THE EFFECTS OF SALINITY INTRUSION ON THE BIOGEOCHEMISTRY OF HUDSON RIVER TIDAL FRESHWATER WETLANDS

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ABSTRACT

RESEARCH PAPER: The Effects of Salinity Intrusion on the Biogeochemistry of Hudson River Tidal Freshwater Wetlands

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Rising sea levels and stronger storm surges associated with climate change may expose tidal freshwater wetlands to saline waters. Previous research documents changes in tidal wetland biogeochemistry with salinity intrusion due to increased sulfate reduction and higher sulfide (H_2S) concentrations. To better understand the effects of salinity intrusion on biogeochemical cycling, descriptive measurements of sediment biogeochemistry in the Hudson River (New York, USA) were measured along a salinity gradient using microelectrodes. Laboratory experiments were also conducted exposing freshwater sediments to varying salinities and measuring sediment O_2 and H_2S dynamics. The higher incidence of H_2S in high salinity sediments ($p < 0.01$), and the subsequent effect on critical nutrient cycles, suggests that exposure to saline water may threaten the quality and sustainability of tidally influenced wetlands in the brackish region of the Hudson River estuary through changes in sediment biogeochemistry.

Introduction

Wetlands perform a multitude of functions that make them invaluable ecosystems not only to the organisms they contain, but also to surrounding environments. In addition to providing habitat for numerous species, wetlands provide a natural means of water filtration and can reduce the effects of floodwaters and storm surges by absorbing water velocity (Mitsch and Gosselink 1993; Gribsholt et al. 2005; Neubauer et al. 2005; Barbier et al. 2008). Another characteristic of wetlands, and a direct result of their placement at the interface of aquatic and terrestrial ecosystems, is that they exhibit higher biogeochemical activity than other strictly aquatic or terrestrial zones. Thus, wetlands are an ideal location for the exchange of chemical species with the atmosphere, groundwater, and surrounding aquatic and terrestrial ecosystems (Megonigal and Neubauer 2009).

Tidal freshwater wetlands (TFWs) are a unique type of wetland environment because they are subject to ocean-generated, lunar tides. TFWs are generally associated with large river systems, occurring at or near the head of an estuary, where salinity typically remains below an average of 0.5 parts per thousand (ppt) (Odum 1988). Because rivers typically constrict from the mouth of the estuary to the headwaters, tidal amplitude is usually greater in freshwater marshes than in downriver, saline marshes (Odum 1988). TFW sediments have high concentrations of dissolved and particulate organic matter and relatively low concentrations of dissolved sulfur (< 1 mg/L; Odum 1988). Because sulfur is scarce in TFWs, methanogenesis is the primary means of organic matter mineralization and the nitrogen cycle favors the removal of nitrate via denitrification (Odum 1988).

With high surface area, anaerobic zones near the sediment surface, and an abundance of

available organic matter, TFWs are an ideal environment for the removal of nitrate via denitrification (Megonigal and Neubauer 2009). Median rates of denitrification in tidal freshwater wetlands are up to 40% higher than rates recorded for other intertidal and aquatic ecosystems (Greene 2005). Denitrification is likely coupled to an influx of nitrate into TFWs from flooding waters (Megonigal and Neubauer 2009). Accordingly, a significant fraction of the nitrate and nitrite produced within the estuary, as well as that from allochthonous sources, is removed via marsh sediment processes (primarily denitrification) before estuarine waters reach the sea (Cai et al. 2000).

Dissimilatory nitrate reduction to ammonium (DNRA) is another pathway of nitrate removal in TFWs, though in this instance nitrogen is not removed from the system. Rather, it is retained as ammonium, a biologically available nitrogen species. DNRA in TFWs can consume as little as 5% or as much as 40% of the total nitrate pool (Bowden 1986; Nebauer et al. 2005). The relative amount of nitrate consumed by DNRA versus denitrification is, in part, a function of the relative amounts of organic matter and nitrate available in the system. DNRA typically predominates in brackish and saline systems, whereas denitrification becomes the major pathway for nitrate removal in freshwater zones, an occurrence likely attributable to the inhibition of denitrification by sulfide (Brunet and Garcia-Gil 1996; An and Gardner 2002).

Tidal freshwater wetlands are also important sites for organic carbon mineralization. Mineralization of organic matter in freshwater sediments occurs predominantly through the processes of methanogenesis (Capone and Kiene 1988). This trend is directly related to the lack of sulfate (and subsequent sulfate reduction) that is characteristic of low salinity freshwaters (Capone and Kiene 1988; Kelley et al. 1990). Organic matter mineralization via methanogenesis

yields less free energy than other pathways such as sulfate reduction, which is more common in saline sediments (Reeburgh and Heggie 1977). Thus, when sulfate becomes available, rates of methanogenesis can be suppressed by as much as 72% due to a shift to sulfate reduction (Bridgham et al. 2006).

Equally important as the overall rate of organic carbon mineralization in TFWs is the accumulation of organic matter. Maintaining a balance between carbon mineralization and accumulation is paramount to the sustainability of TFWs. According to Redfield (1965), the formation of TFWs was made possible by a slowing of sea level rise. Specifically, the accumulation of deposited sediments and organic matter and the storage of these materials allow TFWs to not only form and grow, but also to provide a net sink for carbon, nitrogen, and other nutrients (Morris et al. 2002; Neubauer et al. 2002). For this reason, a balance between loss and gain of organic matter is crucial to the sustainability of TFWs. If the primary pathway of mineralization were to be altered, the persistence and function of these ecosystems might be threatened.

Of the many observed effects of anthropogenic climate change, those concerning changes to patterns of precipitation, evaporation, and evapotranspiration may hold serious consequences for TFWs (Smith et al. 2005; Milly et al. 2005). In conjunction with decreased river discharge, rising sea levels could cause intrusion of saline water into traditionally freshwater portions of coastal estuaries (Hamilton 1990; Knowles 2002). The end result would be an upriver migration of the freshwater-saltwater front yielding inundation of freshwater soils with saline water during flooding tides. Differences in seawater salinity, hydrology, vegetation, and solute concentrations such as sulfate (SO_4^{2-}) and hydrogen sulfide (H_2S) result in marked differences in

biogeochemical cycles between salt and freshwater marshes (Weston et al. 2011). Alterations to key biogeochemical cycles such as denitrification and organic matter mineralization in response to salinity intrusion could threaten the quality and sustainability of TFWs as eutrophication and reduced accretion may result.

Current research suggests increased salinity can decrease denitrification rates (Giblin et al. 2010). Thus, increases in TFW salinity may reduce potential nitrate removal. Of the total amount of ammonium that is released from decaying organic matter and oxidized to nitrate in TFWs, 15-70% is removed via denitrification (Seitzinger 1988). With increased salinity, ammonium can be displaced from sorption sites by cations, such as calcium and magnesium, which are characteristic of seawater. The end result is a decrease in the pool of ammonium available for nitrification as well as reduced rates of coupled nitrification-denitrification. Seitzinger and Sanders (2002) suggested that higher denitrification rates in freshwater sediments may be due to an increased capacity to absorb ammonium. Salinity intrusion is also often accompanied by an increase in sulfide concentrations, due to increased sulfate reduction (Joye and Hollibaugh 1995). Through a direct effect on nitrifiers and denitrifiers, higher sulfide concentrations favor dissimilatory nitrate reduction to ammonium (DNRA) over denitrification (Brunet and Garcia-Gil 1996). Denitrification produces elemental nitrogen (N_2), which is lost from the tidal ecosystem to the atmosphere. In contrast, DNRA produces ammonium, which is retained within the tidal ecosystem, potentially exacerbating negative effects associated with nitrogen enrichment.

Organic matter mineralization is another pathway that may be altered as a result of salinity intrusion. Shifts in this process may result in an overall loss of organic matter from

TFWs (Weston et al. 2011). Organic matter mineralization coupled to sulfate reduction produces greater energy yields than when coupled to methanogenesis. Thus, sulfate reduction becomes more prominent relative to methanogenesis for anaerobic mineralization of organic matter (Weston et al. 2011). Further, sulfate reduction can increase the overall rates of organic carbon mineralization by as much as 49% (Weston et al. 2011). In fact, the loss of organic matter can be greater than the rate of accumulation (Weston et al. 2011). This potential loss of organic matter may threaten the sustainability of TFWs, presenting significant implications associated with the intrusion of saline water. If the loss of organic matter were to continually outpace accumulation, then the accretion and growth necessary for the wetlands to respond to rising sea levels would not be possible and the ecosystems would be lost.

As with all tidally influenced wetlands, the balance between organic matter accumulation and mineralization is a delicate one in the tidal wetlands of the Hudson River estuary (New York, USA). Over the past 500 years, this balance has favored the accumulation of organic matter, facilitating increased acreage of Hudson River tidal wetlands (Kiviat et al. 2006). However, of the 2,900 hectares of tidally influenced wetlands that are currently associated with the Hudson River estuary, downstream areas are highly susceptible to salinity intrusion. This particular region of the estuary constitutes the brackish region, where the water is a mixture of freshwater and seawater, and salinities range from 0.1 to 30 ppt. Due to direct connection with surrounding terrestrial ecosystems, the Hudson River ecosystem is influenced not only by tidal movements, but also by external factors such as nitrogen deposition associated with anthropogenic activities (Kiviat et al. 2006). In this way, the nature of the Hudson River tidal

wetlands inherent biogeochemical processes are susceptible to alterations in response to salinity intrusion fostered by rising sea levels.

The objective of this research was to quantify biogeochemical dynamics in the TFW sediments of the Hudson River in response to increasing salinity using a combination of both *in situ* and *in vitro* techniques. Specifically, sediment nitrogen, oxygen, and sulfide dynamics in tidal sediment were measured. It was hypothesized that the intrusion of saline water would result in increased sulfide concentrations and nitrogen retention within the wetlands due to a direct effect on sediment microbial activity.

Methods

Study Site Description

Five wetland sites spanning the brackish region of the lower Hudson River estuary were selected for measurement of sediment biogeochemistry (Figure 1), including (listed from low to high salinity): Constitution, Con Hook, Manitou, Iona, and Piermont marshes. Vegetation communities were standardized across sites to the maximum extent possible with either stands of cattail (*Typha* spp.) in the freshwater sites or invasive common reed (*Phragmites australis)* in the more saline sites. Species richness was higher in cattail stands. Big cordgrass (*Spartina cynosuroides*), saltmarsh cordgrass (*Spartina alterniflora*), purple loosestrife (*Lythrum salicaria*), spike grass (*Distichlis spicata*), salt-meadow cordgrass (*Spartina patens*), arrow arum (*Peltandra virginica*), and pickerelweed (*Pontederia cordata*) were common at northern sites, which included Constitution, Manitou, and Con Hook marshes. Conversely, common reed

stands, such as Piermont and Iona marshes, typically were not colonized by additional species of vegetation.

Field sampling was conducted in summer 2011 and summer 2012 with two separate sampling events each year to include a sampling event in late spring/early summer (6/27/2011 - 7/6/2011; 5/14/2012 - 5/30/2012) and a sampling event in late summer (8/3/2011- 8/5/2011; 7/27/2012 - 8/2/2012). The timing of the sampling events allowed for the evaluation of sediment under two distinctly different salinity and vegetation conditions. In early summer, vegetation communities were just developing and salinities were low (< 7 ppt). In late summer, vegetation communities were mature and salinities were typically at maximum levels (10 - 15 ppt) as river discharge decreased and the salt front migrated upriver. Due to unfavorable tidal conditions, only Constitution and Piermont marshes were sampled during spring 2012. These sites were selected because they constituted the extreme ends of the salinity gradient and allowed for comparison between the highest and lowest salinity exposure.

In situ descriptive sampling

Microelectrode measurements were conducted using Clark-type dissolved oxygen and hydrogen sulfide microelectrodes (OX-N, OX-500, H2S-N, and H2S-500, Unisense, Aarhus N, Denmark) (Revsbech and Jørgensen 1986; Jeroschewski *et al.* 1996; Kemp and Dodds 2001). These microelectrodes were used to measure *in situ* sediment dissolved oxygen (O_2) and hydrogen sulfide (H_2S) concentrations. Signals detected by the electrodes were received by a customized portable meter (Multimeter, Unisense) where data were stored and transferred to a personal computer. Because of the size of the microelectrodes (10 - 100 µm), disruption of

sediment was negligible during manipulation and measurement. Oxygen microelectrodes were calibrated using tap water saturated with oxygen (100% O_2 saturation) and then saturated with dinitrogen (0% O_2 saturation). Simultaneous measurements of dissolved oxygen were also taken in the water column with a conventional O_2 handheld meter (Oakton; DO6; Acorn Series Dissolved Oxygen/ºC Meter) (mg O_2/L) for field reference points. Hydrogen sulfide microelectrodes were calibrated using sulfur nanohydrate under anaerobic conditions at targeted concentrations (0 - 12.5 mg H_2S/L). Calibration of all microelectrodes occurred prior to and immediately following each field sampling event.

At each field site (N = 5), O_2 and H_2S concentrations were measured by positioning microelectrodes at the sediment surface. Three sediment profiles of O_2 and H_2S concentrations were measured at each site and sampling event. For each sediment profile, measurements were recorded at the sediment surface followed by a sequence of measurements at 250 to 5000 µm vertical increments (based on changes in O_2 and H_2S concentrations) to a final depth of 50,000 µm (5 cm) into the sediment. In 2012, profiles were obtained to a final depth of 100,000 µm (10 cm) to ensure that H_2S was not confined to greater depths, despite the occurrence of anoxic zones in the upper 5 cm of sediment. In general, measurements were made at 1000 µm intervals from the surface throughout the oxic zone. Once oxygen had been depleted, measurements were taken at 2000 µm intervals unless sulfide was detected, in which case measurement intervals were decreased to 1000 µm to gain greater resolution in the H_2S profile.

Bulk water and pore water samples were collected in triplicate at each site and immediately filtered (GF/F 0.7 µm pore size) for subsequent analyses. Bulk water was collected from just below the water surface at all sampling events in 2011 and 2012. Pore water samples

were extracted from sediment cores only in summer 2012. Cores were collected (as described below) and returned to the laboratory, where they were sectioned and centrifuged for collection of supernatant (pore water). Each 5 cm core was sectioned so that two separate pore water samples were obtained, one from the top 2 cm of sediment and one from the bottom 3 cm of sediment. Bulk and pore water samples were analyzed for ammonium (NH_4), sulfate (SO_4), phosphate (PO_4), and nitrate (NO_3) concentrations on a Dionex ion chromatograph using standard methods (DIONEX ICS-3000; Eaton et al. 2005). Ion concentrations below detection were designated as zero in calculations. Detection limits were 0.005 mg/L NH_4, 0.03 mg/L SO_4, 0.01 mg/L PO_4, and 0.01 mg/L NO_3,

In vitro sediment core experiments

In summer 2011, 18 cores were collected from Constitution Marsh, the lowest salinity field site (1 ppt; Figure 1) and used in laboratory experiments. Cores were made of PVC pipe 7 cm diameter and 25 cm in length. To collect samples, cores were placed at the sediment surface and pushed straight down into the sediment while a handsaw was used to simultaneously cut roots and other obstructions within the diameter of the core. After a minimum of 5 cm of sediment had been isolated, the core bottoms were fitted with rubber stoppers. Cores were collected carefully to minimize disturbance and returned to the laboratory on ice within 3 h. Salinity experiments were begun < 24 h following sediment collection. Salinities used in this experiment were modeled after salinity intrusions observed in the Hudson River Environmental Conditions Observing System (HRECOS) record for Piermont Marsh.

Six replicate cores were used for measurement of sediment biogeochemical response to each of three salinity treatments: reference (no increase in salinity, 0.1 ppt); moderate salinity intrusion (10 ppt) and high salinity intrusion (17 ppt) (Table 1). The chronic salinity treatment was similar to salinity levels in Piermont Marsh (the highest salinity field site) in late summer. High salinity treatments reflected maximum salinity levels observed in the Piermont HRECOS record. Cores were held in plastic tanks subjected to "tides" of treatment salinities using peristaltic pumps. Each pump was on a timer and set to flood a particular bucket with 3 gallons of a particular treatment every 12 h. Cores were inundated for 2 h each flood event, at which point the pumps turned back on and the buckets were drained. Initially, all replicates in each treatment received freshwater (0.1 ppt) collected at Norrie Point Marina (Staatsburg, NY, USA). After 3 d, the reference replicates remained under freshwater treatment, while the experimental replicates were treated with freshwater amended with Instant Ocean (Aquarium Systems, SKU: 927988) to 10 ppt. After another 3 d, the high salinity replicates began treatment with freshwater amended with Instant Ocean to 17 ppt. This treatment was continued for 5 d, during which moderate salinity intrusion replicates remained at 10 ppt and reference replicates remained at 0.1 ppt. Sediment oxygen and hydrogen sulfide profiles were measured prior to any salinity treatments and immediately (< 6 h) following each salinity treatment. After all treatments were administered, cores were sectioned for analysis of pore water nutrient concentrations using ion chromatography as above.

Mesocosm experiments

In summer 2012, multiple mesocosm experiments were conducted to measure microbial activity in estuarine sediment exposed to varying salinities. As for sediment core experiments,

mesocosm experiments used sediment and water obtained from Constitution Marsh (< 1 ppt; Figure 1), the lowest salinity field site. Specifically, top sediment (0 - 5cm) was collected from several randomly selected locations within the field site and homogenized with a 2.38 mm sieve. Bulk water was collected from the Hudson River directly adjacent to Constitution Marsh. Two buckets of sediment (5 gallons each) and 2 carboys of river water (5 gallons each) were transported from the field site directly to the laboratory, where they were refrigerated until the start of experiments. Sediment assays were conducted for measurement of nitrification and denitrification rates as well as ammonium and nitrate uptake rates in response to salinity.

Nitrification was measured using nitrapyrin as a nitrification inhibitor (Powell and Prosser, 1985). Glass beaker (250 ml) mesocosms were filled with 30 ml of bulk water and 10 cm^3 of homogenized sediment. A total of 5 salinity treatments were applied: 0, 8, 16, 24, and 30 parts per thousand (ppt) salinity by amending Hudson River bulk water with Instant Ocean (Aquarium Systems, SKU: 927988). Each treatment consisted of 12 randomly paired replicates, 6 of which received 50 µl of nitrapyrin (2-chloro-6-[trichloromethyl]-pyridine), an inhibitor of ammonium monooxygenase, dissolved in dimethyl sulfoxide (DMSO). The remaining 6 replicates of each treatment received 50 µl of DMSO. Samples were incubated for 3 d at room temperature, with manual stirring every day to ensure mesocosms remained oxic. After incubation, 5 ml of 1N potassium chloride (KCl) was added to each mesocosm to extract ammonium from sorption sites. After a 30 min KCl incubation, water samples were collected, filtered (Whatman GF/F, 0.7 µm pore size), and analyzed for ammonium via the phenol hypochlorite method on a Shimadzu dual-beam spectrophotometer (Aminot, et al., 1997; Solarzano 1969; Strauss and Lamberti 2000). Nitrification rates were calculated as the difference

in the NH_4^+-N concentrations between paired nitrapyrin and DMSO sample replicates and expressed per unit of dry mass sediment in each mesocosm.

Net nutrient uptake was measured as change in concentration per unit time and mass (Kemp and Dodds 2002; Bunch and Bernot 2012). Rates of nitrate and ammonium uptake by the sediment microbial community were measured under the same salinity treatments used in the nitrification assay. For each treatment (0, 8, 16, 24, and 30 ppt), 3 replicates were prepared. In 50 ml falcon tubes, 30 ml of river water were added to 10 cm^3 of homogenized sediment. Initial water samples were collected, filtered as above and frozen at the beginning of the experiment. After 3 d incubation at room temperature, final filtered water samples were collected. Nitrate concentrations were analyzed via ion chromatography (Dionex 3000; Eaton et al. 2005) and ammonium concentrations were measured by the phenol hypochlorite method using a Shimadzu dual-beam spectrophotometer (Aminot, et al., 1997; Solarzano 1969; Strauss and Lamberti 2000). Uptake rates for each analyte were calculated as the difference between initial and final concentration divided by incubation time and mass dry sediment.

Denitrification response to salinity was measured using the acetylene inhibition technique (Yoshinari and Knowles, 1976). Salinity treatments were prepared as for the uptake and nitrification assays (Hudson River water amended with Instant Ocean). Treatments consisted of a freshwater treatment (0 ppt), as well as low (7 ppt), medium (15 ppt), and high (30 ppt) salinity treatments. Four replicates of each treatment and 4 controls (no acetylene added) were prepared in 250 ml glass flasks with gas-tight caps equipped with rubber septa. Each flask was prepared with 50 cm^3 of homogenized sediment and then filled to the 150 ml mark with river water of the appropriate salinity. After purging each bottle with nitrogen (N_2) for 5 min, potassium nitrate

was added to achieve a concentration of 1.4 mg KNO_3/L and glucose was added to a concentration of 1 g $C_6H_{12}O_6$/L to ensure nutrient saturation. Acetylene was injected into each flask to obtain a partial pressure of 10 kPa (30 ml C_2H_2 per flask). Flasks were then shaken and allowed to equilibrate for 30 min before initial samples were collected. Extracted initial gas samples (3 ml) were transferred to gas-tight serum vials. Each bottle then received an injection of 3 ml of N_2 with 10% acetylene (C_2H_2) to adjust partial pressure. Samples were incubated at room temperature for 5 h before final samples (T_f) were collected. Samples and standards were analyzed via gas chromatography using a Shimadzu GC-14B gas chromatograph with a Tekmar Dohrmann headspace autosampler 7000.

Statistics

Differences in bulk and pore water nutrient concentrations among field sites were analyzed using Analysis of Variance (ANOVA) followed by Tukey's test for pairwise comparisons. Sediment biogeochemical dynamics were quantified as the mean, minimum, and maximum analyte concentration for each sediment profile and also compared using ANOVA. Changes in microbial activity in response to salinity were assessed using linear and non-linear regression models. All statistical analyses were conducted using Sigmaplot 12.0 graphing and analysis software.

Results

Bulk and pore water chemistry

Bulk water chloride concentrations ranged from 1.00 mg Cl/L at Constitution in spring to 4.47 mg Cl/L at Piermont in summer (Figure 2). Bulk water chloride concentrations did not vary among sites in spring (mean = 1.27 mg Cl/L) but did significantly increase down-river in summer with Constitution having the lowest concentrations (0.91 mg Cl/L) and Piermont having the highest concentrations ($p = 0.031$; Figure 2). Between spring and summer, bulk water chloride concentrations remained relatively consistent at Constitution Marsh (mean = 0.79 mg Cl/L) but at Iona and Piermont marshes, there was a ~4-fold increase in salinity between spring and summer (Figure 2). Pore water chloride concentrations mirrored bulk water patterns and were not significantly different among sites in spring. In summer, pore water chloride concentrations doubled from 0.91 mg Cl/L at Constitution to 6.25 mg Cl/L at Piermont (Figure 2).

Bulk water sulfate concentrations ranged from 0.06 mg SO_4^{2-}/L at Constitution in summer to 0.65 mg SO_4^{2-}/L at Piermont Marsh in summer. Similar to chloride concentrations, bulk and pore water sulfate concentrations did not vary among sites in spring (mean = 0.15 and 0.17 mg SO_4^{2-}/L, respectively; Figure 2). However, in summer, bulk and pore water sulfate concentrations were significantly higher at Piermont marsh. Specifically, Piermont bulk water sulfate concentrations (0.65 mg SO_4^{2-}/L) were ~10 x greater than Constitution Marsh in summer (0.06 mg SO_4^{2-}/L; Figure 2).

No significant differences in nitrate and phosphate concentrations were identified among sites or between seasons ($p > 0.05$; Table 2). Across sites and season, bulk water nitrate ranged from 0.007 – 0.021 mg NO_3/L and phosphate ranged from 0.036 – 0.102 mg PO_4/L. In pore water, nitrate ranged from 0.007 – 0.013 mg NO_3/L and phosphate ranged from 0.037 – 0.147 mg PO_4/L.

Sediment oxygen dynamics

In spring 2011, sediment oxygen concentrations did not vary among study sites ($p > 0.05$; Figure 4). Mean sediment oxygen concentration at Piermont was 0.8 mg O_2/L, while the other 4 sites ranged from 2.2 mg O_2/L (Manitou) to 2.4 mg O_2/L (Constitution; Figure 4). However, in spring 2012, sediments at Piermont Marsh had higher mean oxygen concentrations (3.2 mg O_2/L) than Constitution Marsh (1.5 mg O_2/L; $p < 0.001$; Figure 4). Maximum and minimum O_2 concentrations also followed this trend during spring 2012 sampling. At Piermont, mean maximum concentrations (4.8 mg O_2/L) were nearly 2x higher than at Constitution Marsh (2.9 mg O_2/L; $p = 0.037$; Figure 4). Similarly, minimum values at Piermont Marsh (mean = 3.0 mg O_2/L) were 2 fold higher than the minimum of 1.4 mg O_2/L measured at Constitution ($p < 0.001$; Figure 4).

In both years, summer sampling documented spatial variability in sediment oxygen. In 2011, mean sediment oxygen concentration was higher at Constitution Marsh (4.3 mg O_2/L; $p < 0.001$; Figure 4) relative to the other sites. Specifically, mean sediment oxygen at Constitution was 2x higher than Iona Marsh (1.8 mg O_2/L) and over 3x higher than Con Hook (1.4 mg O_2/L) and Piermont (1.3 mg O_2/L; Figure 4). There was no significant variation in maximum sediment

oxygen concentrations among in summer 2011, with values ranging from 8.2 mg O_2/L (Con Hook) to 10.3 mg O_2/L (Constitution; $p > 0.05$; Figure 4). In contrast to 2011 summer sampling, in summer 2012 Iona Marsh had lower mean oxygen concentrations (0.9 mg O_2/L) compared to other sites (1.6 mg O_2/L; $p < 0.001$). As with mean concentrations, maximum O_2 concentrations only deviated statistically at Iona Marsh ($p < 0.001$). Concentrations at Iona reached a maximum of 10.5 mg O_2/L, but were lower at the remaining 4 sites, which ranged from 2.2 mg O_2/L (Manitou) to 2.5 mg O_2/L (Con Hook; Figure 8). In 2011, sediment oxygen varied temporally only in Piermont Marsh and decreased from spring (1.8 mg O_2/L) to summer (1.3 mg O_2/L; $p < 0.001$; Figure 4).

Sediment hydrogen sulfide dynamics

In spring 2011, a wide range of sulfide concentrations were recorded across study sites. With the exception of Con Hook Marsh (mean = 8.1 mg H_2S/L), sediment H_2S concentrations were lowest in the upstream sites, ranging from 0.64 mg H_2S/L at Iona Marsh to 1.53 mg H_2S/L at Constitution (Figure 6). These gave way to elevated concentrations at the brackish end of the salinity gradient (Piermont Marsh; mean = 5.5 mg H_2S/L; $p < 0.05$; Figure 6). By contrast, mean sediment H_2S concentrations were below the limit of detection at all study sites during spring 2012 sampling (Figure 6). Despite mean concentrations falling below the detectable limit, H_2S was detected in isolated sites at both Constitution and Piermont marshes during spring 2012. Maximum concentrations reached 0.57 mg H_2S/L and 0.19 mg H_2S/L at Constitution and Piermont, respectively, though statistically there was no difference between these values ($p > 0.05$; Figure 6). 2012 spring data are not available for Con Hook, Manitou, or Iona marshes.

Sediment H_2S concentrations measured during summer 2011 did not vary across sites ($p > 0.05$), nor did they vary temporally from spring 2011 values ($p > 0.05$; Figure 6). Sediment H_2S was highest at Iona Marsh (mean = 7.2 mg H_2S/L), while the remaining 3 sites exhibited mean concentrations ranging from 3.7 mg H_2S/L (Constitution) to 6.7 mg H_2S/L at (Con Hook; Figure 6). Summer 2011 data are not available for Manitou Marsh. Similarly to Spring 2012 observations, Summer 2012 sediment H_2S concentrations were below detection limit at all study sites (Figure 6). Unlike Spring 2012, however, there were no detectable spikes in H_2S concentrations in any of the replicate profiles for any of the sites visited during Summer 2012.

In vitro core experiments

Mean sediment O_2 concentrations did not respond to variations in the salinity of overlying water ($p > 0.05$; Figure 8). During all three phases of the experiment, mean O_2 concentrations were not influenced by seawater manipulation. The lowest mean concentration was measured in the freshwater replicates (0.1 ppt) during days 4 – 6 (phase II) of the experiment (mean = 1.48 mg O_2/L) and concentrations peaked in cores flooded with a salinity of 10 ppt during days 7 – 11 (phase III; mean = 2.32 mg O_2/L; Figure 8). In addition to limited variation within each phase of the experiment, the individual treatment groups also did not differ across phases of the experiment. Mean O_2 concentrations in freshwater replicates ranged from 1.48 mg O_2/L (phase two; days 4 - 6) to 1.9 mg O_2/L (phase one; days 1 – 3; Figure 8). In moderate salinity treatments (10 ppt), mean core oxygen ranged from 2.2 mg O_2/L (phase two; days 4 - 6) to 2.32 mg O_2/L (phase three; days 7 – 11; Figure 8). Lastly, the range of mean O_2 concentrations in high salinity replicates was 1.66 mg O_2/L (phase one; days 1 - 3) to 2.17 mg O_2/L (phase two; days 4 -6; Figure 8).

Unlike sediment O_2, sediment H_2S concentrations in experimental cores responded consistently to salinity treatments. During all three phases, H_2S concentrations in the freshwater replicates were below the detection limit of the equipment (~0.01 mg H_2S/L; Figure 8). Replicates exposed to a moderate salinity treatment did not vary from phase I to phase II, ranging from below detection limit during phase II to 0.1 mg H_2S/L in phase I. However, during phase III, H_2S concentrations increased 5 fold in moderated salinity cores to 0.6 mg H_2S/L ($p < 0.01$; Figure 8). The high salinity treatment group responded similarly. Specifically, concentrations of sediment H_2S were similar during phase I (mean = 0.61 mg H_2S/L) and phase II (mean = 0.41 mg H_2S/L), but concentrations measured during phase III were 2x higher than those in either of the initial two phases (mean = 1.2 mg H_2S/L; $p < 0.01$; Figure 8).

Mesocosm experiments

Nitrification rates in freshwater sediments were higher than rates observed in sediments flooded with saline water (mean = 0.4 µg NH_4^+-N gdm^{-1} d^{-1}; $p < 0.001$; Figure 9). The three middle salinity treatments (8, 16, and 24 ppt) did not differ from one another ($p > 0.05$). Calculated rates were below zero in each of these sediments, indicating the absence of nitrification ($R^2 = 0.753$; $p < 0.001$; Figure 9).

Similar to nitrification, denitrification in mesocosm sediments were also affected by salinity treatments ($p < 0.001$; $R^2 = 0.91$; Figure 9). The highest denitrification rates were observed in freshwater sediments (mean = 6.12 µg N_2O-N gdm^{-1} d^{-1}; Figure 9). Rates then decreased as the overlying water became more saline. Sediments in the low salinity treatment (7 ppt) denitrified at a rate of 3.84 µg H_2S/L, while those subjected to the moderate treatment of 15

ppt had mean denitrification of 2.84 µg H_2S/L (Figure 9). Finally, denitrification rates reached minimum levels when sediments were subjected to the high salinity treatment of 30 ppt (mean = 1.57 µg H_2S/L; Figure 9).

Unlike nitrification and denitrification, net assimilation of both NO_3^- and NH_4^+ were not influenced by changes in the salinity of overlying water ($p > 0.05$). Rates of net NO_3^- uptake ranged from negative values (net remineralization; -0.001 µg NO_3^--N gdm^{-1} d^{-1}; 24 ppt) to 0.07 NO_3^--N gdm^{-1} d^{-1} (8 ppt; Figure 9). With respect to net NH_4^+ uptake, the highest rates were measured in the 24 ppt treatment (mean = 6.26 NH_4^+-N gdm^{-1} d^{-1}), while mesocoms exposed to a salinity of 30 ppt had net negative uptake of NH_4^+ (mean = -32.93 $NH4^+$-N gdm^{-1} d^{-1}), indicating a net remineralization of NH_4^+ in these sediments (Figure 9).

Discussion

Pore-water analysis

Analysis of pore-water chemistry illustrated the contrast in chemical concentrations between the northern end of the salinity gradient and the southern end. In many cases, such as with chloride, sulfate, and nitrate, the three northernmost sites (Iona, Con Hook, and Constitution) had similar pore-water concentrations, whereas Piermont Marsh had significantly different concentrations. The higher chloride and sulfate concentrations in Piermont were expected, as these are the two major ions in salt water and Piermont Marsh contains the highest salinity waters across the study sites. However, Piermont sediments also had higher nitrate concentrations, which would not be directly influenced by saltwater but may be the result of changes in microbial activity (Magalhães et al. 1980). Similarly, pulsed salinity sediment cores

exhibited concentrations of chloride, sulfate and nitrate that were higher than the three northernmost sites and comparable to Piermont marsh. Chloride concentrations were higher in Piermont, but sulfate was higher in pulsed cores. Some variation in chemical composition would be expected between artificial seawater and seawater from a natural system. Higher nitrate levels in the higher salinity pulsed core sediments further suggest a relationship between salinity and nitrate concentrations.

The lack of variation in pore-water chemistry among the three northernmost sites (Constitution, Iona, and Con Hook) may be explained by the proximity of these sites to one another (Figure 1). At a distance of nearly 10 miles downstream, Piermont Marsh is by far the southernmost site of the four, whereas Constitution, Con Hook, and Iona Marshes all exist within ~3 miles of one another at the extreme north end of the sampling region. This likely explains the lack of statistical differences between these sites in terms of chloride, sulfate, and nitrate concentrations.

Sediment sulfide concentrations did not follow the trend of higher concentrations at Constitution. Rather, significantly higher sediment sulfide concentrations were measured at Iona Marsh relative to other sites, which was not expected. One possible explanation is that Iona Marsh may retain more water than other sites. As a result, it may be that less sulfide is lost from these sediments, allowing for an accumulation over time and accounting for these higher concentrations.

In situ descriptive sampling: Sediment oxygen dynamics

The oxygen dynamics reported in the field data are what would be expected, both in terms of maximum and mean O_2 concentrations. Maximum oxygen concentrations were lower at all sites in the August sampling relative to the June sampling. These data suggest that as the summer progressed, either increased temperatures and/or sediment microbial respiration depleted available oxygen yielding lower oxygen concentrations.

In situ descriptive sampling: Sediment sulfide dynamics

Neither mean nor maximum sediment H_2S concentrations varied along the anticipated salinity gradient. This lack of variation may be due to all sites having similar sediment microbial communities and potential for reducing sulfate to hydrogen sulfide. However, because Piermont Marsh was the only site in which sulfide was always present (i.e. never below detection level), regular exposure to higher salinity waters may result in greater retention of sulfide by wetland sediments.

In vitro sediment core experiments

Cores undergoing pulsed salinity treatments exhibited similar biogeochemical activity to Piermont Marsh (highest salinity) sediments. Specifically, maximum and mean oxygen concentrations were similar; however, chronic salinity cores became anoxic at greater sediment depths relative to Piermont Marsh sediment (Figure 8). This may have been an experimental

artifact, as oxygen may not have diffused as well through experimental sediments contained in the PVC cores during the experiments. Alternatively, the decrease in oxygen diffusion may be the result of the high salinity water flooding the cores, as increased salinity has been shown to decrease oxygen solubility in water (Carpenter 1966).

Sediment sulfide concentrations were also similar between Piermont Marsh and pulsed salinity cores. In addition to comparable mean and maximum sediment sulfide concentrations, these two sediments were the only instances in which sulfide was never completely depleted (Figure 8). Further, sulfide levels in these sediments mimic those reported by previous research. DeLaune et al. (1982) reported sulfide concentrations of 6 mg H_2S/L in brackish water sediments (0.5-18 ppt) and 20 mgH_2S/L in sediments regularly exposed to seawater (18-30 ppt). Additionally, Baldwin and Mendelssohn (1998) have shown average hydrogen sulfide concentrations of 6.7 mg H_2S/L corresponding to a salinity of 6 ppt. Salinities at Piermont Marsh rarely exceeded these levels, as this was an unusually wet year in regard to rainfall.

Mesocosm experiments

Treatment of wetland sediments with saline water altered sediment nitrogen cycling. Decreases in denitrification appear to be more pronounced as salinity increases. However, the effect of salinity on nitrification seems only to depend on the presence or absence of saline water, with no real difference in the effect amongst treatments of various salinities (Figure 9). Interestingly, these two critical alterations to the nitrogen cycle occur despite no change in the net uptake of either ammonium or nitrate. The fact that NH_4^+ concentrations remain relatively

constant during treatment with saline water, despite the fact that denitrification slows, is a strong indication that DNRA has become a dominant pathway (relative to denitrification) during salinity intrusion.

Conclusions

These data present potential implications associated with higher salinity waters in tidal freshwater wetland sediments as a result of increases in both nitrate and sulfide concentrations. Exposure to occasional salinity increases and the resultant sulfate reduction is not uncommon throughout the brackish region of the Hudson River estuary; however, consistent exposure to high salinities, as seen in Piermont Marsh, may lead to a greater retention of sulfide, most likely as a result of more constant sulfate reduction. Further, resulting higher concentrations of sulfide will put these wetlands at risk for increased nitrogen retention through a favoring of dissimilatory nitrate reduction to ammonia over denitrification. Also, if the increased sulfate reduction that typically results in high sulfide concentrations is an indication of greater mineralization of organic matter, steady rates of accretion may not be maintained in these wetlands. Furthermore, the continued outpacing of accretion by mineralization may result in the loss of tidally influenced freshwater wetlands of the Hudson River to rising sea levels.

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Table 1. Salinity treatments applied during *in vitro* sediment core experiments. Treatments were administered every 12 h for 11 days.

Day	Freshwater Salinity (ppt)	Chronic Salinity (ppt)	Pulsed Salinity (ppt)
1-3	0.1	0.1	0.1
4	0.1	10.2	10.0
5	0.1	10.0	10.0
6	0.1	10.5	10.5
7	0.1	10.5	17.3
8	0.1	10.3	17.3
9	0.1	9.9	17.5
10	0.1	10.2	17.2
11	0.1	10.3	17.2

Table 2. Mean bulk and pore water nitrate (NO_3) and phosphate (PO_4) concentrations in spring and summer along a salinity gradient. Standard deviation in parentheses. There were no significant differences in nitrate and phosphate concentrations between water type, seasons, or sites (ANOVA; $p>0.05$).

Site	NO_3 (mg/L)		PO_4 (mg/L)	
	Bulk	***Pore***	***Bulk***	***Pore***
Spring				
Constitution	0.010	0.012	0.056	0.089
Piermont	0.013	0.013	0.102	0.037
Summer				
Constitution	0.007	0.007	0.037	0.147
Con Hook	0.021	0.012	0.051	0.063
Manitou	0.010	0.013	0.036	0.064
Iona	0.009	0.011	0.046	0.065
Piermont	0.012	0.011	0.035	0.070

Figure Legends

Figure 1. Location of study sites throughout the brackish region of the lower Hudson River estuary, New York, USA.

Figure 2. Mean bulk and pore water chloride and sulfate concentrations across seasons and sites measured in 2011 and 2012. N = 6 ± SE except in spring at Con Hook, Manitou, and Iona where N = 3 ± SE. Pairwise letters denote significant site differences within a season. Significant differences in chloride and sulfate concentrations across sites were identified in summer ($p < 0.001$) but not in spring ($p > 0.05$).

Figure 3. Example sediment oxygen profiles in summer from the lowest salinity site (Constitution) and the highest salinity site (Piermont) measured with microelectrodes.

Figure 4. Maximum, mean, and minimum sediment oxygen concentrations across seasons and sites in 2011 and 2012. N = 6 sediment profiles at each site except in spring at Con Hook, Manitou, and Iona where N = 3 sediment profiles. Values are across profiles ± SE. Pairwise letters denote significant site differences within a season ($p < 0.05$). No significant differences were identified in maximum and mean oxygen concentrations in summer or minimum oxygen concentrations in spring or summer ($p > 0.05$).

Figure 5. Example sediment sulfide profiles in summer from the lowest salinity site (Constitution) and the highest salinity site (Piermont) measured with microelectrodes.

Figure 6. Maximum and mean sediment sulfide concentrations across seasons and sites in 2011 and 2012. N = 6 sediment profiles at each site except in spring at Con Hook, Manitou, and Iona where N = 3 sediment profiles. Values are across profiles ± SE. Significant differences within a season denoted by * ($p < 0.05$). No significant differences were identified in maximum sulfide concentrations in spring or summer ($p > 0.05$).

Figure 7. *In situ* pore water sulfide concentrations in top sediment (0-5 cm) and bottom sediment (5-10 cm) in August 2012. N = 3.

Figure 8. *In vitro* sediment core experiment oxygen and sulfide dynamics in response to salinity treatments (Table 1). Significant differences within a measurement phase denoted by * ($p < 0.05$).

Figure 9. *In situ* sediment microbial activity in response to salinity treatments.

Figures

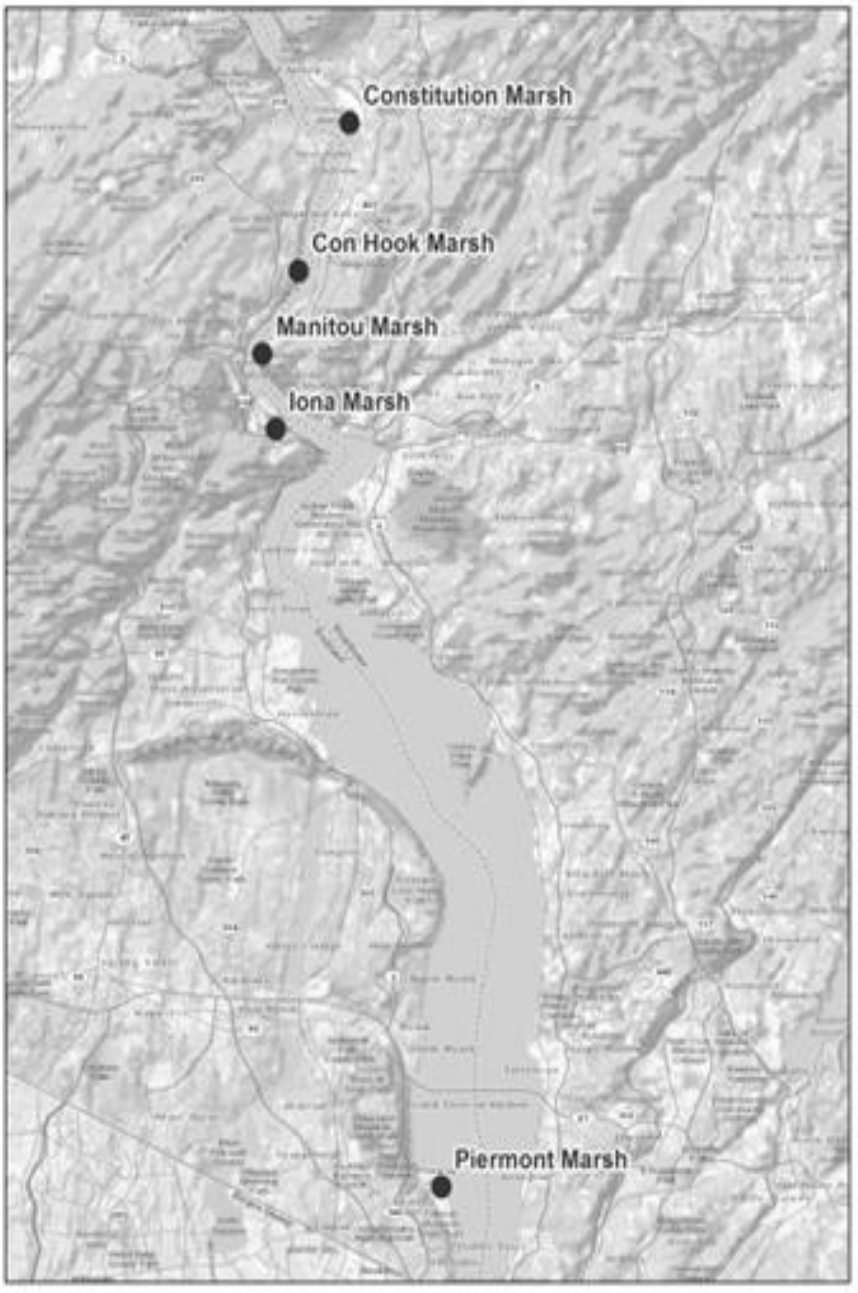


Figure 1

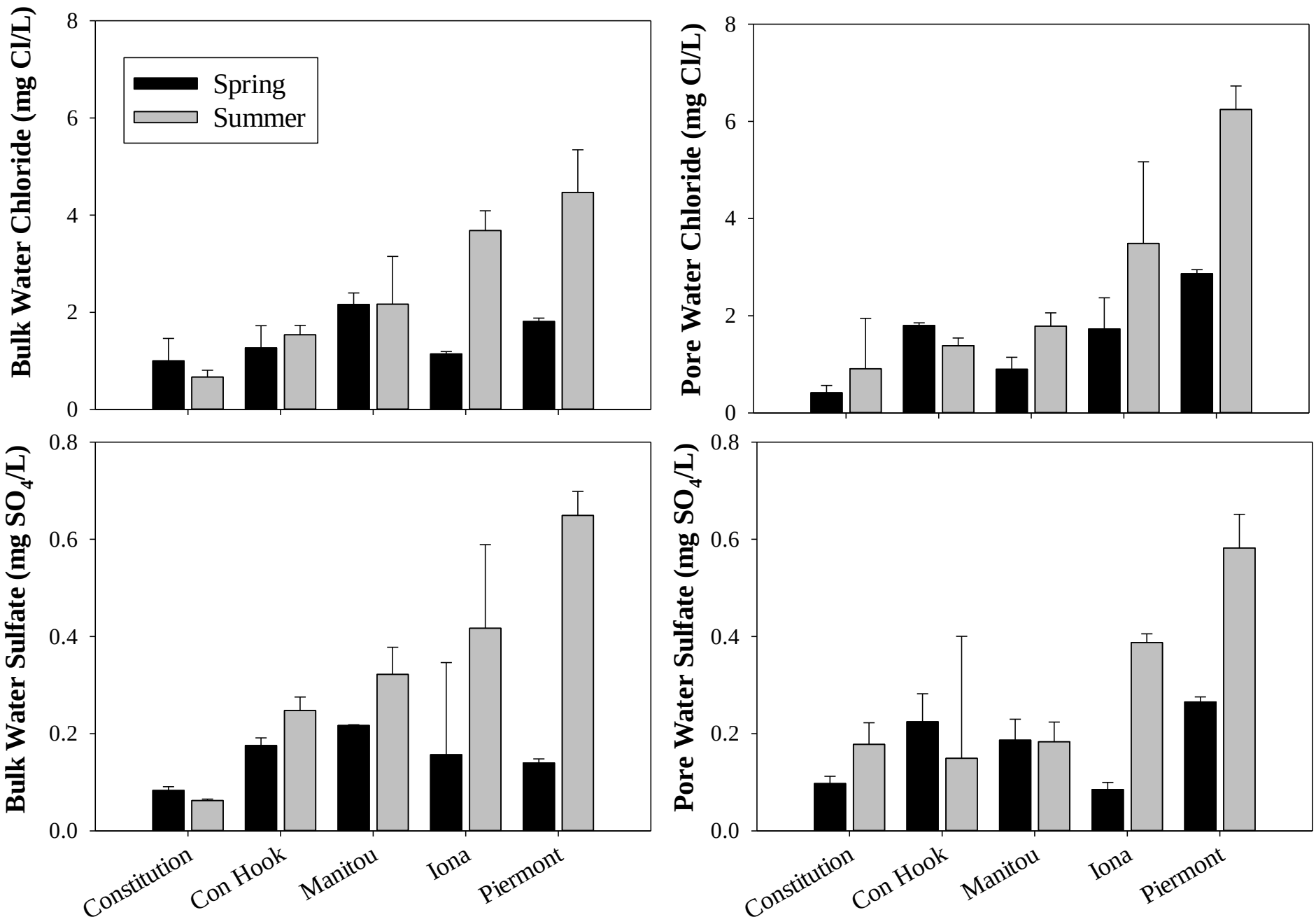

Bulk Water Chloride (mg Cl/L)
Pore Water Chloride (mg Cl/L)
Bulk Water Sulfate (mg SO4/L)
Pore Water Sulfate (mg SO4/L)
Spring
Summer
0
2
4
6
8
0.0
0.2
0.4
0.6
0.8
Constitution
Con Hook
Manitou
Iona
Piermont

Figure 2

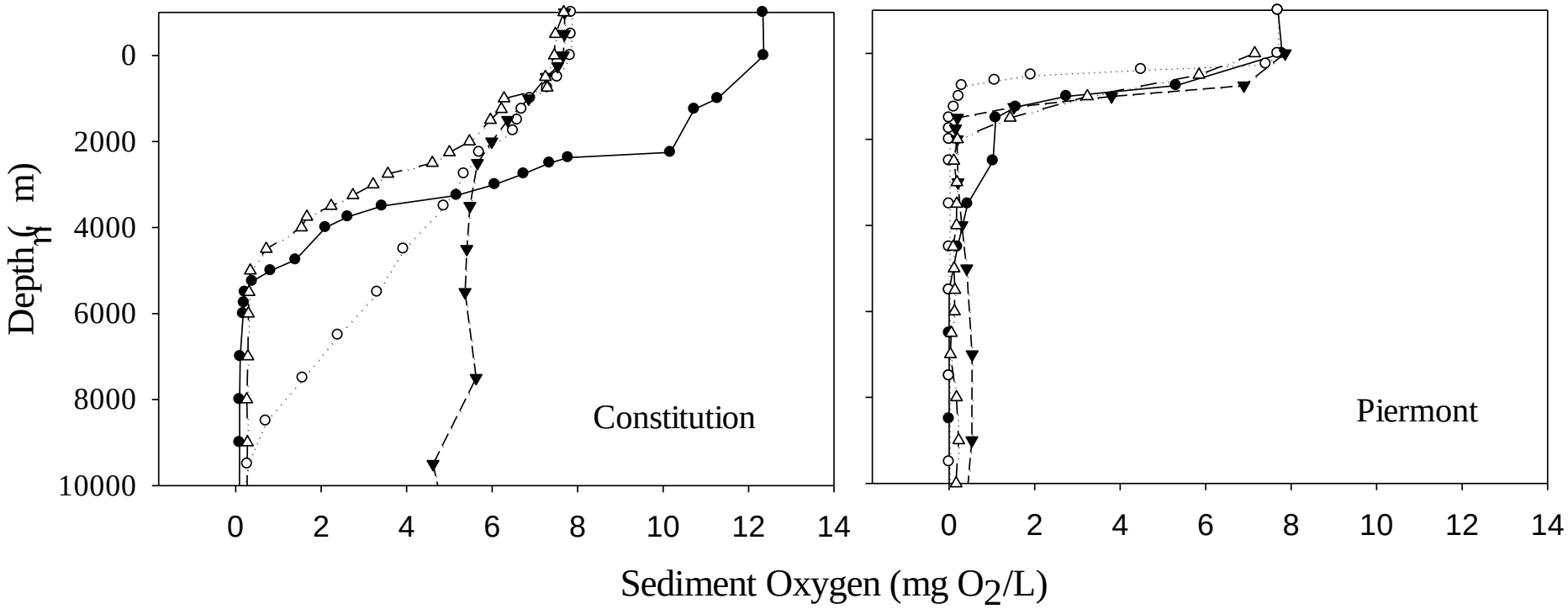

Depth (m)
0
2000
4000
6000
8000
10000
Constitution
Piermont
0
2
4
6
8
10
12
14
Sediment Oxygen (mg O2/L)

Figure 3

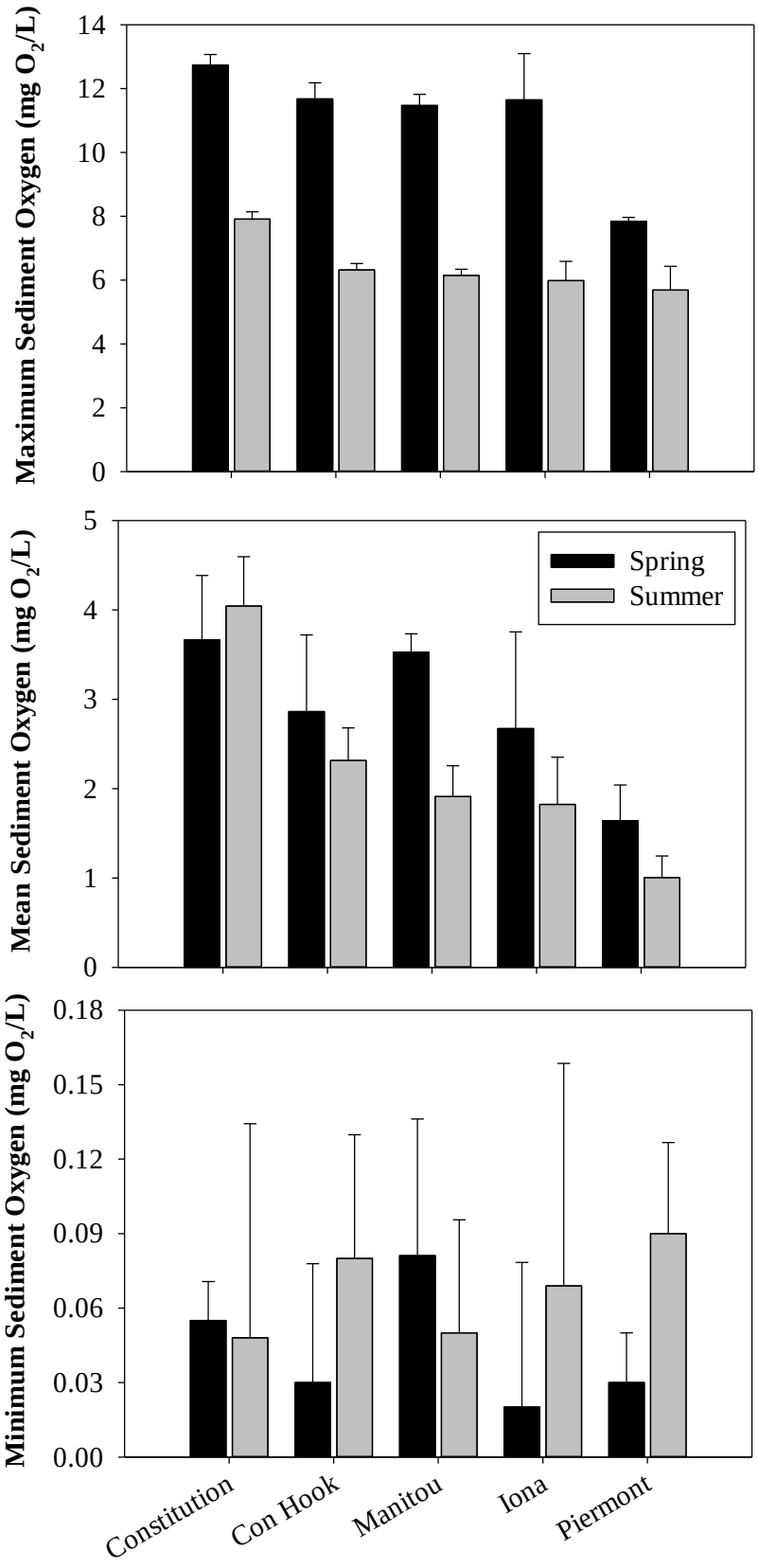

Maximum Sediment Oxygen (mg O2/L)
14
12
10
8
6
4
2
0
Mean Sediment Oxygen (mg O2/L)
5
4
3
2
1
0
Spring
Summer
Minimum Sediment Oxygen (mg O2/L)
0.18
0.15
0.12
0.09
0.06
0.03
0.00
Constitution
Con Hook
Manitou
Iona
Piermont

Figure 4

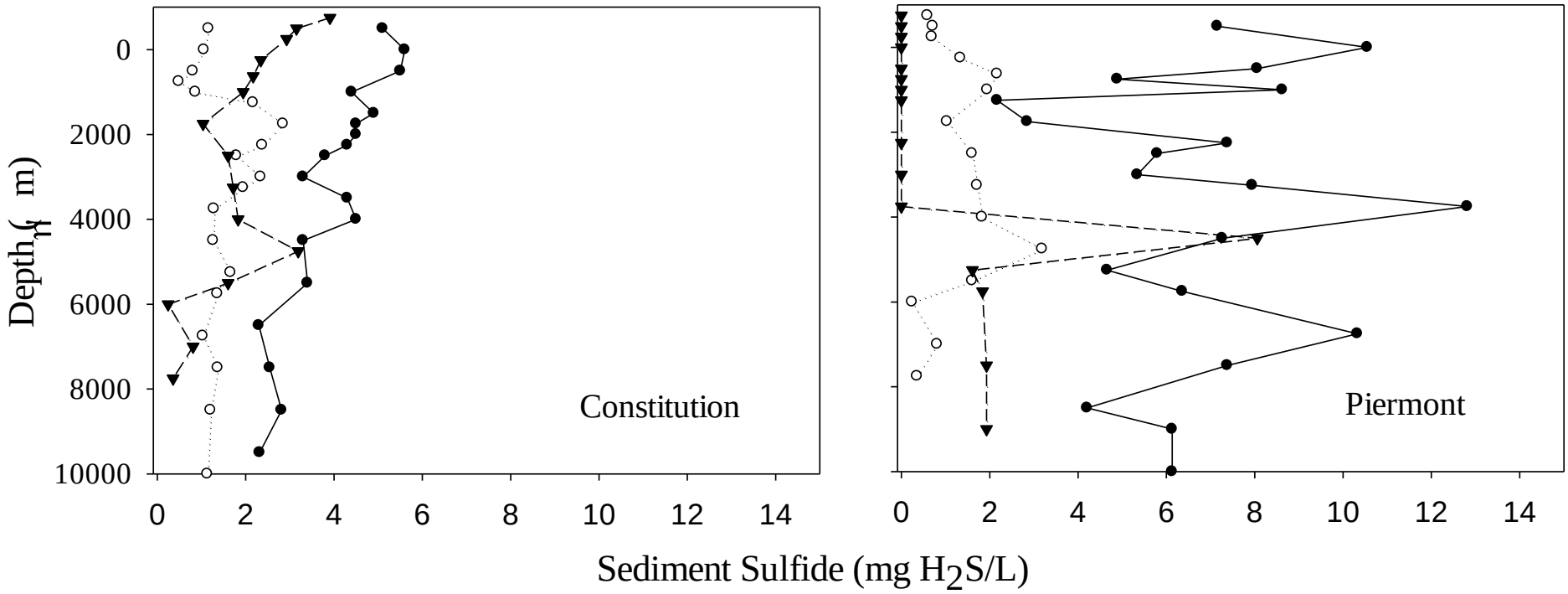

Depth (m)
0
2000
4000
6000
8000
10000
0
2
4
6
8
10
12
14
Constitution
Piermont
Sediment Sulfide (mg H2S/L)

Figure 5

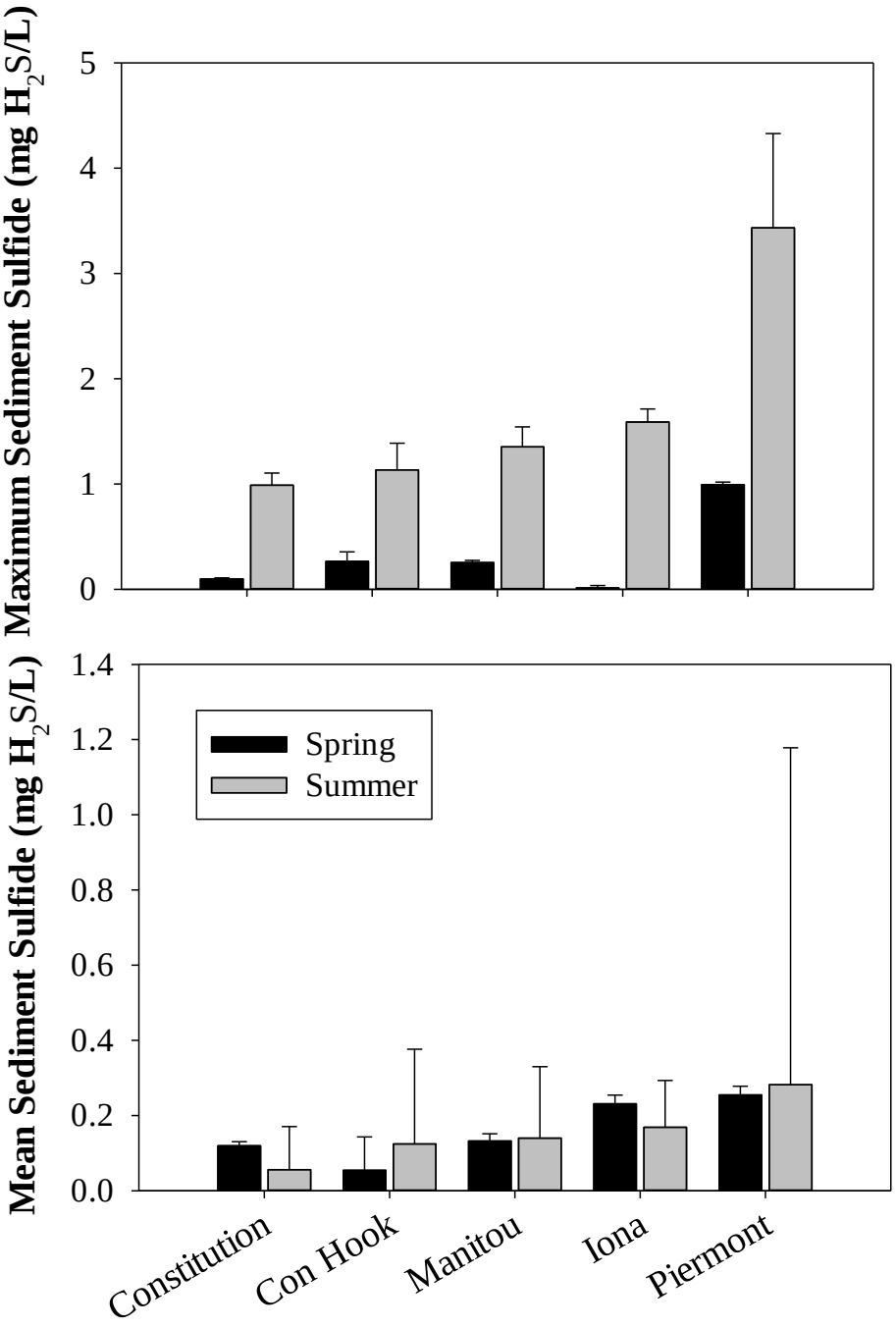

Maximum Sediment Sulfide (mg H_2S/L)
5
4
3
2
1
0
Mean Sediment Sulfide (mg H_2S/L)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Spring
Summer
Constitution
Con Hook
Manitou
Iona
Piermont

Figure 6

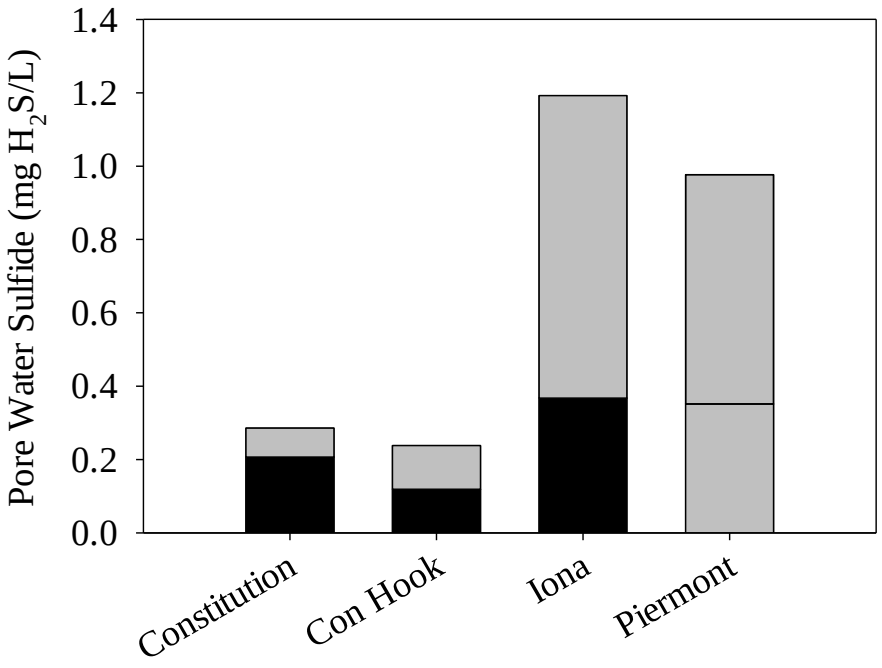
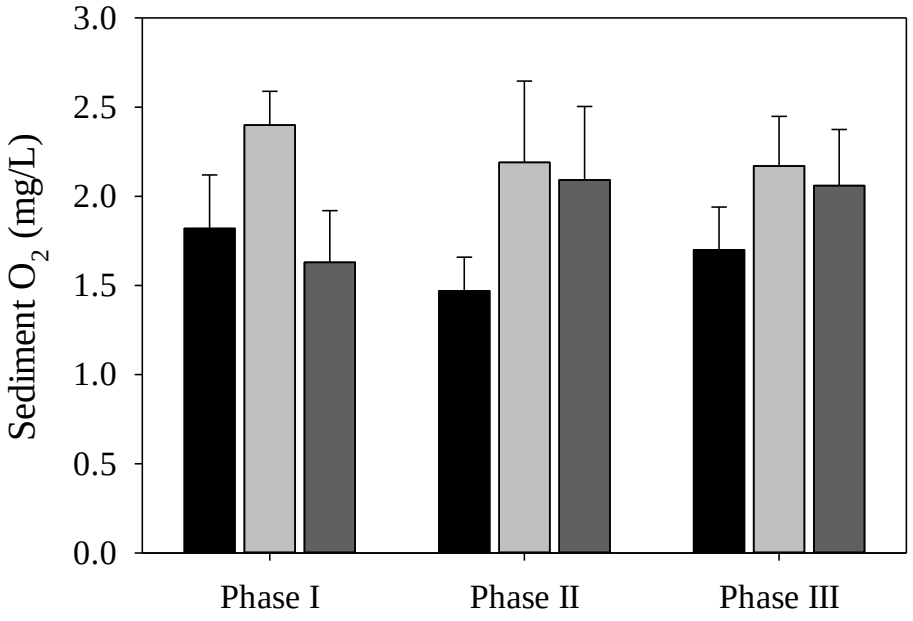

Pore Water Sulfide (mg H_2S/L)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Constitution
Con Hook
Iona
Piermont

Figure 7


3.0
2.5
2.0
1.5
1.0
0.5
0.0
Sediment O_2 (mg/L)
Phase I
Phase II
Phase III

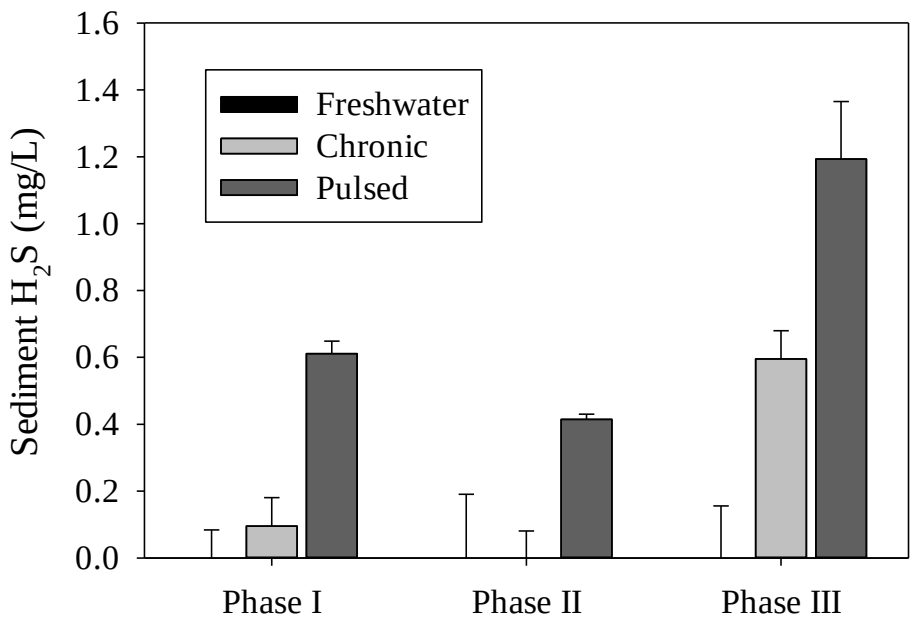

1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Sediment H_2S (mg/L)
Freshwater
Chronic
Pulsed
Phase I
Phase II
Phase III

Figure 8

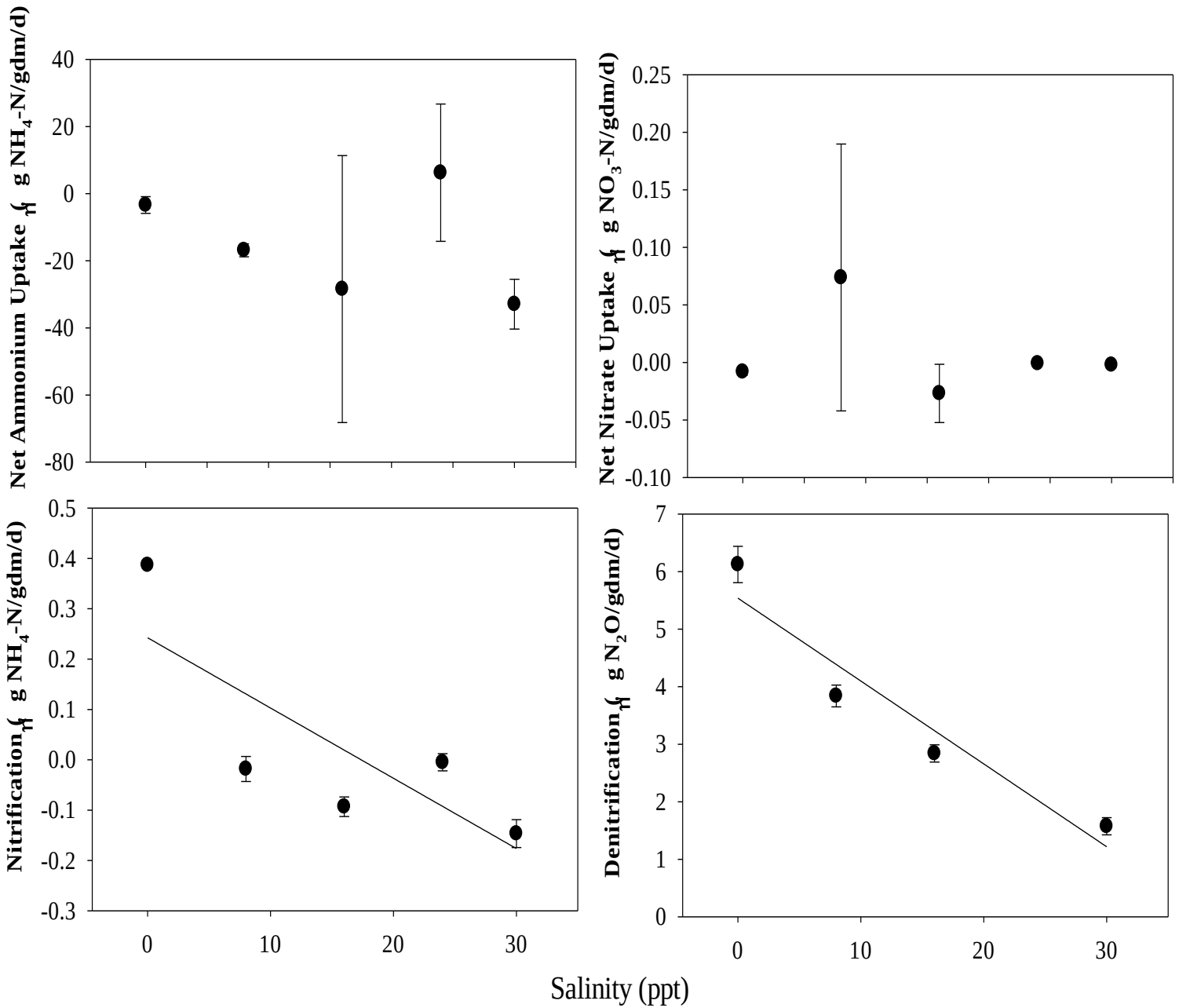

Net Ammonium Uptake (µg NH4-N/gdm/d)
40
20
0
-20
-40
-60
-80
Net Nitrate Uptake (µg NO3-N/gdm/d)
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
Nitrification (µg NH4-N/gdm/d)
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
Denitrification (µg N2O/gdm/d)
7
6
5
4
3
2
1
0
0
10
20
30
Salinity (ppt)

Figure 9