Europe, Canada, and the U.S. (European Task Force 2002, Environment Canada 2012, USGS 2012). In some areas, the salt is prewetted to make melting more efficient. This prewetting agent is often NaCl brine, but $CaCl_2$ can also be used. At approximately -4º C, NaCl takes approximately twenty minutes to embed in ice or snow, but when wetted with 32% calcium chloride solution, NaCl immediately adheres to the roads and reduces the need for repeated applications (Morris Chemicals Inc, 2011). $CaCl_2$ used for deicing roads can be applied as a solid or brine. The price of $CaCl_2$ is up to six times more than NaCl, so it is most commonly used as a prewetting agent rather than as the primary deicer. In Sweden, research has shown that $CaCl_2$ is associated with concrete and vegetation damage. Consequently, it is not allowed to be used as a road deicer in Sweden (European Task Force, 2002). A survey by the National Transportation Research Board (TRB) found that out of twenty-eight highway departments surveyed in the U.S. and Canada, 95% of them used NaCl. Calcium chloride was used as a prewetting agent or primary salt by 60% of all of the departments surveyed (TRB, 2007).

Road salt deicer has been proven to make roads safer and reduce accidents (Salt Institute 2013), but it has also been shown to have adverse impacts on the environment. For example, NaCl deicers have been associated with corrosion in automobiles, and damage to vegetation and aquatic systems (Murray and Ernst 1976). Road salt can also alter the chemistry and density structure of lakes (Löfgren 2001, Judd et al. 2005, Novotny et al. 2008, Novotny and Stefan 2010, Sibert et al. 2014). Contamination of drinking water supplies is also a concern, especially for those on salt restricted diets (Huling and Hollacher 1972). The EPA recommends that drinking water should have no more than 20 mg/L of sodium. However, many studies have suggested that there is a large amount of sodium contributed to groundwater near roads that have been treated with NaCl. In New Jersey in 2015, United Water measured 108 mg/L Na in their water supply, which is approximately five times more than the EPA recommended level of sodium. Studies have also shown that road salt harms terrestrial animals in at least two ways, through increased vehicular collision and direct poisoning. Many animals have a sodium deficient diet and can therefore be attracted to salted roadways (Schulkin, 1991). Moose, deer, sheep, and birds have a higher mortality rate near roads that have been salted (Environment Canada, 2001).

Chloride can also lower the quality of drinking water. Background concentrations of Cl are normally low: usually less than 10 mg/L (Jones and Jeffery, 1992). Concentrations of chloride greater than 250 mg/L give water a noticeably salty taste. Therefore, 250 mg/L is the secondary maximum contaminant limit for public drinking water set by the U.S. EPA (U.S. EPA, 1989). The U.S. EPA has stated that chloride poses a risk at concentrations over than 230 mg/L for aquatic organisms over long-term exposures of more than an hour and that is poses an acute risk at concentrations of 860 mg/L for aquatic organisms (US EPA 1988). Groundwater near roads treated with deicers can contain chloride concentrations up to 1400 mg/L which is enough to pose significant acute risk to biota; chloride concentrations in groundwater in Toronto have been measured in concentrations of up to 275 mg/L (Williams et al., 2000, Environment Canada 2001). Chloride concentrations in groundwater from a study by the USGS measured concentrations greater than 250 mg/L in 2.5% of land use wells and 1.7% of drinking wells in a study area in the Midwest (Mullaney et al. 2009). In the Great Lakes (aside from Lake Superior), chloride concentrations have increased exponentially over the first six decades of the 20th Century and this trend is continuing for Lake Michigan and the bulk of the concentration is coming from road salt deicers (Chapra et al. 2009).

Chloride can accumulate in near surface aquatic systems near roads that are deiced, but reducing the amount of salt used by 10% can reduce soil loading by 50% and groundwater concentrations by 45% (Environment Canada 2001). Some practices to reduce salt loading include considering the sensitivity of particular environments, and using less salt in those areas. The same amount of $CaCl_2$ or $MgCl_2$ will deliver twice as much chloride to the environment compared to the same amount of NaCl, so NaCl could potentially be a better choice in sensitive areas. Sand can be used in environmentally sensitive areas. However, it can be blown off the road after application and it can turn into airborne particulates potentially causing respiratory problems and turbidity in surface waters in the spring (European Task Force 2002, Ramakrishna and Viraraghaven 2005). Calcium magnesium acetate (CMA) can also be used in sensitive areas. CMA has been shown to stabilize soil structure, buffer pH, and can help decrease sediment loading by causing the flocculation of clays (Amrhein and Strong 1990). However, CMA is very expensive: on an equal weight basis $1.00 of NaCl is equal to $19.30 of CMA (Cary Institute 2010).

Road salt deicers are commonly found in association with other significant contaminants, including heavy metals linked to automobiles. These heavy metals can come from a variety of sources: lead from gasoline; diesel fuel and tire attrition can lead to cadmium deposition; and stainless steel attrition can contribute chromium to the environment particularly close to roads (Amrhein et al. 1992). Laboratory studies have shown that NaCl increases the mobility and possibly the toxicity of heavy metals including cadmium, chromium, and lead in soil (Amrhein and Strong 1990, Amrhein et al 1992, Mayer et al. 2007, Nelson et al. 2009). Calcium and magnesium are better competitors than sodium for cation exchange sites held by trace metals, thus calcium chloride and magnesium chloride used in road deicers may displace more metals from cation exchange sites than sodium chloride. Heavy metals can be mobilized not only by cation exchange but also by the formation of aqueous complexes and by colloid dispersion (Norrström and Jacks 1998). Aqueous complexes can make heavy metals more mobile because the complexes stay in solution and resist adsorption to soil particles. Colloid dispersion increases heavy metal mobilization by distributing the small particles of metal evenly throughout solution. The solution, as it moves, carries the heavy metals along with it (Norrström and Jacks 1998).

This study will focus on three heavy metals: cadmium, lead, and chromium. The EPA maximum contaminant level for cadmium in drinking water is 0.005 mg/L. Exposure to higher levels of cadmium can eventually cause kidney damage which can lead to death (U.S. EPA 2013). Cadmium is being studied because it is one of the most mobile heavy metals. This is because it tends to be present in aqueous complexes in soil solutions, particularly chloride complexes, which decrease adsorption of Cd to soil particulates (Amrhein et al. 1992, Norrström and Jacks 1998, Mayer et al. 2008, Nelson et al. 2009). The mobility of cadmium in soils and ground water is largely due to cation exchange processes and complexation with chloride ions. It is not typically associated with the abundance of organic matter found in most soils. In road dust, one study found that 20-26% of Cd (Miller and McFee 1993) was readily exchangeable compared to 1.5% of lead (Harrison et al. 1981). Mayer et al. (2008) also found that cadmium is most abundant in sediment in the exchangeable fraction, from which it can readily exchange with ions in solution.

The EPA action level in drinking water for lead is 0.015 mg/L. Exposure to lead can cause delays in physical or mental development and cause kidney problems and high blood pressure. Lead is considered one of the least mobile metals in roadside soils, because it chemisorbs strongly to available particulate surface sites, especially Fe and Mn oxides or organic matter (McBride 1994, Harrison et al. 1985). For this reason, it is often found closer to salted roadsides than cadmium and is often associated with Fe or Mn oxides (Harrison et al. 1985). Deicers can also influence lead mobility. For example, Nelson et al. (2009) showed that NaCl facilitated a more significant mobilization of lead than $MgCl_2$. They state that the most probable mechanism for this is sodium facilitated dispersion of clays or metal oxides. However, deicers could also decrease lead mobility due to the formation of insoluble lead chlorides.

Chromium is another heavy metal of concern. Chromium is commonly found in near surface environments in two valence states, Cr(VI) and Cr(III). Chromium (VI) is the more toxic form. Drinking water standards from the EPA require total chromium (Cr(VI) and Cr(III)) in drinking water to be less than 0.1 mg/L. Over a long period of time, exposure to chromium in drinking water or the environment can cause allergic dermatitis or, at high levels, cancer. The

World Health Organization (1996) states that 1-5 grams of chromate can cause humans to suffer severe acute effects such as gastrointestinal disorders, convulsions and death from cardiovascular problems. Cr(III) is more stable in reducing environments; however it can be oxidized to Cr(VI) in an oxidizing environment (Bartlett 1991). The mobility of chromium can depend on a number of different variables. For example, organic matter can reduce Cr(VI) to Cr(III), which is less mobile and also less toxic (Bolan et al. 2003). Chromium is typically most mobile in neutral to alkaline groundwater because adsorption of Cr(VI), which forms an anion in solution, decreases with increasing pH. In contrast, Cr(III) forms a cation and can be more readily adsorbed onto cation exchange sites, charged surface sites, or precipitated out as $Cr(OH)_3$ or in iron hydroxides (Banks et al. 2006). Chromium has been found in higher concentrations in roadside soils in Albany and Buffalo than in soils taken from nearby areas where there was no deicer used (Amrhein and Strong, 1990). The deicer can act as an agent to mobilize chromium from automobiles into the soil.

Kim and Koretsky (2012) conducted a study to investigate the effects of road salt deicers, particularly sodium chloride (NaCl) and calcium chloride ($CaCl_2$), on wetland biogeochemistry. They found that road salt deicers resulted in significant changes in biogeochemistry. Dissolved Mn(II) and Fe(II) increased with time in cores treated with both NaCl and $CaCl_2$. The accumulation of these solutes in the treated cores suggested that anaerobic respiration is stimulated by the addition of NaCl or $CaCl_2$. Microbial mats were observed on the surface of cores incubated in both road salt deicer solutions but not on control cores incubated in ultrapure water. This could mean that the decomposition of the organic matter in the mats added to the total concentration of the Mn(II) and the Fe(II) in the core pore waters by stimulating Fe(III) and Mn(IV) reduction. Evidence of cation exchange between NaCl and $CaCl_2$ with the organic matter or clay minerals in the soil was also observed, with increased concentrations of dissolved Mg, K, Na, and/or Ca in treated when compared to the control cores.

The purpose of this study is to assess changes in pore water and solid phase geochemistry when $CaCl_2$ is applied to wetland soils together with Cd, Cr(VI), and Pb. Cores were incubated in three different solutions: ultrapure water, 5 g/L $CaCl_2$, and 5 g/L of $CaCl_2$ with approximately 1 ppm each of Cd, Cr(VI), and Pb. Cores were sacrificed periodically from each treatment to monitor pore water and solid phase geochemistry. Levels of Mn(II) and Fe(II) from anaerobic respiration and K, Mg, and Na yielded from cation exchange, are expected to increase more rapidly with time in cores incubated in $CaCl_2$ than in the control (ultrapure water) cores. In all three treatments, phosphate should increase over time due to anaerobic respiration, and pore water pH should decrease over time due to oxidation of more reduced solutes and the precipitation of carbonates. Cadmium is expected to mostly remain in solution, due to formation of aqueous cadmium chloride complexes, whereas Pb will likely bind to organic matter or Fe(III) oxides. Cr(IV) may remain in solution, unless it is reduced to Cr(III) and taken up by organic matter in the cores.

Site:

Sediments were collected from a wetland on the southwest side of Asylum Lake (Kalamazoo County) on December 12, 2014 (Figure 1). Sediments were collected in the same general area that Kim and Koretsky (2012) collected sediment for incubation. It was 35º F and overcast. The site was vegetated with cattails, trees, and other plants. There was about a centimeter of water over the sediment at the sampling site. Water was observed filling the holes that were created by sampling. Previous studies demonstrate that sediment pore waters from the south shore of Asylum Lake are strongly redox-stratified (Koretsky et al. 2006).

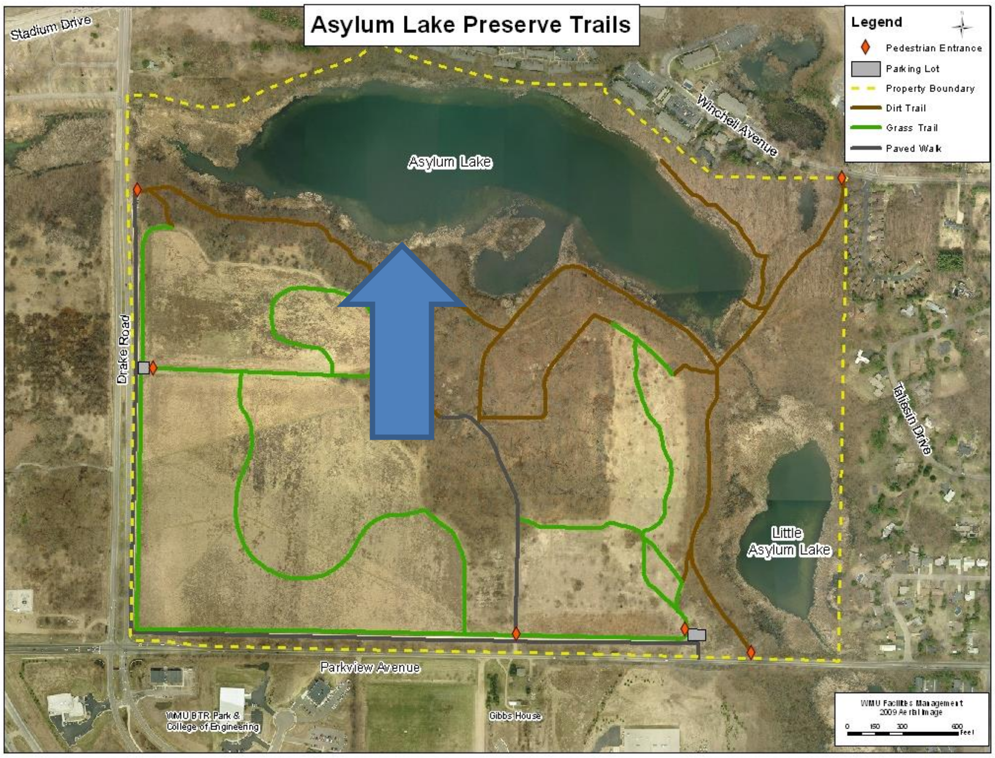

Figure 1.Location of sampling site, Asylum Lake, Kalamazoo, MI

Methods:

Sediment was collected from the surface to a depth of 25 cm using a metal shovel at nine sites located in an area of ~3 m radius. It was immediately sealed in nine 1-gallon ziploc bags, each of which was about two-thirds full. These were immediately transported to the lab and refrigerated. The next day the sediment was homogenized by mixing the sediment in the bag by hand. The homogenized sediment was then packed into 2-1/2 inch long, 1-1/2 inch diameter PVC tubes. Three 2-gallon buckets were prepared, i.e. one for each of the three treatments, with eight cores placed inside each bucket. Three additional cores were packed and set aside for initial testing. One sample bag was used per bucket to pack the cores. The control bucket was filled with 2 L of ultrapure water (>18 MegaOhm). The second bucket contained 2 L of a 5 g/L solution of $CaCl_2$ to simulate roadside deicer concentrations. The third bucket contained 2 L of a 5 g/L solution of $CaCl_2$ with approximately 1 ppm each of Cd, Pb, and Cr(VI) to simulate roadside heavy metal and deicer accumulations. The bucket containing $CaCl_2$ only was titrated to an initial pH of 5.16 using 3 drops of 5 M HCl added periodically while stirring with a stir bar. The heavy metals came in an acidic solution so the $CaCl_2$ solution was titrated to the same starting pH to make sure that initial conditions would be the same for both treatments. Evaporative loss of water was reduced by placing plastic shower caps over the buckets. The pH of the overlying solution was measured weekly. Every 25 days, for 100 days, two cores were sacrificed from each bucket. Pore waters were removed from each core via vacuum filtration under a nitrogen atmosphere and the filtrates were then passed through a .45 μm syringe-filter. Conductivity, pH, and redox-sensitive species (Mn(II), alkalinity, Fe(II), and total inorganic phosphate) were measured on the same day as the extraction. UV-Vis spectrophotometric methods were used to measure total alkalinity (bromophenol blue; Sarazin et al. 1998), phosphate (molybdate blue; Greenberg et al. 1992), Fe(II) (ferrozine, Stookey 1970), and Mn(II) (formaldoxime; Koroleff 1983). Alkalinity standards were matrix-matched for the filtrates from the $CaCl_2$ treatments. Samples to be analyzed by ICP-OES for major and trace elements (Na, K, Mg, Cd, Pb, and total Cr) were preserved in trace-metal grade nitric acid and refrigerated. The samples were then spiked with internal standards (1,000 ppb Y) before analysis. Loss on ignition tests were performed to assess changes in organic matter content of the sediments. Sediments were first freeze dried for two days, and then ~2-3 grams of sediment were weighed exactly and heated at 550ºC for two hours. Samples were cooled and reweighed to determine the percent of organic matter (Heiri et al. 2001). Visual MINTEQ version 3.0 was used for calculation of saturation indices. pH, alkalinity, Mn(II), Fe(II), Cr(VI), Cd, Pb, and phosphate concentrations were entered into MINTEQ and then MINTEQ was used, with the default thermodynamic database, to calculate saturation indices for the minerals that could form from these species.

Results:

Major and trace elements (Na, Mg, K, Pb, Cd, Cr) could not be analyzed due to mechanical problems with the ICP-OES. Samples have been acidified and refrigerated and will be analyzed as soon as possible.

The pH of the overlying solution in the buckets treated with $CaCl_2$ is lower by ~1-1.5 pH compared to the control treatment (Figure 2). pH in the control solution increases dramatically after the first 25 days from an initial pH of 6.56 to 7.08 at 26 days. The pH of the $CaCl_2$ treatment also increases in the first 25 days, but then fluctuates between 5.3 and 6.0 for the remainder of the experiment. The pH of the $CaCl_2$ treatment with Cd, Pb, Cr(VI) starts out at the same pH as the $CaCl_2$ treatment and also increases in the first 25 days to 5.85, but then decreases to 5.16-5.26 at 100 days.

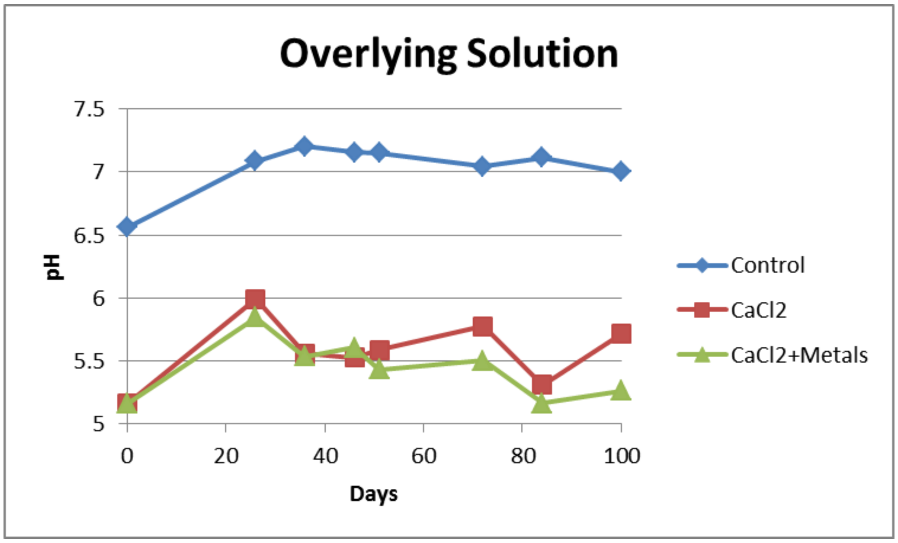

Figure 2. pH as a function of time in the overlying solutions of the three treatments

The cores in the $CaCl_2$ and heavy metals solution always had a higher conductivity in the porewater than the porewater from the cores in the solution containing only $CaCl_2$ (Figure 3). As expected, cores in both $CaCl_2$ treatments had much higher conductivity compared to the control cores. There was an overall trend of increasing conductivity until 75 days, from ~5500-7000 µS/cm, in porewaters incubated in both $CaCl_2$ treatments followed by a slight decrease between 80 and 100 days. Conductivity in the control cores decreased over time, starting at 800 µS/cm and decreasing to 345 µS/cm

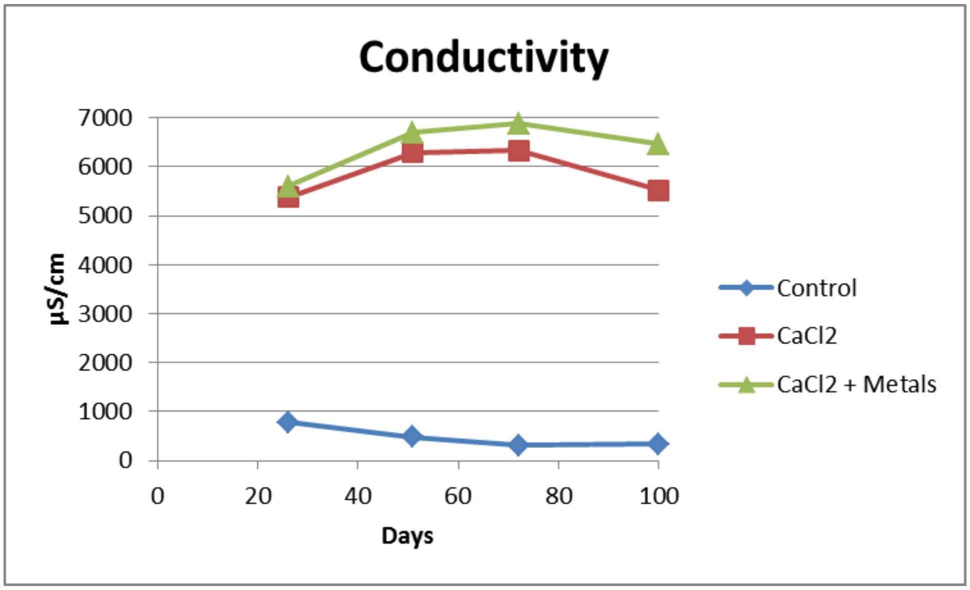

Figure 3. Conductivity in the porewater as a function of time in all three treatments

Average concentrations of dissolved solutes in pore waters extracted from duplicate cores extracted are shown in Figures 4-8. pH is much lower in the pore waters of the $CaCl_2$ treated cores compared to the control treatment, remaining relatively constant with time at ~8 in the control cores and ~6.5 in the $CaCl_2$ treatments for the first 50 days of the experiment. After this the pH starts to decline with time, with the lowest values in each treatment occurring at 100 days (Figure 4).

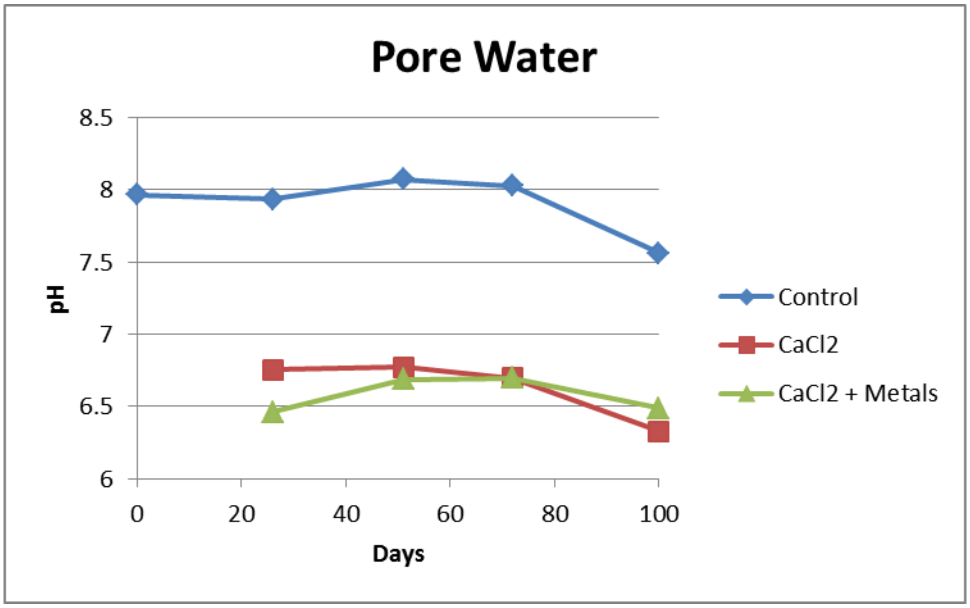

Figure 4. Porewater pH as a function of time in all three treatments

Alkalinity levels generally decrease with time in pore water extracted from all of the treatments (Figure 5). In the control the initial alkalinity is ~8 mM declining to ~3 mM by 100 days. Matrix-matched standards were not utilized for the initial sampling or at day 25: matrix-matching increased the development of color in the $CaCl_2$, suggesting that the calculated alkalinity for the initial points may be overestimated in the $CaCl_2$ treatments. As in the control, alkalinity declined with time in treatments with $CaCl_2$, reaching even lower levels (~1 mM) by 100 days.

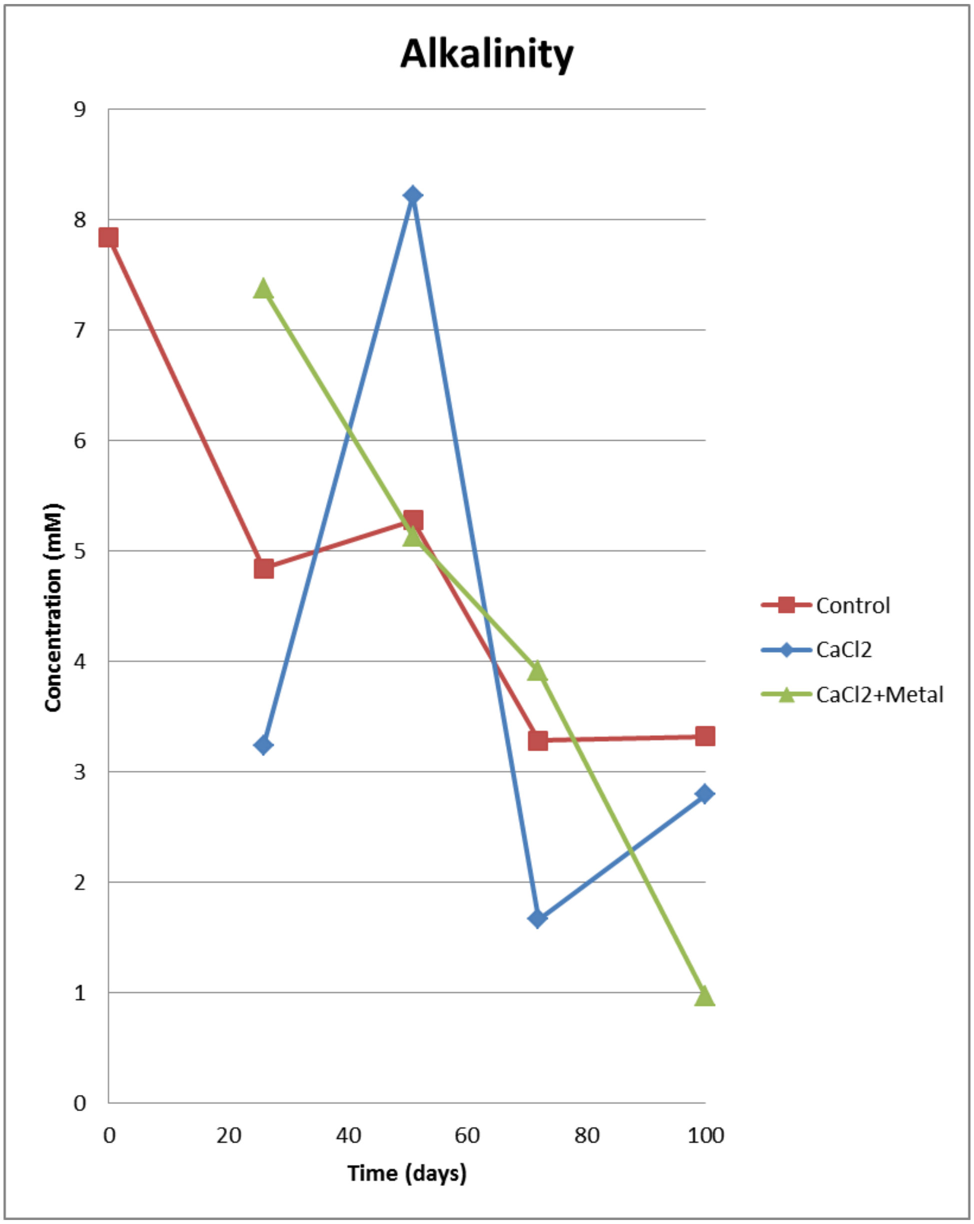

Figure 5. Pore water alkalinity as a function of time in all three treatments

Phosphate concentrations were typically less than 2 µM in the control and the $CaCl_2$ treatments (Figure 6). A large spike in phosphate (~18 µM) was measured at 72 days in the control; however, duplicate cores were not analyzed for the control on this date. The control cores typically had the highest phosphate levels in the pore water, while phosphate concentrations in the $CaCl_2$ treatments were always close to the detection limit of 0.5 µM.

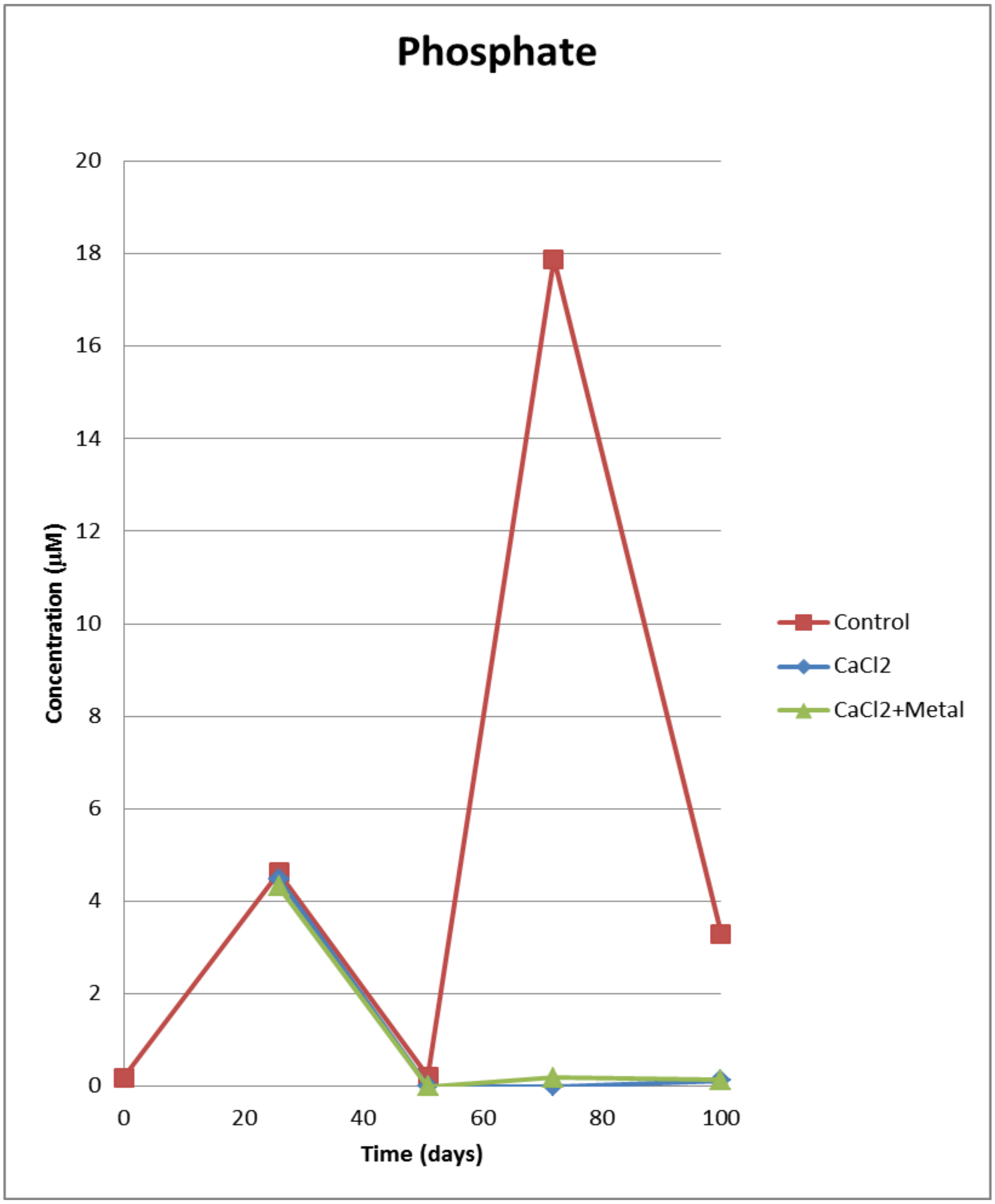

Figure 6. Pore water concentration of phosphate as a function of time in all three treatments

Dissolved Fe(II) concentrations in the control core pore water were near detection limits of 3.5 µM throughout the incubation with maximum levels of ~23 µM at 51 days (Figure 7). Fe(II) increased dramatically in both $CaCl_2$ treatments during the first 50 days of the incubation, reaching ~1500 µM at 51 days. Between 75 and 100 days, the concentrations decrease to ~300 µM.

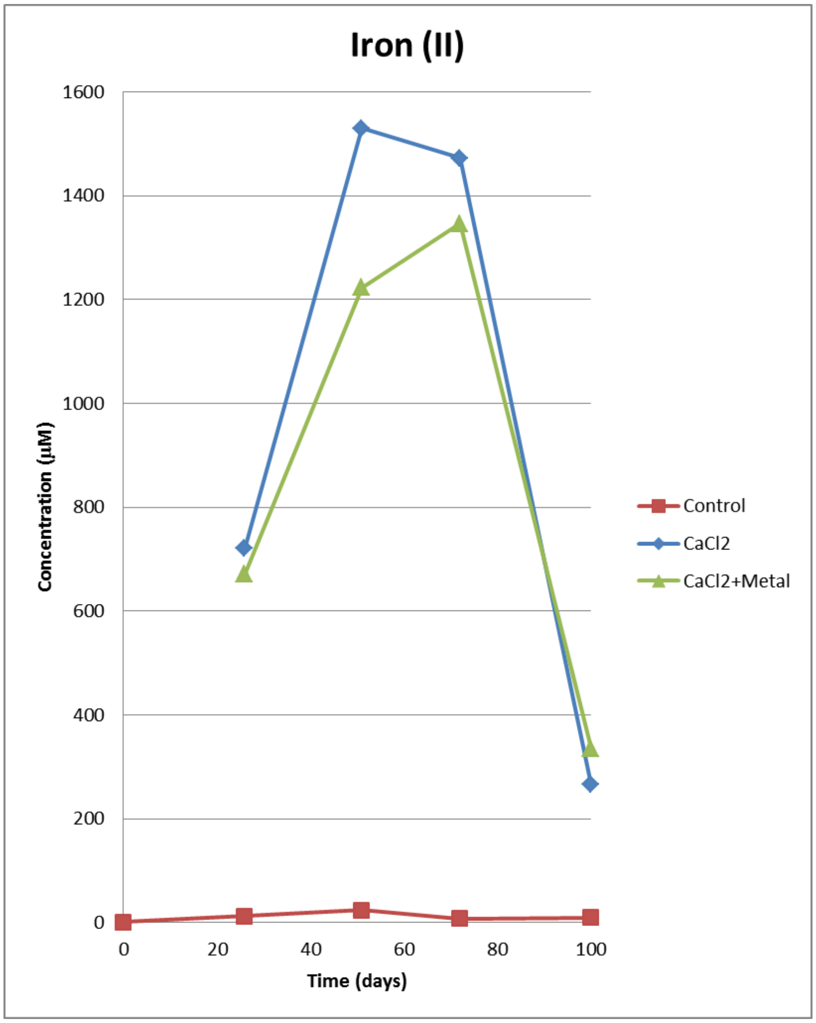

Figure 7. Pore water concentrations of Fe(II) as a function of time in all three treatments

Dissolved Mn(II) concentrations followed the same general trend as the Fe(II) concentrations (Figure 8). Concentrations in the control cores were much lower than in the cores treated with $CaCl_2$. Mn(II) levels in control core porewaters peaked at ~230 µM at 26 days and then decreased steadily to a level of 26 µM at 100 days. Like Fe(II), concentrations of Mn(II) increased dramatically in the $CaCl_2$ core porewaters peaking at ~1600 µM at 76 days and then decreased precipitously to ~330 µM at 100 days.

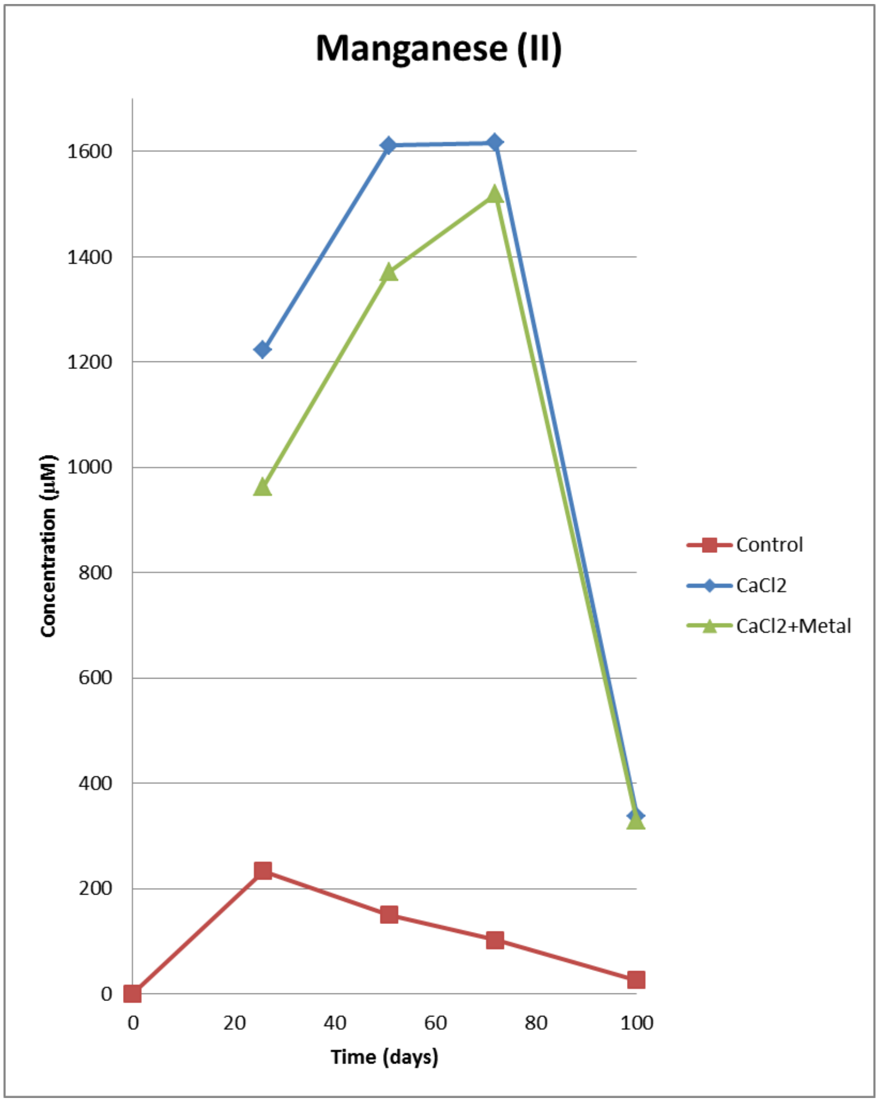

Figure 8. Pore water concentration of Mn(II) as a function of time in all three treatments

LOI tests are usually considered to provide a rough estimate of the quantity of organic matter in the solid sediment. The organic matter content in the control cores decreased steadily with time; the sediment initially had ~7.8% organic matter and decreased to ~4.1% at 100 days (Figure 9). The $CaCl_2$ sediment had higher organic matter content than the other two treatments. The sediment initially started out with ~8.6%, and the organic matter level decreased at 26 days to ~7.9%. The organic matter concentration then increased at 72 days to ~8.7% and dropped again to ~8.5% at 100 days. The sediment from the cores in the $CaCl_2$ and heavy metals treatment had a similar trend: organic matter was initially ~7.8%, but then increased to ~8.3% at 72 days and then decreased dramatically to ~6.9% at 100 days.

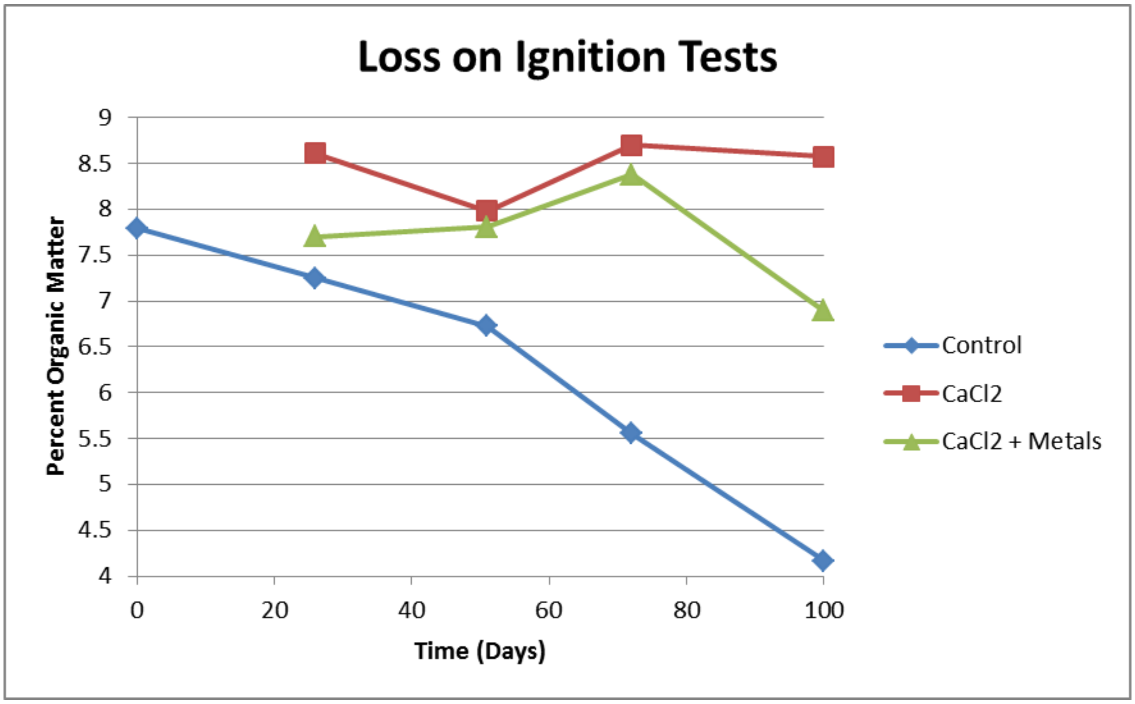

Figure 8. Percent organic matter in sediment as a function of time from all three treatments

Discussion:

Anaerobic Respiration

Microbial respiration of organic matter in oxic conditions is typically coupled to oxygen as the electron acceptor, according to:

$$\boxed{CH_2O + O_2 \rightarrow CO_2 + H_2O}$$

Equation 1. Where "CH_2O" represents organic matter

However, when oxygen is not present, organic matter can be respired using alternate terminal electron acceptors (Ehrlich 2002). For example, Mn(IV) or Fe(III) can be used as the terminal electron acceptors according to the half reactions:

$$\boxed{MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O}$$

Equation 2

and

$$\boxed{Fe(OH)_3 + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O}$$ Equation 3.

Organic matter is degraded (oxidized) via a series of electron acceptors which are generally used in sequence according to the energetic favorability of the reactions and the availability of electron acceptors (Figure 10; Ohren 2010). The sequence of electron acceptors use is generally O_2, NO_3^-, Mn(IV), Fe(III), and then SO_4^-, but these reactions can occur simultaneously or in different orders, especially in dynamic, heterogeneous systems.

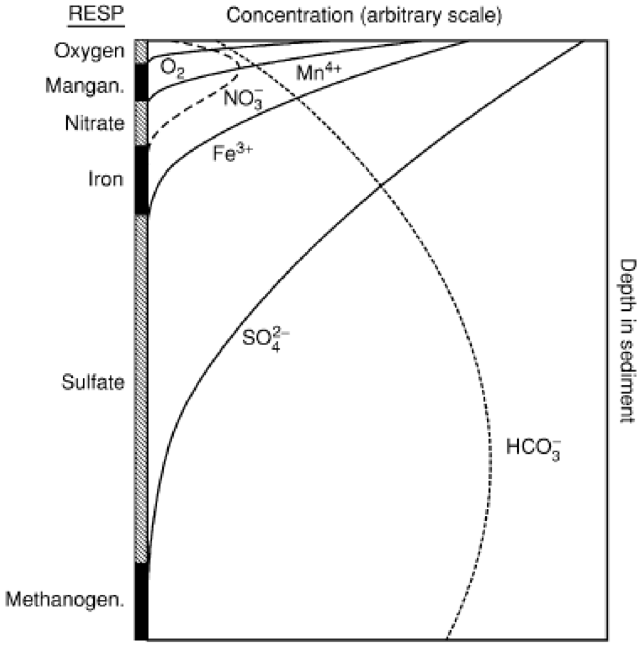

Figure 10. Idealized vertical distribution of electron acceptors in marine sediments (Adapted from Canfield et al. 2005)

According to Figure 10, the first sign of anaerobic respiration would be the absence of dissolved oxygen and the presence of aqueous Mn(II), followed by Fe(II) in the sediment pore waters. Mn(IV) releases more energy when reduced compared to Fe(III) and therefore is typically reduced before Fe(III) (Davison 1993). In cores treated with $CaCl_2$, Mn(II) and Fe(II) concentrations in the pore waters increased significantly with time until 72 days, and then decreased. The control cores had less dissolved Mn(II) and Fe(II) throughout the experiments and did not show the same dramatic increase and decrease in porewater concentrations of these (Figures 7, 8). The significant accumulation of dissolved Mn(II) and Fe(II) suggests that the addition of $CaCl_2$ stimulates anaerobic microbial respiration, specifically, the reduction of Fe(III) and Mn(IV). Orange microbial mats developed on the surface of the cores treated by $CaCl_2$ but not on those in the control or the heavy metal solution (Figures 11-13).

Figure 11. Control core at 43 days

Figure 12. $CaCl_2$ + heavy metals at 43 days

Figure 13. $CaCl_2$ core at 52 days

The presence of the mats in the $CaCl_2$ treatment but not the $CaCl_2$ with heavy metals treatments suggests that the mats are not directly responsible for the reduction of Mn(IV) and Fe(III), as there was a large accumulation of Mn(II) and Fe(II) in both treatments. These mats started forming within two weeks of incubation. If these mats produce labile organic matter via photosynthesis, anaerobic oxidation of the produced organic matter coupled to Mn(IV) and Fe(III) reduction could explain the accumulation of dissolved Mn(II) and Fe(II). However, this does not explain the high concentrations of Mn(II) and Fe(II) in the $CaCl_2$ and heavy metals treatment, which were nearly as high as in the $CaCl_2$ only treatment, and were much larger than the control. The LOI tests show that organic matter decreased steadily in the control cores (Figure 8) suggesting that oxidation of organic material did occur in these cores. The increase in organic material in the $CaCl_2$ treatment could be due to growth from the microbial mat observed, which may have produced enough organic matter to compensate for degradation of organic matter via Mn(IV) and Fe(III) reduction. The $CaCl_2$ and heavy metals treatment had a similar increase in organic matter, which suggests that organic matter production also counterbalanced degradation via Mn(II) and Fe(II) reduction in these cores.

Degradation of P-containing organic compounds should also result in the release of phosphorous as dissolved phosphate. However, little phosphate accumulation is observed in any of the treatments, especially the treatments with $CaCl_2$ (Figure 6). This suggests that phosphate is immediately taken up from the solution, either as a nutrient, or through precipitation of solids such as $MnHPO_4$, vivianite ($Fe^{2+}{}_3(PO_4)_2 \cdot 8H_2O$), hydroxylpyromorphite ($Pb_5(PO_4)_3OH$), or chloropyromorphite($Pb_5(PO_4)_3Cl$). For example, MINTEQ calculations showed that $MnHPO_4$ in the $CaCl_2$ treatment became increasingly less saturated as the experiment proceeded, with an initial saturation index of 3.626 at 25 days to 1.47 at 100 days (Table 2). Vivianite in the $CaCl_2$

treatment went from being highly supersaturated (3.995 at 25 days to highly undersaturated (-1.337 at 100 days). The $CaCl_2$ with heavy metals treatment also followed the trend of decreasing saturation indices of phosphate minerals over time. This could explain why there were higher levels of phosphate in the pore waters of the control cores compared to the pore waters of the $CaCl_2$ treatments, in spite of the evidence for greater anaerobic respiration in these treatments.

Table 1. Saturation indices over time for phosphate minerals in $CaCl_2$ and heavy metals treatment. Calculations assume 1 ppm of Cd, Pb, and Cr(VI) persists in the porewaters.

Saturation Index over time					
Mineral	Formula	26 days	52 days	72 days	100 days
Chloropyromorphite	$Pb_5(PO_4)_3Cl$	11.507	-19.41	8.814	10.53
Vivianite	$Fe^{2+}{}_3(PO_4)_2•8H_2O$	2.979	-17.035	1.6	1.623
$MnHPO_4$	$MnHPO_4$	3.357	-1.5	2.186	-0.354
Hydroxylpyromorphite	$Pb_5(PO_4)_3OH$	0.534	-30.1	-1.296	-0.426

Table 2. Saturation indices over time for phosphate minerals in $CaCl_2$ treatment

Saturation index over time					
Mineral	Formula	26 days	52 days	72 days	100 days
Vivianite	$Fe^{2+}{}_3(PO_4)_2•8H_2O$	3.995	-16.68	-16.86	-1.337
$MnHPO_4$	$MnHPO_4$	3.626	-7.896	-7.071	1.47

Carbonate Precipitation

Carbonate precipitation is controlled by pH, alkalinity, and the speciation of calcium, magnesium, iron, and other cations that may form carbonates (Amjad 1999). Some ions, such as dissolved Fe, can influence precipitation of calcium carbonate, calcium sulfate, and calcium phosphates, even when present at relatively low concentrations (Katz and Parsiegla 1995). Common carbonates include not only calcite and aragonite (polymorphs of $CaCO_3$) but also cerrusite ($PbCO_3$), rhodochrosite ($MnCO_3$), siderite ($FeCO_3$) and many others. In addition, many cations can form partial solid solutions with calcite or aragonite. Alkalinity can be used as a proxy for dissolved carbonate concentrations in systems that do not have high levels of other alkalinity-generating ions, such as organic anions, borate, and phosphate (US EPA 1992). Alkalinity varied significantly with time in all treatments, tending to trend downward as the experiments proceeded (Figure 5). This could be due to carbonate precipitation, which could also remove Fe(II) and Mn(II) through the formation of siderite and rhodochrosite respectively. Anaerobic respiration consumes hydrogen ions, resulting in increased pH, whereas aerobic releases hydrogen ions to solution (Equations 1-3), further suggesting that carbonate precipitation caused the decreased pH observed with time in all of the cores (Figure 4).

In addition, MINTEQ calculations show that many carbonate minerals, while supersaturated at the beginning of the experiment, became less supersaturated or undersaturated at the end of the experiment (Tables 3 and 4). This suggests that carbonate precipitated out of solution over time in these experiments. pH could have been lowered by the aerobic respiration occurring in the microbial mats on top of the $CaCl_2$ cores. Because the mats are located on the core-surface solution interface, they may have had sufficient oxygen to perform aerobic respiration, which lowered the pH of the overlying solution and the pore water.

Table 3. Saturation indices over time for carbonate minerals in $CaCl_2$ and heavy metals treatment. Calculations assume 1 ppm of Cd, Pb, and Cr(VI) persists in the porewaters.

		Saturation Index over time in $CaCl_2$ + metals treatment			
Mineral	Mineral Formula	26 days	52 days	72 days	100 days
Cerrusite	$PbCO_3$	0.823	0.943	0.919	0.604
$MnCO_3$	amorphous	1.228	1.447	1.382	0.042
Otavite	$CdCO_3$	0.685	0.759	0.652	-0.021
Rhodochrosite	$MnCO_3$	1.728	1.947	1.882	0.542
Siderite	$FeCO_3$	1.187	1.512	1.438	0.144

Table 4. Saturations indices over time for carbonate minerals in $CaCl_2$ solution

		Saturation Index as a function of time in $CaCl_2$			
Mineral	Mineral Formula	26 days	52 days	76 days	100 days
$MnCO_3$	amorphous	1.297	1.75	1.059	0.315
Rhodochrosite	$MnCO_3$	1.797	2.25	1.559	0.815
Siderite	$FeCO_3$	1.174	1.857	1.116	0.31

Conclusions

The addition of $CaCl_2$, a common road salt deicer, to wetland soils resulted in significant biogeochemical changes. The salt treatment stimulated the growth of a microbial mat, and a large increase in the production of Fe(II) and Mn(II). Porewater pH decreased over time, possibly due to carbonate precipitation or organic matter degradation and via aerobic respiration.

The use of road salt deicer continues to increase internationally, particularly in the U.S., Canada, and Europe. This study demonstrates that the addition of $CaCl_2$ to wetland sediments can influence the biogeochemistry of the sediments. The reduction of Mn(IV) and Fe(III) oxides could release adsorbed metals into pore water and the sediment. Roadside sediment can receive a large amount of road salt deicer in the winter, and is also susceptible to higher metal concentrations from the runoff of leaded gasoline or other heavy metals included in automobile parts. Future work will include BCR extractions (Rauret et al. 2000) to assess the speciation of metals in the sediment solids and ICP-OES analyses to determine the concentrations of Na, Mg, K, Pb, Cr(total), and Cd in pore waters. Future research could focus on other road salt deicers and their effect on the mobility of metals.

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