

2018

# Salt retention in wetland soils and effects on dissolved organic carbon export

Kayla Marie McGuire

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SALT RETENTION IN WETLAND SOILS AND EFFECTS ON DISSOLVED ORGANIC  
CARBON EXPORT

by

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Thesis

Submitted to the Department of Biology

Eastern Michigan University

In partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

in

Biology

concentration in Ecology and Organismal Biology

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July 8, 2018

Ypsilanti, Michigan

## ACKNOWLEDGEMENTS

I would like to give my thanks to all my family and friends who kept me focused and gave me constant support throughout this process. Without your patience and guidance, finishing this project would not have seemed possible. I would also like to thank my advisor, Kristin Judd, who was always ready to give invaluable advice and insight. She was willing to spend hours with me both in the lab and in the field and knew how to communicate things in a way we both understood. The level of support and encouragement she was always willing to give enabled me to become a better scientific thinker and problem-solver, and I cannot thank her enough. The members of my committee, Steven Francoeur and Katy Greenwald, also provided me with support, wisdom, and guidance outside of my immediate academic focus which served to give this thesis a well-rounded and comprehensive tone.

Funding for this project was provided by the Eastern Michigan University Department of Biology and the Graduate School. Additional support was given from the Michigan Department of Transportation, who generously provided road deicing salt from Detroit, Michigan, which allowed me to conduct research to the highest degree of accuracy.

## ABSTRACT

Deicing salt runoff has negative effects on ecosystems. Wetland ecosystems can act as important filters for runoff pollution (e.g., nutrients), mitigating damage to plants and microbes. Wetlands are important sinks for nutrients and pollutants (e.g., road salt) and transformation spots for many nutrients including carbon. The interactions between deicing salt runoff and wetland soil carbon were explored by measuring chloride export and retention, dissolved organic carbon (DOC) export, and carbon quality using mesocosm experiments. Net retention of  $\text{Cl}^-$  was highest in soils receiving high salt treatments (5.0 g/L NaCl), although percent retention of  $\text{Cl}^-$  was greater in soils receiving moderate salt treatments (2.5 g/L NaCl), indicating a retention cap for  $\text{Cl}^-$ . The export of DOC was significantly lower upon addition of salt for two of three wetland sites. The quality of carbon exported was not affected by salt addition. The storage of salt found could further alter the biogeochemistry of wetland ecosystems.

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## INTRODUCTION

### **Background: Ecological impacts of road salting**

Since 1975, the annual usage of deicing salts in the United States increased from around 8 million tons to 22 million (Mullaney et al. 2009). The widespread usage of deicing salts has negative effects on many types of ecosystems (e.g., Kayama et al. 2003; Green et al. 2008; Munck et al. 2009). For example, salt runoff causes harm to many species of upland plants (e.g., Kayama et al. 2003; Bryson and Barker 2006; Munck et al. 2009; Findlay et al. 2011). Some species of pine and sumac surveyed near roadways in the Northeastern U.S. exhibited burnt or browning plant tissue and contained salt concentrations many times higher than those recorded in healthy plants of those species. In some regions, surface water concentrations of deicing salts (specifically NaCl) have been found to reach levels toxic to freshwater biota near the source of input and near urban environments (Kaushal et al. 2005).

Additionally, lab and field studies suggest that deicing salts create adverse conditions in aquatic ecosystems. For example, deicing salt runoff leads decreases overall aquatic biodiversity (Bridgeman et al. 2000; Ramakrishna and Viraraghavan 2005; Cañedo-Argüelles et al. 2013). Salt-based runoff has also been linked to developmental issues in amphibians (Sanzo and Hecnar 2006; Karraker et al. 2008; Karraker and Ruthig 2009; Hopkins et al. 2013) and benthic macroinvertebrates (Silver et al. 2009). Other studies on aquatic systems suggest that salt runoff alters the chemistry and density structures of lakes affecting lake turnover and altering chemical balances (Kjensmo 1997; Judd et al. 2005).

Widespread use of deicing salts can result in landscape-level changes in biogeochemical cycling. Some studies suggest that deicing salt application can result in trace metal mobility in soils, fluctuation in nutrient bioavailability (e.g., Bäckström et al. 2004; Mayer et al. 2008;

Nelson et al. 2009) and changes in soil chemistry (e.g., Norrström and Bergstedt 2001; Green et al. 2008). Changes in soil chemistry via salt application can also alter soil microbial community composition (e.g., Tiquia et al. 2007). Saline soil conditions can affect ecosystem-level nutrient cycling by eliminating or displacing salt-intolerant bacteria that are integral to the transformation of nutrients that are present in those soils.

The salinization of drinking water supplies by salt infiltration is an increasing concern as the amount of deicing salts that are used in the United States continues to rise (Mullaney et al. 2009). It is predicted that at the current rate of urbanization (increasing percentage of impervious surface) management practices will not be enough to stop most surface water in the Northeastern United States from becoming undrinkable and toxic to freshwater life before the end of the century (Kaushal et al. 2005). Recent links between chloride levels and corrosivity of surface water are also of concern. The dissociation of salt into its respective ions gives runoff corrosive properties. Increases in the corrosive potential of water in distribution systems, due to a combination of chloride inputs and environmental factors, may lead to issues within water infrastructure and efficacy of water distribution (Stets et al. 2017). In addition, corrosivity of salt ions can be attributed to the transport of heavy metals such as lead within water infrastructure further polluting water supplies. This has been seen clearly in the case of Flint, Michigan. Without appropriate treatments to the infrastructure, the result was widespread pollution of drinking water supplies due to pipe corrosion and subsequent mobility of lead. Not only is this dangerous for water consumers, the early replacement of water infrastructure has negative economic impacts on the affected region. Compounded with excessive road salt usage, trends of corrosivity could become exaggerated and become even more of an issue in the coming decades.

Although increases in chloride levels have been found to exacerbate issues surrounding water potability and safety, the quantity of road deicing salts used in the continental United States has increased greatly over the past decades (Mullaney 2009). Evidence of road salt application increasing freshwater salinity is accumulating. In a New York stream system, for example, over an 18-year period (1986-2005) increases in sodium and chloride concentrations accumulated to 0.9 mg/L and 1.5 mg/L respectively. Similarly, export of those ions from the stream increased 20,000 kg/year and 33,000 kg/year, respectively, since 1986. Long-term deicing salt application is estimated to account for 91% of those increases (Kelly et al. 2008). Studies such as these illustrate an important relationship between salt input trends over time and the amount of salt that is now being released into surface waters as a result.

Road runoff also contributes to alkalinization. The freshwater salinization syndrome, caused by both salt pollution and human-increased weathering, is an issue of increasing concern, especially in the Midwestern United States (Kaushal et al. 2017). A large percentage of freshwater systems in the United States have seen increases in pH (90%) and specific conductance (37%). The release of cations from soils due to displacement by road salts combined with displacement of cations by acid rain accelerate weathering resulting in even more salinization of waterways. This positive feedback could have severe implications for nutrient balances (e.g., loss of nitrogen from soils), ecosystem services (e.g., heavy metal sequestration), and water infrastructure and potability. Continued application of road salt would serve to exacerbate a problem that is quickly becoming global in scale.

### **Movement of deicing salt through soils and watersheds**

Understanding the pathways taken by runoff is important for predicting environmental impacts and useful for planning effective management systems. Chloride from deicing salt runoff

can move through a watershed via surface water or groundwater pathways. Effects of surface runoff are more immediate and can result in sharp peaks in streamwater salinity during melt events. Chloride inputs in surface waters are usually attributed to human impacts such as urbanization and the construction of impervious surfaces (Rhodes et al. 2001; Crockett et al. 2003; Ramstack et al. 2004; Kaushal et al. 2005).  $\text{Na}^+$  and  $\text{Cl}^-$  ion inputs to surface waters spike immediately after salt application and will generally decrease as precipitation flushes the watershed throughout the spring and summer seasons (Kaushal et al. 2014). During storm water surge events and snow melts, these salt concentrations may reach concentrations of over 5 g/L due to the contribution from deicing salt usage. Surface water runoff has the most pronounced impact on aquatic systems immediately after snowmelt. In general, levels of both  $\text{Na}^+$  and  $\text{Cl}^-$  downstream from highways are extremely elevated in surface waters.

While runoff immediately impacts the salinity of surface waters, groundwater moves through the soil where it interacts with soil particles to determine flow patterns. The movement of water through groundwater pathways leads to deposition of chloride and many other minerals in soil pores and in aquifers where it may sit until excessive flooding or soil disturbance. Salinization of ground water can elevate salinity in streams during baseflow conditions. Some studies have observed elevated salinity during the summer and attribute it to salinization of ground water (Kelly et al. 2007). Groundwater movement generally contributes a low concentration of salt initially and will steadily increase salt release to soils and aquatic systems over time (Kelly et al. 2008; Cooper et al. 2014). Unlike surface waters, where elevated salt concentration is typically short-lived, ground water inputs may exceed chloride tolerance limits of biota over longer periods of time. This capacity to store salt ions may be a result of retention mechanisms in soils (Kelly et al. 2008; Cooper et al. 2014). Recent studies show that little salt

was released from soils during the early years of retention monitoring (net retention of salt). Over time, however, the amount of salt released becomes equal to that of the initial input and may stabilize if salt use ceases (Kelly et al. 2008). Once salt builds up in soils, high levels of salt ions may be released into streams during summer months long after the initial input of salt. Although salt is seasonally washed out of soils, overall increases in the salinity of watersheds have been observed since the early 1950's, supporting a retention mechanism that may not allow all of the salt to exit the soil matrices (Mullaney et al. 2009). These observations are attributed to and are consistent with long-term salt use and subsurface accumulation of salt across a watershed. Understanding the way salt interacts with soils can help to predict long-term impacts of salting practices on these ecosystems.

Although chloride is generally considered to be unreactive in ecosystems, there is evidence that chloride can be retained in soils (e.g., Norton et al. 1999; Rhodes et al. 2001; Svensson et al. 2012; Lovett et al. 2005). Several mechanisms for chloride retention in soils have been proposed. One potential mechanism is the formation of chlorinated organic compounds. Chloride has been found to integrate into soil organic matter by forming organic chlorine compounds, preventing flushing of chloride during precipitation events (Rhodes et al. 2001; Bastviken et al. 2006). Further, high levels of organic matter can result in the storage of chloride in organic compounds and microbial metabolites. Other mechanisms include physical retention of chloride ions in soil micropores. Soils that have high bulk densities, low hydraulic conductivities or high concentrations of cations may retain more salt by this mechanism. Because abiotic factors such as bulk density and hydraulic conductivity can change over time, large quantities of stored chloride could be released with changes in local conditions or seasonally.

## **Wetlands: Ecologically important sinks and filters**

Wetland ecosystems are famous for their ability to retain nutrient and to filter out pollutants. For example, coastal wetlands often intercept and retain agrochemicals and nutrients that have traveled downstream from agricultural fields (Noe and Hupp 2005). Before nutrients, pollutants, and minerals are released into aquatic ecosystems, they are often stored, transformed or filtered out by wetland ecosystems. Nutrient retention occurs in wetlands due to the settling of particles (and attached nutrients) and plant uptake. Wetland ecosystems experience low rates of decomposition due to frequent anoxic conditions where nutrients can become trapped in detritus for long periods of time. These nutrients will then either remain in plant biomass or be exported from the wetland to groundwater storage or downstream aquatic systems. In similar ways, heavy metals, and contaminants (e.g., byproducts from industry) are accumulated in wetland ecosystems. Studies have highlighted the capacity of wetlands to filter out contaminants received in runoff (Knight et al. 1999; Mishra and Tripathi 2008). In fact, wetlands are commonly used for purposes such as wastewater treatment or heavy metal decontamination (Knight et al. 1999). Several wetland characteristics make them effective natural filters. They often lack the extensive mineral soil layers that are characteristic to uplands, and instead have larger pore spaces and loosely packed sediments. These physical attributes allow for the efficient filtration of contaminants by retention in soils or plants. Additionally, many plants that grow in wetlands are efficient gas exchangers (e.g., *Phragmites australis*) (Mitsch and Gosselink 2007), facilitate storage of carbon within the ecosystem (e.g., *Typha spp.*) and thus are able to store carbon that would otherwise make it back into the atmosphere as a greenhouse gas (e.g., CO<sub>2</sub>, CH<sub>4</sub>).

Although wetlands are well-known as filters for various pollutants, not much is known regarding their interactions with salt inputs. Because of their position in the landscape, their

ability to filter materials from runoff, and high organic matter content wetlands may have important interactions with salt runoff. Soil characteristics common to wetlands could be conducive to the retention of salt. For example, wetlands often contain high amounts of organic matter. The formation of organic chlorine compounds may be more likely in such wetland systems and could result in the retention of chloride ions. Inland wetland soils often consist of particles that are finer (e.g., silt, clay) that give the soil a lower hydraulic conductivity. This may result in micropores that trap chloride instead of directly releasing it. Given these wetland soil characteristics, it is possible that wetlands may have the capacity to filter chloride ions from road salt runoff.

### **Salt and dissolved organic carbon**

Upland ecosystem research has shown that salt inputs prompt the release of dissolved organic carbon (DOC) from these soils (Evans 2005; Green et al. 2008). DOC is the fraction of the organic carbon pool that passes through a 0.45-micron filter. Dissolved organic carbon originates from various sources including decaying plant matter leachate, soil organic matter (SOM) and microbial exudates. It can be classified as a heterogenous mix of carbon-containing molecules that differ in size and chemical composition. More specifically, these different types of molecules are categorized as either labile or recalcitrant. Labile DOC is readily consumed by microbial communities and is respired as CO<sub>2</sub> or incorporated into microbial biomass (Mandal et al. 2008). In contrast, recalcitrant DOC is not easily consumed by microbes. This form of DOC can remain undegraded in systems for long periods of time, impacting global carbon budgets by “locking up” carbon and preventing return to the atmosphere (Paul et al. 2001).

The carbon transformations that occur within wetland ecosystems (Figure 1) contribute to the global carbon cycle. Carbon taken up by plants is either stored in soils or released as gas

(e.g., CO<sub>2</sub>, CH<sub>4</sub>). The balance between carbon uptake and release is typically negative (carbon sink), due to low rates of decomposition in saturated soils with low oxygen availability. In fact, wetlands, which make up only about 5 - 9% of the land area, account for 20 - 25% of global terrestrial carbon stores (Mitsch and Gosselink 2007). In aquatic systems, labile DOC is an important energy source for bacteria (Raymond and Bauer 2001) while recalcitrant DOC can limit light and UV penetration through the water column (Boyer et al. 1997).

Dissolved organic carbon export from soils in the Northeastern United States has increased over the past few decades (Boyer et al. 1997; Monteith et al. 2007; Evans et al. 2005; Green et al. 2008). Upland studies in both the Northern and Eastern U.S. have shown that the concentration of DOC flushed from watersheds was ten percent higher on average than measurements taken a decade prior (Boyer et al. 1997). These large-scale changes in DOC export may reflect a large-scale cause for the mobilization of DOC from areas that used to store carbon. Possible reasons for the increased mobility of DOC include global temperature increases, land use changes, hydrological changes, increases in atmospheric CO<sub>2</sub> and colloid dispersion due to displacement of cations from salt exposure (Evans et al. 2005). However, more work is needed to target an effector for the increase in DOC mobility. If these export trends continue, carbon sinks could quickly turn into carbon sources and would ultimately release high amounts of carbon back into the atmosphere as CO<sub>2</sub>. Further, prior studies have suggested a link between dissolved organic carbon export and prior soil salt exposure (Boyer et al. 1997; Green et al. 2008; Kim and Koretsky 2012). Salt retention in soils long after application may also play a role in such a relationship by triggering a long-term release of DOC from ecosystems long after salt application was initiated (Kelly et al. 2008; Cooper et al. 2014). The possible relationships between recent

DOC export trends and increases in salt application and storage in soils could have large-scale implications for wetlands as carbon sinks and the overall health of aquatic systems.

The objectives of this study were to investigate the potential mechanisms of salt retention and export in wetland soils and explore possible relationships between salt and DOC export. I hypothesized that salt would be retained in wetlands due to low bulk density and high organic matter content of soils. Additionally, I hypothesized that as soil salt concentrations increased, DOC export would increase due to cation displacement following salt exposure. Base cations such as  $Mg^{+2}$  and  $Ca^{+2}$  are exported from soil matrices in favor of ions like  $Na^{+}$  which adsorb to soil particles. This destabilizes the soil structure which prompts colloid dispersion, and, thus, dispersion of DOC. To test these hypotheses, a mesocosm approach was used in which wetland sediments were irrigated with varying concentrations of salt solutions (every three days for seven flushes), followed by irrigation with salt-free water. Soil chloride concentrations were measured at the beginning and end of the experiment to determine net and percent salt retention. To determine chloride and DOC export from soils, the effluent was analyzed for chloride and DOC concentration. The quality of carbon (i.e., whether it was labile or recalcitrant) released was also assessed to determine if any connection exists between the application of road salts and the quality of DOC that is exported from the system.

## METHODS

### Site selection

Soils were collected from three inland wetland sites in Southeast Michigan: Independence Marsh (IM), Paint Creek (PC), and Parker Mill Park (PMP). Sites were selected to include a range of soil and vegetation types. Soils were collected during the first week of June 2016. Independence Marsh is dominated by native *Typha spp.* Other plant species at this site were mostly herbaceous (*Carex spp.*, *Eutrochium spp.*, *Solidago spp.*) in addition to a few woody shrubs and trees (*Salix spp.*, *Cephalanthus occidentalis*). Independence Marsh is located within Independence Lake County Park, bordered completely by forested area. The soils are high in organic matter (OM) (Table 1) and were saturated at the time of collection. Independence Marsh water inputs drain into the Huron River watershed and its drainage area is only 1.4% impervious surface area.

Paint Creek is a constructed wetland dominated by invasive cattail (*Typha x glauca*, *Typha angustifolia*) with patches of *Phragmites australis*. Soils contain a moderate (~35 - 40%) amount of OM and sand, due to frequent flooding. Paint Creek drains directly into a retention pond that periodically floods into the marsh and eventually flows into the Stoney Creek Watershed. Paint Creek wetland drains into an area that is 40.3% impervious surface by area, although it is not in direct contact with any road system.

Parker Mill Park is a county park located in a riparian forested wetland. *Carex spp.*, *Pilea pumila*, *Impatiens capensis*, and *Salix spp.* are the dominant herbaceous vegetation. Some *Quercus spp.*, *Carya sp.*, and *Acer spp.* are also present. The soils obtained at Parker Mill Park originated near a peat mound adjacent to Fleming Creek, approximately 75 meters from the creek. Soils from this area are sandy from periodic flooding and have a lower organic content (~25% OM). This area is a floodplain and often inundated. The flood water from this area drains

back into Fleming Creek, part of the lower Huron River watershed. The impervious land type cover surrounding the Parker Mill Park site accounts for 11.5% of the total land use area though no immediate roadways are present at the site.

### **Experimental design**

Landscape-level trends are often difficult to describe using field experiments due to confounding variables. To more easily measure wetland chloride retention and DOC export in response to chloride (road salt) input, a mesocosm approach was used. The experimental design consisted of a 3 x 3 factorial treatment design ( $n = 5$ ). Soil from each wetland site was placed into PVC mesocosms that were then flushed with NaCl solutions of varying concentrations once every three days for 12 days (four flushes), followed by three water flushes (no salt). Subsequent measurements of chloride, DOC, and DOC quality were taken.

At each site soil cores were collected with a standard bulb planter along a transect. Soil cores were collected in pairs every 5 meters, for 30 meters to attempt to capture heterogeneity. Soils were placed on ice and refrigerated upon return to the lab. To prepare soils for loading into mesocosms, they were first homogenized by site. Rocks, rhizomes, and woody materials were removed. Because the soils from each site differed in texture, porosity, and saturation level, soils were weighed to a mass that would fill the mesocosm to a standard 15 cm in height. The mass of soil required to reach this height varied by site (Paint Creek = 200 g, Parker Mill Park = 300 g, Independence Marsh = 375 g). The mesocosms used were constructed from two-inch PVC piping (20 cm height, 1.6 cm diameter), #10 rubber stoppers, gravel, mesh screening and an outlet of plastic tubing to allow the drainage of effluent. Pooled soil cores from each of the three sites were then divided into 15 mesocosms per site. Subsamples were taken and dried for determination of organic matter content (Table 1). Each set of 15 mesocosms were then assigned

to one of three experimental treatments for five mesocosms per treatment: control (0g/L Cl<sup>-</sup>), medium (2.5 g/L Cl<sup>-</sup>), high (5.0 g/L Cl<sup>-</sup>). After the mesocosms were filled with soil, each was saturated with deionized water (DI) to control for differences in pre-experiment saturation levels. The first flush occurred 24 hours later (Day 0).

Over the course of 18 days, mesocosms were filled with 75 mL of water once every three days for a total of seven flushes (Figure 2). A flush consisted of water addition and 72 hours of settling time to allow water to percolate through the soil column. The first four flushes consisted of medium and high salt treatments (or DI water in the controls). For the last three flushes, all treatments received 75 mL DI water in order to detect if salt would continue to flush out to completion. After each flush was complete the effluent was drained and collected into acid washed beakers for further analysis.

### **Effluent analysis**

#### ***Sample preparation***

Effluent was transferred from a collecting beaker to an acid washed syringe and filtered through a glass fiber filter (GF/F) to remove particulates. A small volume (< 5 mL) of the effluent was used to rinse the filter and syringe before collection. Filtrate was collected in two 20 ml scintillation vials in 10 mL volumes. Half of the collected scintillation vials of filtrate were diluted with DI water (1:1) and then acidified with 20 µl of trace-metal grade HCl while the other half were set aside for chloride and spectroscopy analysis.

### **Salt retention and export from soils**

To determine the extent of salt retained in or exported from soils, soil salt concentration was compared before and after the experiment. Soil sub-samples taken from pooled samples were collected to determine baseline Cl<sup>-</sup> concentration. After the irrigation experiment was

completed, soil samples were collected from each mesocosm. All soil samples were stored in a refrigerator until they were sent to Michigan State University (MSU)'s Department of Plant, Soil and Microbial Sciences for chloride measurements. Net Cl<sup>-</sup> retention of each treatment and each site was then calculated using baseline Cl<sup>-</sup> concentrations and final Cl<sup>-</sup> concentrations. Chloride mass was determined using a wet-to-dry conversion for soil mass and then multiplying this value by grams of soil in each mesocosm. Net retention was then calculated (equation 1).

$$(1) \quad \text{Net retention} \left( \frac{g \text{ Cl}^-}{g \text{ soil}} \right) = \frac{\text{Cl}^- (g)}{(10^{-6})(\text{Bulk density} (kg/m^3)) \left( \frac{1}{3} \pi (r_1^2 + r_1 r_2 + r_2^2) h (cm^3) \right)}$$

Percent of Cl<sup>-</sup> added to each mesocosm that was retained by soils was also calculated (equation 2).

$$(2) \quad \text{Percent retention} = \frac{\text{Cl}^- (g)}{\text{Total Cl}^- \text{ added} (g)} \times 100$$

### **Bulk density and loss-on-ignition**

Five sub-samples of soil per site were analyzed for bulk density. Bulk density was determined for each set of samples using a standard drying method (Dean 1974). Samples were weighed after being fully dried at 60°C (n = 5). Using the volume of a truncated cone, bulk density was then calculated (equation 3).

$$(3) \quad \text{Bulk density} \left( \frac{kg}{m^3} \right) = \frac{\text{soil dry weight} (kg)}{\text{soil volume} (m^3)}$$

The percentage of OM present in the soil samples from each site was assessed using a loss-on-ignition method (LOI). Five samples from each site were weighed into tins and dried at 60°C. The dry weights of each tin were taken and then each sample was combusted at 500°C. The percentage of OM was then calculated (equation 4).

$$(4) \quad \%OM = \frac{\text{pre ignition wt.}(g) - \text{post ignition wt.}(g)}{\text{pre ignition wt.}(g)} \times 100$$

In addition, the percentage of carbon in samples was determined by dividing the percent OM in half.

### **Chloride analysis**

To determine effluent chloride concentration, ion conductivity (mV) was measured using an Orion 710 A<sup>+</sup> ISE/pH meter with an Accumet™ Chloride Combination ISE ion probe using one vial of collected filtrate. Before each reading 160 µl of ion strength adjuster buffer (ISA) was added to the vial of filtrate to allow for the stabilization and uniform distribution of ions throughout the filtrate. Chloride concentrations were determined by comparing conductivity measurements of samples to a standard curve. These values were used along with flush volume to determine the mass of chloride exported with each flush.

### **Dissolved organic carbon and specific UV absorbance determination**

To determine the impact of salt addition on DOC export from wetland soils, DOC concentration was measured on a Shimadzu TOC 2000. A set of DOC standards made with potassium hydrogen phthalate were used to construct standard curves. The DOC concentration and the effluent volume were used to determine the mass of DOC exported over the course of the experiment.

Specific UV absorbance at 254 nm (SUVA<sub>254</sub>) was measured for each sample to assess the quality of the DOC. Sample absorbance at 254 nm was corrected for by the DOC concentration. Low SUVA values are characteristic of labile forms of DOC, while higher values are characteristic of more recalcitrant DOC (Potter and Wimsatt 2005). Absorbance readings were corrected for the addition of ISA buffer by subtracting the absorbance value of DI water plus ISA. SUVA<sub>254</sub> was calculated according to Potter and Wimsatt (equation 5).

$$(5) \quad SUVA_{254}\left(\frac{L}{mg-M}\right) = \frac{UVA(cm^{-1})}{DOC\left(\frac{mg}{L}\right)100\left(\frac{cm}{M}\right)}$$

### **Statistical analysis**

Because the same soil cores were subjected to multiple treatments over time, a repeated-measures analysis of variance (RM ANOVA) was used to determine if chloride, DOC export and SUVA differed significantly with respect to time, site, and treatment. Data were log transformed as needed to achieve normality. Mauchly's test of sphericity was performed to confirm data fell within appropriate sphericity restrictions. An outlier test within SPSS 24 used a boxplot and mean to identify three outliers for both SUVA and DOC data sets (all three points were in the Independence Marsh dataset, flush seven). Sphericity, RM ANOVA analyses, and outlier tests were performed in IBM SPSS Statistics 24.

## RESULTS

### **Soil characteristics**

The percentage of OM present in wetland sites ranged from 25.8% to 80.5% (Table 1). Independence Marsh soils had twice the OM of either Parker Mill Park or Paint Creek, and OM levels at Parker Mill Park and Paint Creek were similar. Soil carbon in IM soils was also twice that of Parker Mill Park or Paint Creek.

Bulk density of soils from wetland sites was variable (Table 1). Soils from Independence Marsh and Paint Creek had similar bulk densities, but soils from Parker Mill Park had an average bulk density about three times that of soils from Independence Marsh or Paint Creek.

### **Salt retention of soils**

Baseline soil chloride levels were similar at Independence Marsh and Parker Mill Park; however, baseline soil chloride levels at Paint Creek were about three greater times those of the other two sites (Table 1). Upon completion of the experiment (four flushes with 0, 2.5, or 5.0 g/L NaCl followed by three flushes with DI water), final soil chloride concentrations were much higher than the baseline levels in both 2.5 g/L and 5.0 g/L NaCl treatments across all sites. The degree to which chloride concentration increased, however, differed with treatment. At the end of the experiment, wetland soils from each site had retained  $\text{Cl}^-$  indicating that not all salt was released (Figure 3a). As the concentration of NaCl applied to soils increased, net  $\text{Cl}^-$  retention also increased. Independence Marsh retained nearly two times as much NaCl among for both treatments as the other two sites. Although both salt treatments resulted in retention of chloride, the 2.5 g/L treatment resulted in the highest percent retention for all sites (Figure 3b). Overall, percent retention of chloride ranged from 4.5% to 13.1%. Percent salt retention was highest at the Parker Mill Park site, and salt retention at Independence Marsh was comparable to Parker

Mill Park. However, Paint Creek percent salt retention was less than half of values measured for Parker Mill Park or Independence Marsh. All sites retained the most salt after 2.5 g/L treatments, indicating a potential retention cap.

### **Soil organic matter and retention**

Net  $\text{Cl}^-$  retention and soil organic matter appear to be in a positive relationship (Figure 4). As the percent of soil organic matter increases, the amount of  $\text{Cl}^-$  total retained in those soils also increases. The soils with the highest net retention were from Independence Marsh (80.54% OM) and retention was similar at Parker Mill Park and Paint Creek (25.81% and 34.26% OM, respectively). The relationship between soil organic matter content and overall retention capability of those soils may help explain mechanisms by which wetland soils could be retaining salt.

### **Salt export from soils**

Across all sites, soils receiving NaCl treatments steadily exported  $\text{Cl}^-$  during salt treatments. The concentration of  $\text{Cl}^-$  exported during treatments steadily rose at all sites then gradually released less over time (Table 2). Although salt export from Independence Marsh was more delayed than in Parker Mill Park and Paint Creek soils, export from all sites decreased over time ( $p < 0.01$ ). Salt export from Independence Marsh was greater during salt treatments across all treatments imposed, and the decrease in export after the addition of freshwater was less compared to both Paint Creek and Parker Mill Park (Figure 5).

## **DOC export**

Cumulative export of DOC was lower in soils receiving salt treatments (versus controls) for two of the three sites studied ( $p < 0.01$ ). Soils from Independence Marsh and Paint Creek exported less DOC with addition of salt (both 2.5 and 5.0 g/L) compared to controls, whereas Parker Mill Park soils showed no difference ( $p > 0.05$ ) in DOC export between controls and salt treatments (Figure 6, Table 2). The start of fresh water flushes (day 12) did not appear to affect DOC export. Independence Marsh soils exported the most DOC total across all treatments, with the control exporting the highest mass of DOC. Paint Creek and Parker Mill Park soils also exported more DOC in the controls than in treatments.

## **Specific ultraviolet absorbance**

The SUVA values at each of the sites increased over time, indicating that exported DOC was more recalcitrant over time, but less so at IM (Figure 7). No significant difference in SUVA was found between DOC export from salt treatments and controls at both Paint Creek and Parker Mill Park ( $p > 0.05$ ). Independence Marsh controls exhibited higher SUVA values than either treatment ( $p > 0.05$ ) (Figure 7c), although the difference between treatments and controls was not significant (Table 2). SUVA was higher for DOC from Paint Creek and Parker Mill Park than Independence Marsh. SUVA values recorded from Independence Marsh soils were approximately half of those found at the other sites for each treatment type over the duration of the experiment. The lowest SUVA values were found during the first half of the experiment prior to DI flushes (Figures 7 a,b).

## DISCUSSION

These results suggest wetland ecosystems can act as sinks for salt inputs, supporting the prediction that wetland soils would retain salt due to high organic content. Net retention was highest in soils treated with 5.0 g/L NaCl; however, by percentage salt added, soils retained only 4 -14% of total salt added. The percentage of salt retention was maximal within soils treated with 2.5 g/L salt, suggesting that there may be a limit to the amount of salt wetland soils can retain. The export of chloride from wetland soils significantly decreased after salt treatments ceased for all sites as retention increased. Although this was the case, salt continued to be flushed over the duration of the experiment. Most of the salt added did wash out of experimental mesocosms. Surprisingly, we found that wetland soils exported significantly less DOC over time and decreases in export occurred with increases in salt treatment concentrations contrary to what was predicted. With repeated flushing, the quality of carbon exported from wetland soils shifted to lower quality, regardless of treatment or site. Interestingly, at two sites, DOC quality increased significantly with the medium salt treatment (but not the high salt treatment). These findings suggest that road salt addition to ecosystems could accumulate in wetland soils and affect wetland biogeochemistry. The relationships between salt and DOC may play a role in the amount and quality of DOC exported from wetland ecosystems and thereby impact downstream aquatic systems.

### **Salt retention and export**

Previous studies have described chloride movement through soils as “conservative.” However, an increasing number of recent studies indicate that chloride does not always behave conservatively (e.g., Svennson et al. 2007; Lovett et al. 2012). In accordance with more recent studies, this experiment found that chloride retention occurred in wetland soils. Retention of Cl<sup>-</sup>

occurred at all wetland sites and was greatest at the Independence Marsh site. Up to 14% of salt added to soils was retained, the highest retention occurring in the soil with the most organic matter (OM) (Figure 3b). As Independence Marsh was the site with the highest level of OM (Figure 4), this suggests that there could be an interaction between the organic components of wetland soil and NaCl. Some studies have found that chlorine participates in complex interactions with humic (highly organic) soils (e.g., Redon et al. 2011; Chambers et al. 2013). It is possible that the interactions between the soil organic matter and Cl<sup>-</sup> ions have caused the formation of organic chlorine compounds which are then retained in soil instead of flushing out (e.g., Redon et al. 2011). The inorganic chloride ions are incorporated into organic compounds that are used by microbes and become a part of the carbon cycle. These reactions, however, are determined by a number of biotic and abiotic factors such as pH, temperature and microorganisms present and would likely have different impacts on salt retention.

Other studies have assessed the assimilation of inorganic chloride (Cl<sup>-</sup>) into microorganisms and organic compounds, highlighting the importance of microorganisms for salt retention. Their results showed a 5% incorporation rate of added inorganic Cl<sup>-</sup> into organic Cl<sup>-</sup> found in peat after an incubation period of eight weeks (Silk et al. 1997). Additionally, it was found that incorporation of chloride by microbial respiration and chlorination of soil organic matter (SOM) is rapid and could lead to soil acting as chloride sinks. In fact, sterilization of soil in these experiments lead to a much lower rate of chlorination (2% of added Cl<sup>-</sup>), suggesting that microbial communities play a vital role in the formation of organic chlorine in systems with high levels of organic matter. Other studies have since found incorporation rates ranging from 4% to 40% of added inorganic Cl<sup>-</sup> (Bastviken et al. 2006, 2007). These findings are consistent with retention rates observed in our experiment (4% - 14% retention) (Figure 3b). However, it should

be noted that our study does not distinguish between inorganic chlorine assimilation and organic chlorine compound formation. Future studies may be able to assess these mechanisms more thoroughly to determine which, if either, may be driving the trends seen in this experiment.

The amount of chloride introduced into the system impacts the chlorination rate of SOM (Lugo et al. 1988; Bastviken et al. 2006, 2007). Large amounts of chloride lead to higher rates of chlorination. The percent retention results of our experiment indicate that while chloride is retained in greater quantities when more salt is applied, there may be a limit to what a particular soil type can hold. This may indicate that bulk density is an important factor when determining overall retention of chloride in a given soil. Salt retention may have varied among sites based on antecedent chloride conditions (or baseline  $\text{Cl}^-$ ). The site with the highest baseline  $\text{Cl}^-$  (Table 1), Paint Creek, also retained the least amount of salt over the duration of the experiment, which may be due to saturation of the soils. In addition, all sites retained a lower percentage of salt when treatment levels were increased (5.0 g/L). These results suggest there is a “retention cap” that for salt. This saturation threshold may be determined by qualities of the soils such as anion exclusion.

Salt export, the consequence of salt retention, was expected to decrease with increasing salt retention, reflecting non-conservative movement of chloride. Although it was found that salt export from wetland soils increased with higher salt treatments, it was gradual at all sites and continued to flush even after ceasing salt addition (Figure 3a). At Parker Mill Park and Paint Creek, initial export decreased then continued increasing after the first flush. While these patterns were less pronounced, the IM export decreased more sharply and experienced a more gradual increase over time. Site dissimilarities in bulk density and organic matter could be responsible for differences in  $\text{Cl}^-$  export. Organic matter and salt export results of our experiment

indicate that the level organic matter at each site could be facilitating an interaction with salt ions causing a gradual release of chloride rather than a rapid release. This is reflected in the retention results where Independence Marsh retained the most chloride.

Although salt retention occurred in all soils, it is important to note that the majority of added salt was exported. Most of the salt inputs added to soils could wash out of wetland ecosystems resulting in landscape-level implications. Salt that is flushed out would eventually find itself in nearby surface waters, promoting alkalinization and further salinization of these freshwater systems. The salt storage seen in this experiment may be long- or short-lived; salt could continue to flush into fresh water long after the salting season is over. The effects of delayed export may not be seen for seasons or years and could be difficult to quantify or predict.

### **DOC export**

Based on the findings of previous studies, we predicted that salt treatment would increase DOC export (Boyer et al. 1997; Green et al. 2008; Kim and Koretsky 2012). However, DOC release unexpectedly decreased upon addition of salt treatments to wetland soils in two out of three wetland sites ( $p < 0.01$ ) (Figures 6 a,c). In another recent study, similar results were obtained by the addition of brackish water (13 g/L) to freshwater marsh soils. Brackish salt addition caused a significant decrease in DOC release (Chambers et al. 2013). These, as well as our experimental patterns, could be a result of several factors. Because the soil core mesocosms were frequently flushed during the experiment, this may have encouraged microbial decomposition. During aerobic respiration the efficiency of microbes to transform carbon is increased (Freeman et al. 1993). It is possible that differences in soil hydraulic conductivity from sites used may have prompted differential rates of respiration and carbon transformations. Given the biogeochemical pathways available for carbon in wetlands, it is possible that DOC was being

used as a substrate for respiration and therefore was not exported in the form predicted (Freeman et al. 1997). The shift from DOC export to respiration could help explain the lowered rates of DOC export found in soils receiving salt treatments.

Interestingly, the site that did not experience a significant decrease in DOC export, Parker Mill Park, was also the site that had soils containing the least amount of OM (Table 1), which supports the idea that shifts in microbial respiration may be the cause of reduced DOC export. It is also possible that if OM/Cl<sup>-</sup> interactions dominate DOC export trends, the low level of OM present in the soils affected how many organic chlorine compounds were formed. This could have resulted in more DOC leaving the system, free from chlorine ion interactions. These results suggest that wetland ecosystems are processing salt inputs differently than are terrestrial systems.

The quality of carbon exported from sites was not affected by treatments ( $p > 0.05$ ) (Figures 7 a,b,c). The SUVA values increased with successive flushing events, indicating that the quality of DOC flushed from mesocosms decreased (more recalcitrant) over time. SUVA values of Paint Creek and Parker Mill Park DOC were similar, over twice those found at IM, indicating that the DOC from Independence Marsh had greater bioavailability (more labile). At both Paint Creek and Parker Mill Park, SUVA values during salt flushes increased more rapidly than after freshwater addition began. A more dramatic increase in loss of aromatic (recalcitrant) carbon suggests that salt may be triggering the early export of labile carbon rendering it unavailable to bacteria. To address this question, an extension of this experiment could label the loss of carbon as respiration substrate by following it through processes like CO<sub>2</sub> flux.

Research has monitored microbial respiration via CO<sub>2</sub> flux by recording the export of carbon to repeated irrigations of salt treatments (Chambers et al. 2013). The results indicate that

a large portion of soil organic carbon is lost through soil respiration and methanogenesis when exposed to salt under saturated conditions. Implementing techniques that detect CO<sub>2</sub> and CH<sub>4</sub> fluxes could demonstrate that carbon may be leaving the system in forms different than were recorded by this experiment (Chambers et al. 2013). The loss of carbon via other pathways could be explained by ionic displacement of Fe<sup>2+</sup> and other redox cations for Na<sup>2+</sup>. When NaCl is exposed to a soil matrix, the sudden release of cations like Fe<sup>2+</sup> into porewater could increase nutrient supplies for soil microbial respiration to occur more rapidly. Over time, however, it is possible for microbial communities which are maladapted to saline conditions to suffer from osmotic stress and become unable to respire (Ikenaga et al. 2010). This would be reflected in a short-term increase in CO<sub>2</sub> flux from soils, which could be measured in future experiments.

## CONCLUSIONS

Our findings suggest that the salinization of wetland ecosystems could lead to an overall storage of salt within these systems. However, there is a cap on the amount of salt wetland soils could retain, and overall retention in soils with high salt inputs is low. The gradual release of salt post-salt application indicates that wetlands could be a steady source of salt to downstream systems after the introduction of salt. In contrast to what we expected, salt treatments did not increase DOC export. Instead, lower DOC export was found. In addition, salt treatments increased the bioavailability of the exported DOC in two of three soils. This continued storage of salt could further alter the biogeochemistry of wetland ecosystems and downstream receiving waters by shifting bacterial community structure, limiting productivity and subsequently altering dominant plant and algal communities both within wetlands and surrounding aquatic systems. A series of cascading effects, such as change in soil pH and nutrient availability, could alter nutrient cycling into adjacent aquatic systems and within wetland ecosystems. This is subsequently affect carbon and other nutrient cycling on a much larger scale.

Additionally, an influx of  $\text{Na}^+$  due to salt storage could eventually displace many base cations at exchange sites on soil. These displaced cations can exacerbate already extant alkalization processes and perpetuate neutralization of acidic inputs to surface waters. The implications of such a feedback system could impact freshwater quality, water infrastructure stability and, ultimately, contribute to the freshwater salinization syndrome currently active throughout the continental United States.

While it seems possible to use wetland area as a filter for salt runoff, the ecological ramifications studied here may influence the decision to use one for this purpose. Although these results indicate that wetlands can retain salt, salt will still be flushed out of the system and impact

downstream aquatic ecosystems. Placing salt-tolerant wetland plants and deeply rooted plants for soil stability would be necessary to the success of any mitigation wetland. The environmental factors associated with the potential wetland site would need to be monitored closely and often to ensure that the chemistry within the system is conducive to salt storage. Ultimately, the local environment would be an important determining factor when deciding to use wetlands to slow the dispersal and damage associated with salt runoff.

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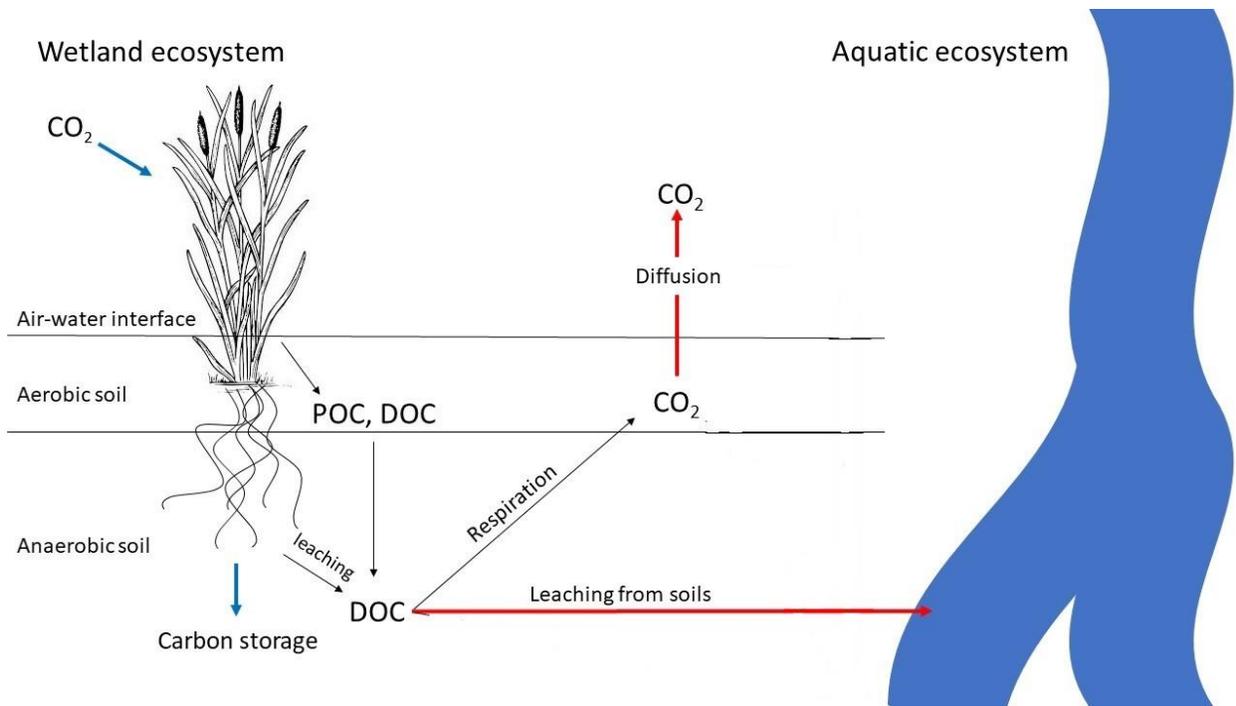
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**Table 1.** Organic matter, soil carbon, bulk density (n = 5), baseline chloride (homogenized soils, n = 1) levels of wetland soils. All data are reported as mean ( $\pm$  1 SD) except for baseline chloride.

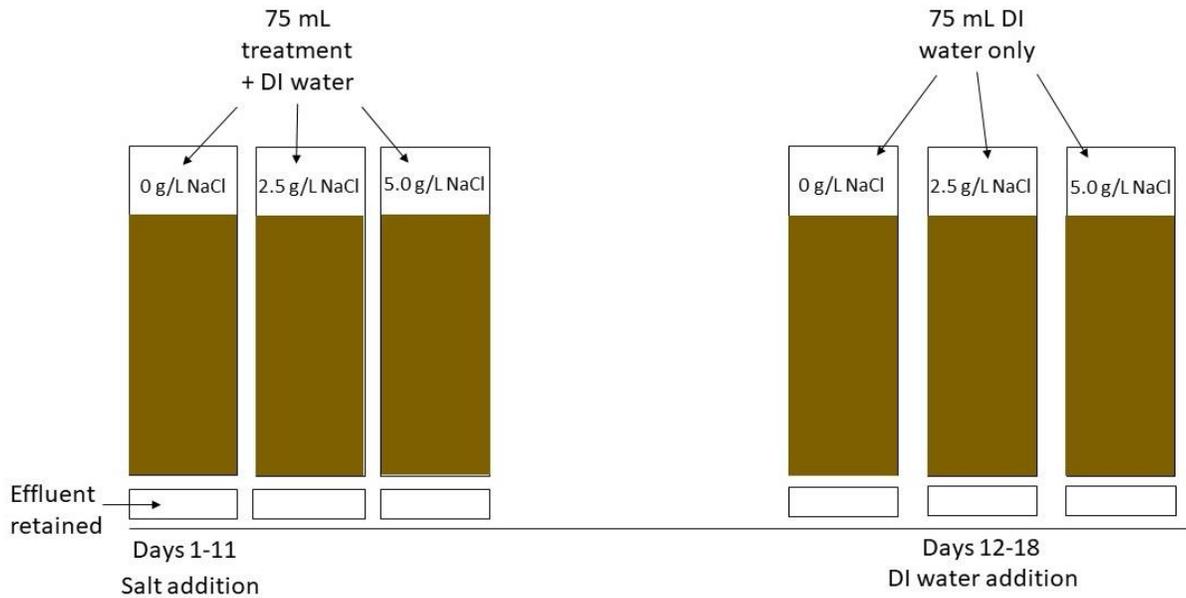
	<b>Parker Mill Park</b>	<b>Paint Creek</b>	<b>Independence Marsh</b>
<b>Organic matter (%)</b>	25.82 $\pm$ 0.86	34.26 $\pm$ 4.65	80.55 $\pm$ 1.28
<b>Soil carbon (%)</b>	12.91 $\pm$ 0.43	17.13 $\pm$ 2.32	40.27 $\pm$ 0.64
<b>Bulk density (g/m<sup>3</sup>)</b>	310.62 $\pm$ 33.50	107.29 $\pm$ 26.40	122.64 $\pm$ 44.35
<b>Baseline chloride (ppm)</b>	166	411	134

**Table 2.** Significance values for multiple comparisons between treatment and corresponding response variables. Same letters indicate treatments within one site that are statistically similar to controls.

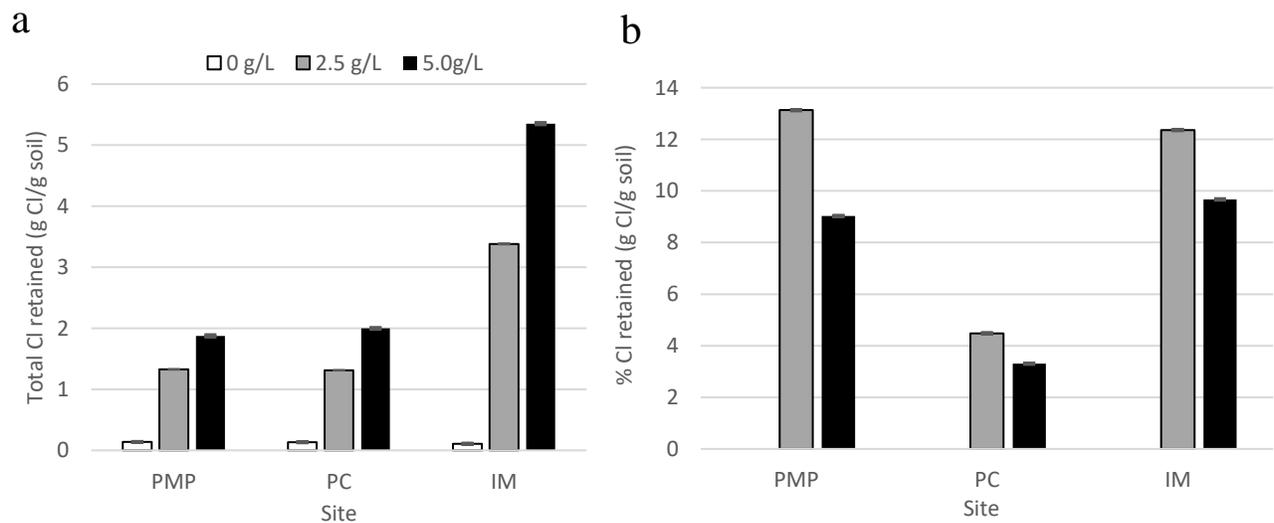
<b>Dependent variable</b>	<b>Site</b>	<b>Treatment</b>	<b>p-value</b>
Chloride export	IM	0.0 g/L NaCl	0.000 <sup>a</sup>
		2.5 g/L NaCl	0.000 <sup>b</sup>
		5.0 g/L NaCl	0.000 <sup>c</sup>
	PC	0.0 g/L NaCl	0.000 <sup>a</sup>
		2.5 g/L NaCl	0.000 <sup>b</sup>
		5.0 g/L NaCl	0.000 <sup>c</sup>
	PMP	0.0 g/L NaCl	0.000 <sup>a</sup>
		2.5 g/L NaCl	0.000 <sup>b</sup>
		5.0 g/L NaCl	0.000 <sup>c</sup>
DOC export	IM	0.0 g/L NaCl	0.041 <sup>a</sup>
		2.5 g/L NaCl	0.041 <sup>b</sup>
		5.0 g/L NaCl	0.008 <sup>c</sup>
	PC	0.0 g/L NaCl	0.048 <sup>a</sup>
		2.5 g/L NaCl	0.048 <sup>b</sup>
		5.0 g/L NaCl	0.009 <sup>c</sup>
	PMP	0.0 g/L NaCl	0.041 <sup>a</sup>
		2.5 g/L NaCl	0.041 <sup>b</sup>
		5.0 g/L NaCl	0.009 <sup>c</sup>
SUVA (Carbon quality)	IM	0.0 g/L NaCl	0.028 <sup>a</sup>
		2.5 g/L NaCl	0.028 <sup>a</sup>
		5.0 g/L NaCl	0.256 <sup>b</sup>
	PC	0.0 g/L NaCl	0.122 <sup>a</sup>
		2.5 g/L NaCl	0.122 <sup>b</sup>
		5.0 g/L NaCl	0.001 <sup>c</sup>
	PMP	0.0 g/L NaCl	0.232 <sup>a</sup>
		2.5 g/L NaCl	0.232 <sup>a</sup>
		5.0 g/L NaCl	0.056 <sup>a</sup>



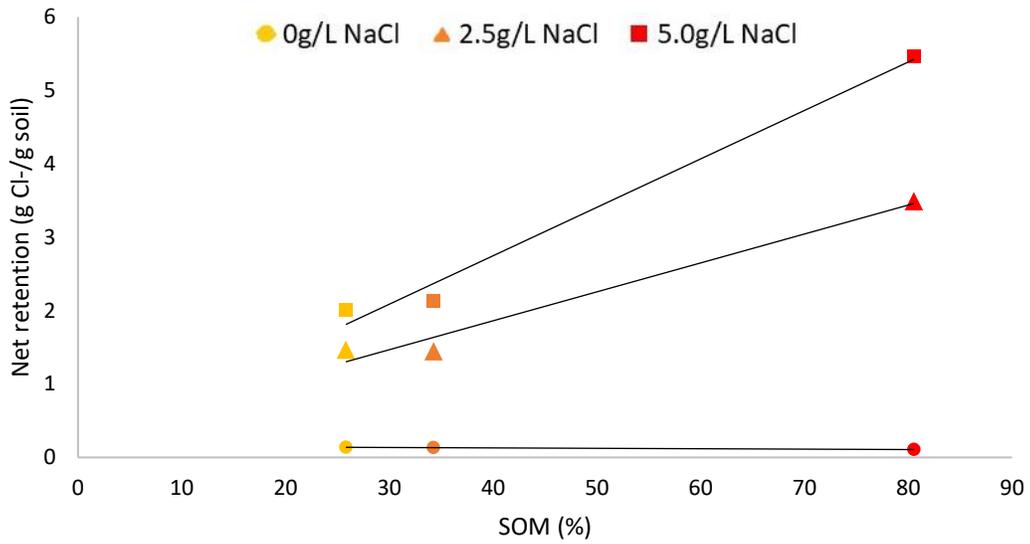
**Figure 1.** Conceptual diagram of carbon transformations in a wetland ecosystem. Blue arrows indicate inputs of carbon and red arrows indicate carbon outputs. In this diagram, carbon enters into the system as POC (particulate organic carbon) and DOC (dissolved organic carbon) carbon leaves the system as DOC via leaching into nearby aquatic systems thereby influencing the biological dynamics of the aquatic ecosystem.



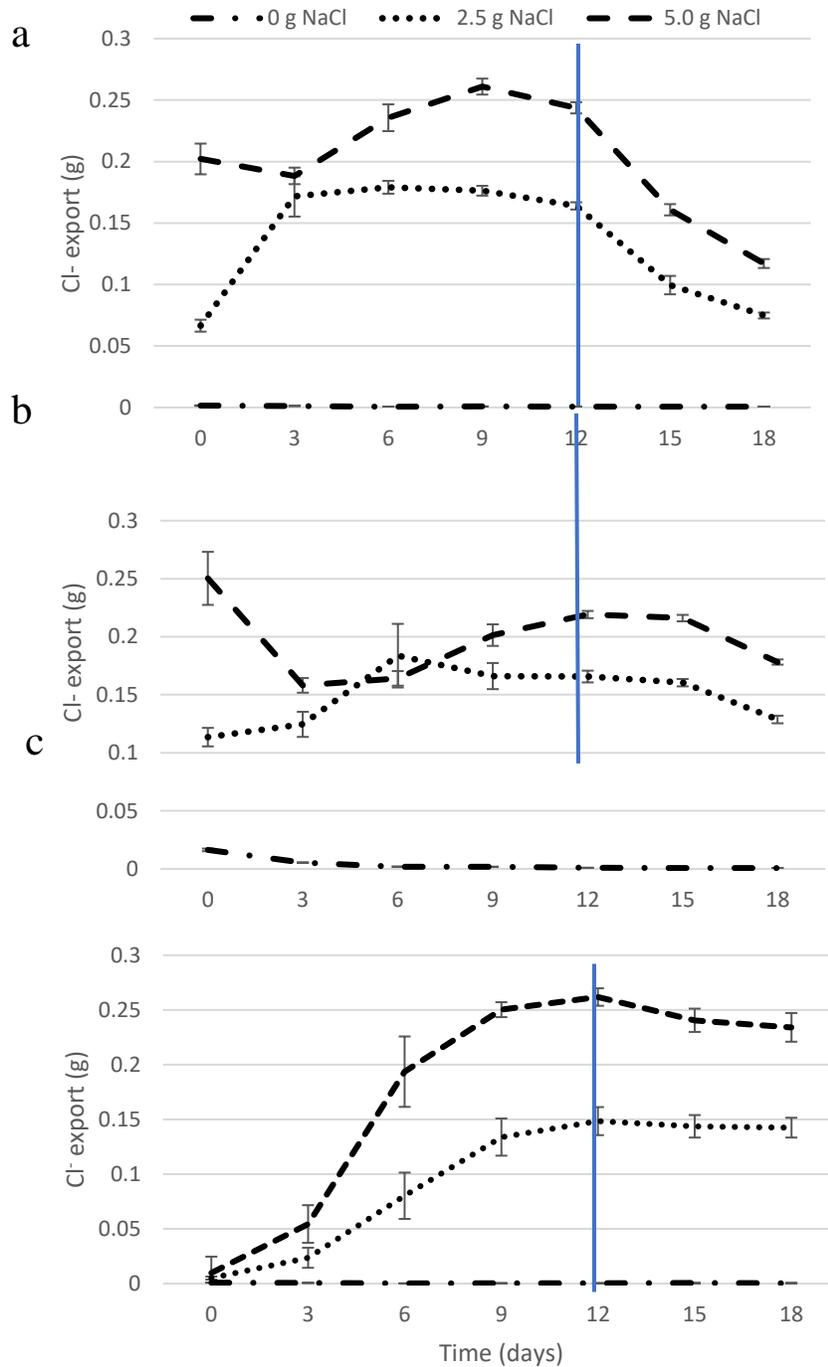
**Figure 2.** Diagram of mesocosm experiment setup. Days 1-11 of flushing were carried out using 75 mL salt water treatments. Days 12-18 of flushing consisted of 75 mL DI water only. Effluent was collected after each flush was performed.



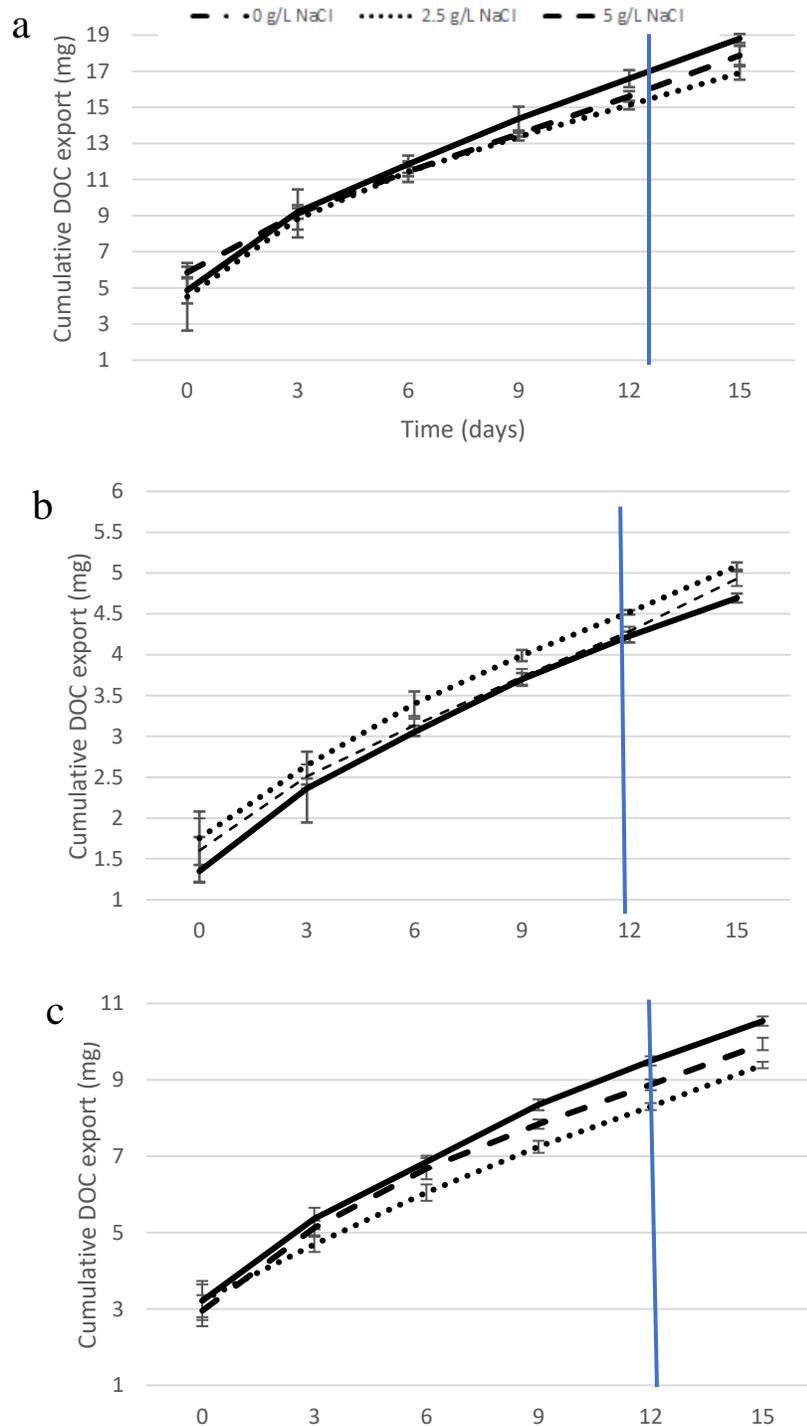
**Figure 3.** Net Cl<sup>-</sup> retention (a) and percent retention of Cl<sup>-</sup> by wetland soils (b). Bars show mean values ( $\pm 1$  SE) (n=5).



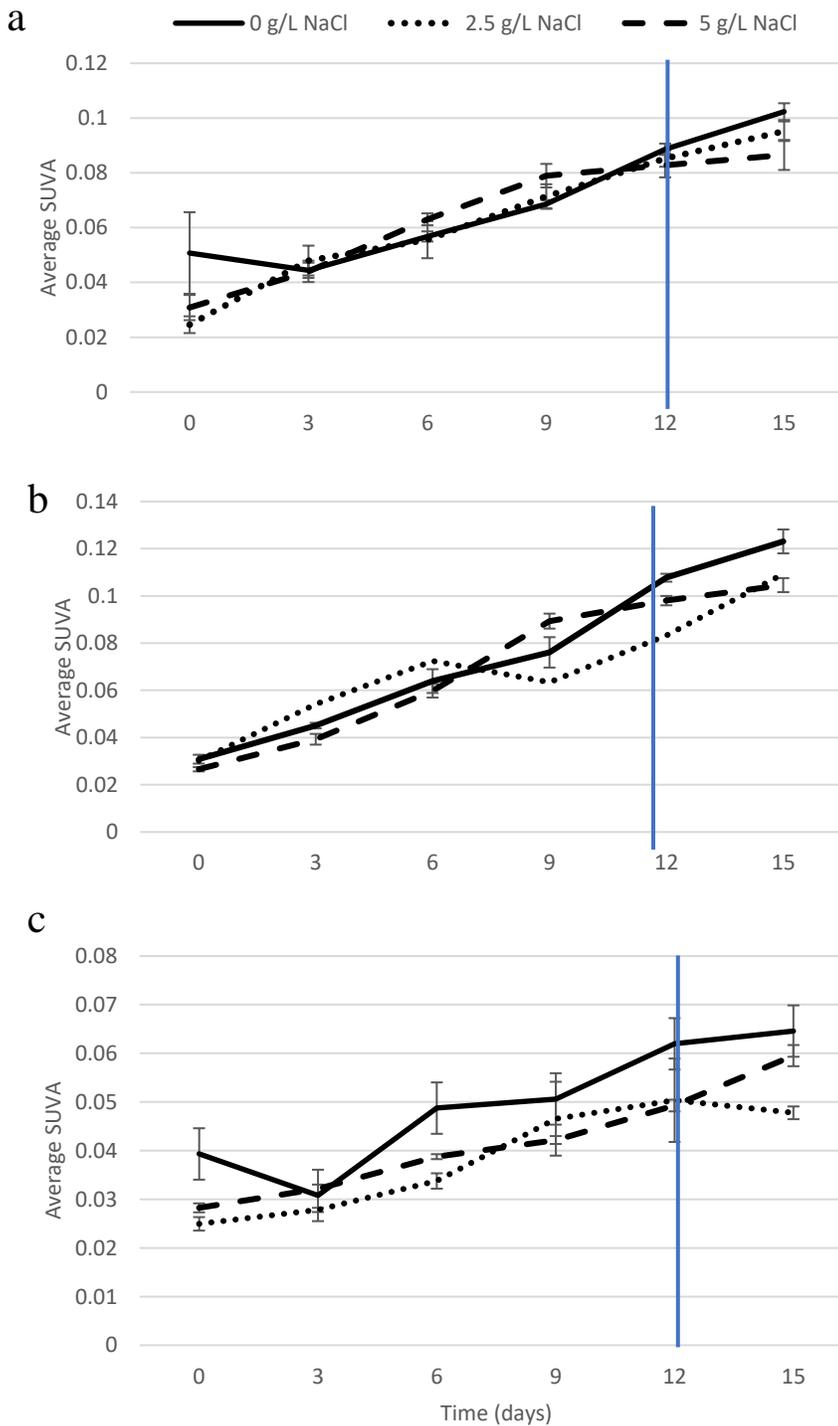
**Figure 4.** *Net retention* of Cl<sup>-</sup> increases as soil organic matter increases. Independence Marsh showed the highest overall retention with the highest percent of organic matter. Shapes indicate treatment level (see key in figure) and color indicates site. Independence Marsh is seen in red, Paint Creek in orange and Parker Mill Park in yellow.



**Figure 5.** Chloride export from wetland soils with each flush. Parker Mill, Paint Creek and Independence Marsh are represented by letters a, b, and c respectively. Vertical line indicates switch to DI water treatments. Bars indicate  $\pm 1$  SE (n=5). Note that graphs show export at each flush—not cumulative chloride values.



**Figure 6.** Cumulative DOC export from wetland soils. Vertical line indicates switch from salt treatments to DI water treatments. Graphs a, b, and c indicate sites at Parker Mill, Paint Creek, Independence Marsh respectively. Note the difference in Y-axis scales, day 18 data not included because of outlying data. Error bars indicate  $\pm 1$  SE (n = 5).



**Figure 7.** Average SUVA in effluent from soils from Parker Mill (a), Paint Creek (b), and Independence Marsh (c) during salt treatments (left of line) and DI flushes (right of line). Note the difference in Y-axis scale for each graph. Vertical line indicates the ceasing of salt additions. Error bars indicate  $\pm 1$  SE (n = 5). Day 18 data not shown on figure due to outlying data.