

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

A Final Report of the Tibor T. Polgar Fellowship Program

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ABSTRACT

Rising sea levels and stronger storm surges may cause a northward migration of the saltwater front in the lower Hudson River estuary, exposing tidally influenced freshwater wetlands to saline waters. Previous research has documented changes in tidal wetland biogeochemistry in response to salinity intrusion due to increased sulfate reduction and resulting sulfide concentrations. Sulfide not only favors a shift from denitrification to the dissimilatory reduction of nitrate to ammonia (DNRA), but can also increase organic matter mineralization, resulting in a net loss of organic material and subsequent decreases in elevation. Without continued accretion of organic matter, the tidal freshwater wetlands of the Hudson River will not keep pace with rising sea levels. To better understand the effects of salinity intrusion on biogeochemical cycling, descriptive measurements of sediment biogeochemistry along the Hudson River salinity gradient were conducted using microelectrodes during two field sampling events (June and August 2011). Additionally, a series of laboratory experiments were conducted exposing freshwater sediments to varying salinities with subsequent measurement of sediment oxygen and hydrogen sulfide profiles. Mean maximum oxygen concentrations varied from 12 mg O₂/L in June to <8 mg O₂/L in August. Sulfide was present in all field site sediments with significantly higher retention in more saline sites (p<0.01). Higher sulfide concentrations were also measured in sediment cores experimentally subjected to salinity intrusion (17 psu). These data suggest 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.

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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 also provide a natural means of filtration for freshwater and can help reduce the effects of floodwaters and storm surges by absorbing water velocity (Barbier et al. 2008; Gribsholt et al. 2005; Mitsch and Gosselink 1993; Neubauer et al. 2005). 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 ecosystems. Thus, wetlands are an ideal location for the exchange of water, solutes, solids, and gases with the atmosphere, groundwater, and surrounding aquatic and terrestrial ecosystems (Megonigal and Neubaum 2009).

Tidal freshwater wetlands (TFWs) are key locations of nitrate removal and organic matter decay (Arrigoni et al. 2008). With high surface areas, anaerobic zones near the sediment surface and an abundance of available organic matter, TFWs present an ideal environment for the removal of nitrate via denitrification (Megonigal and Neubaum 2009). Median rates for denitrification in tidal freshwater wetlands are ~60% higher than rates recorded for other intertidal and aquatic ecosystems (Greene 2005). Denitrification is likely coupled to an influx of nitrate into TFWs (Megonigal and Neubaum 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).

Tidal freshwater wetlands are also important sites for organic carbon mineralization. Mineralization of organic matter occurs predominantly through the process of methanogenesis (both acetoclastic and hydrogenotrophic). This trend is directly related to the lack of sulfate (and ensuing sulfate reduction) that is characteristic of low salinity freshwaters (Capone and Kiene 1988; Kelley et al. 1990). Methanogenesis is a less efficient means of mineralizing organic matter than other pathways such as sulfate reduction, which is more common in saline sediments. Equally as important as the overall rate of organic carbon mineralization in TFWs is the accumulation of organic matter. Further, maintaining a balance between these two processes is paramount. 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 form and grow (Morris 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 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 inland migration of the freshwater-saltwater front yielding inundation of freshwater soils with saline water during flooding tides. Differences in seawater salinity and solute concentrations such as sulfate (SO_4^{2-}) and hydrogen sulfide

(H₂S) result in marked differences in biogeochemical cycles between salt and freshwater marshes (Weston et al. 2010). Alterations to key biogeochemical cycles such as denitrification and organic matter mineralization could threaten the quality and sustainability of TFWs as eutrophication and reduced accretion could 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, organic matter derived ammonium that is released from sediments and nitrified is reduced, ultimately resulting in a decreased rate of nitrate removal via denitrification. Seitzinger and Sanders (2002) suggested that higher observed 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 higher 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). With denitrification, the product is elemental nitrogen, 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 TFW's (Weston et al. 2010). 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. 2010). Further, in saline water, sulfate reducers and methanogens are both stimulated, rather than competing for the same substrates, resulting in a greater loss of organic matter than would otherwise be expected. In fact, the loss of organic matter can be greater than the rate of accumulation (Weston et al. 2010). This potential increased 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.

Of the 2,900 hectares of tidally influenced wetlands in the Hudson River estuary, downstream areas have the most elevated risk of salinity intrusion. This region, where the water is a mixture of freshwater and seawater (salinities ranging from 0.1 to 30 psu), constitutes the brackish portion of the estuary. The total acreage of Hudson River tidal wetlands has increased in the last 500 years, correlating with accumulation of organic matter (Kiviat et al. 2006). The Hudson River ecosystem is influenced by both tidal movements and external factors due to direct connection with the surrounding terrestrial ecosystems. Sedimentation processes in Hudson River tidal wetlands are driven by tidal exchanges between the wetlands and the main channel of the river (Kiviat et al. 2006). In this way, the nature of the Hudson River tidal wetlands and the processes that govern them may make them susceptible to the effects of salinity intrusion fostered by rising sea levels.

This objective of this research was to quantify biogeochemical dynamics in the tidal freshwater wetland sediments of the Hudson River by addressing one broad question using a combination of both *in situ* and *in vitro* techniques. Specifically, this research addresses how salinity intrusion influences sediment nitrogen, oxygen, and sulfide dynamics in tidal sediment. It was hypothesized that the intrusion of saline water would result in increases in sulfide concentrations and nitrogen retention within the wetlands due to a direct effect on sediment microbial activity. Increased sulfide concentrations indicative of sulfate reduction would suggest the possibility of wetland loss while greater nitrogen retention would exacerbate the effects of anthropogenic nitrogen enrichment in the estuary.

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). Vegetation communities were standardized to the maximum extent possible, choosing either stands of cattail (*Typha* spp.) or invasive common reed (*Phragmites australis*).

All field sampling took place on two separate sampling events, one occurring in late June/early July (6/27/2011 to 7/6/2011) and another occurring in early August (8/3/2011 to 8/5/2011). The timing of these sampling events allowed for the evaluation of sediment under two distinctly different conditions. In early summer, vegetation communities are just developing and salinities are low (<7 psu). In late summer,

vegetation communities are mature and salinities are typically at maximum levels (10-15 psu).

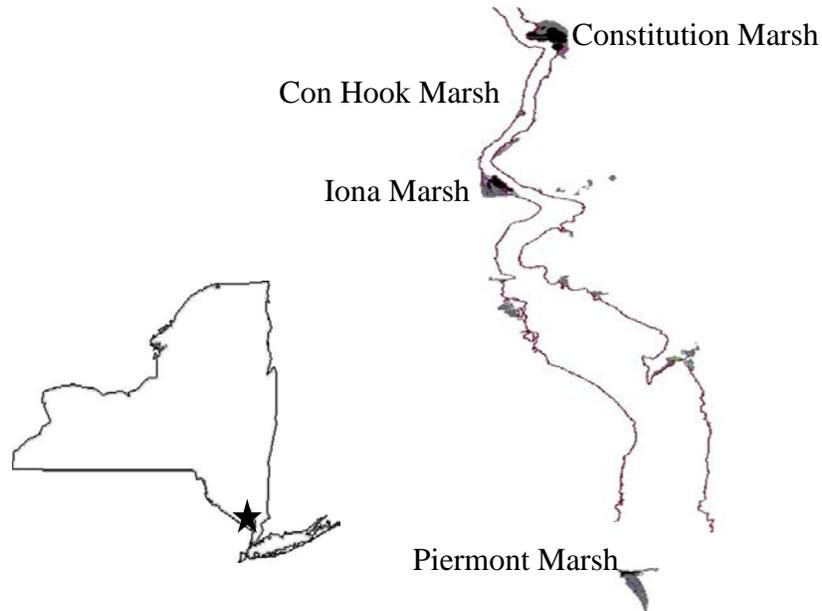


Figure 1. Location of study sites throughout the brackish region of the lower Hudson River estuary in New York, USA.

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 dissolved oxygen (O₂) and hydrogen sulfide (H₂S) concentrations in sediments *in situ*. 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, disruption of sediment is negligible during manipulation and measurement. The microelectrodes are not sensitive to water velocity and can be used without stirring. Oxygen microelectrodes were calibrated using tap water saturated with oxygen (100% O₂ saturation) and then saturated with nitrogen (0% O₂ saturation). Simultaneous measurements of dissolved oxygen were taken with a conventional O₂ handheld meter (Oakton; DO6; Acorn Series Dissolved Oxygen/°C Meter) (mg O₂/L) for field reference points. Hydrogen sulfide microelectrodes were calibrated using sulfur nanohydrate under anaerobic conditions at targeted concentrations (0 to 12.5 mg H₂S/L). Calibration of all microelectrodes occurred prior to and immediately following each field sampling event. Due to instrument malfunction, sulfide concentrations measured during the June sampling event are not valid.

At field sites (N=5), oxygen and sulfide concentrations were measured by positioning microelectrodes at the sediment surface. Concentrations were then recorded at the surface followed by a sequence of measurements at 250 to 5000 μm vertical increments (based on changes in oxygen and hydrogen sulfide concentrations) to a final depth of 5 cm into the sediment. Biogeochemical activity was then assessed by calculating the change in analyte concentration with respect to sediment depth as well as the maximum and minimum values measured. During the first sampling event, pore-water (0-5 cm sediment) was collected using a syringe and hypodermic needle (~5 ml collected from top 5-10 cm sediment). Due to complications arising from sediment consistencies and pore-water availability, pore-water samples were extracted from

sediment cores during the second sampling event. 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.

In vitro sediment core experiments

Eighteen cores were collected from Constitution Marsh, the lowest salinity field site (~2 psu; Figure 1) and used in the 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 within a few hours. Salinity experiments were begun <24 hours 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 psu); chronic salinity intrusion (~10 psu) and pulsed salinity intrusion (~17 psu) (Table 1). The chronic salinity treatment is similar to typical, daily salinity levels in Piermont Marsh (the highest salinity field site) in late summer, representing a baseline exposure to saline

water. Pulsed treatments reflected maximum salinity levels observed in the Piermont HRECOS record. Cores were held in plastic tanks subjected to “tides” of varying salinity 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 hours. Cores were inundated for 2 hours per flood event, at which point the pumps turned back on and the buckets were drained. Initially all replicates in each treatment received freshwater from water collected at Norrie Point (~0.1 psu). After 3 days, 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 psu. After another 3 days, the pulsed salinity replicates began treatment with freshwater amended with Instant Ocean to 17 psu. This treatment was continued for 5 days, during which chronic replicates remained at 10 psu and reference replicates remained at 0.1 psu.

Sediment oxygen and hydrogen sulfide profiles were measured prior to any salinity treatments and immediately (<6 hours) following each salinity treatment. After all treatments were administered, cores were sectioned for analysis of pore-water nutrient concentration using ion chromatography (DIONEX 3000) and organic matter content via combustion.

Statistics

Differences in pore water nutrient concentrations were analyzed using Analysis of Variance (ANOVA) followed by pairwise comparisons. Sediment biogeochemical dynamics were quantified as the mean, minimum, and maximum analyte concentration

for each sediment profile and also compared using ANOVA. All statistical analyses were conducted using SAS Statistical Software.

Table 1. Salinity treatments applied during in vitro core experiments. Treatments were administered every 12 hours (8:00 and 20:00) for 11 days. Salinity changes occurred on 24 July 2011 for the chronic and pulsed treatments and again on 27 July 2011 for the pulsed treatments only. The reference treatments (freshwater) remained at a constant salinity throughout the experiment.

Date	Time	Freshwater Salinity (ppt)	Chronic Salinity (ppt)	Pulsed Salinity (ppt)
7/21/2011	20:00	0.1	0.1	0.1
7/22/2011	08:00	0.1	0.1	0.1
7/22/2011	20:00	0.1	0.1	0.1
7/23/2011	08:00	0.1	0.1	0.1
7/23/2011	20:00	0.1	0.1	0.1
7/24/2011	08:00	0.1	0.1	0.1
7/24/2011	20:00	0.1	10.1	10.0
7/25/2011	08:00	0.1	10.3	9.9
7/25/2011	20:00	0.1	10.1	10.1
7/26/2011	08:00	0.1	10.0	10.0
7/26/2011	20:00	0.1	10.4	10.4
7/27/2011	08:00	0.1	10.5	10.5
7/27/2011	20:00	0.1	10.4	17.3
7/28/2011	08:00	0.1	10.5	17.2
7/28/2011	20:00	0.1	10.5	17.1
7/29/2011	08:00	0.1	10.0	17.5
7/29/2011	20:00	0.1	10.0	17.2
7/30/2011	08:00	0.1	9.7	17.7
7/30/2011	20:00	0.1	10.0	17.3
7/31/2011	08:00	0.1	10.4	17.2
7/31/2011	20:00	0.1	10.5	17.3
8/1/2011	08:00	0.1	10.0	17.1

RESULTS

In situ descriptive sampling: Pore-water chemistry

Chloride concentrations in August were significantly higher in Piermont Marsh, the southernmost site, relative to other sites, with concentrations averaging 6000 mg Cl⁻/L in sediments (Figure 2; p<0.01). The three northernmost sites had average pore water chloride concentrations ranging from 1900 mg Cl⁻/L in Con Hook Marsh to 2600 mg Cl⁻/L in both Constitution and Iona Marshes (Figure 2).

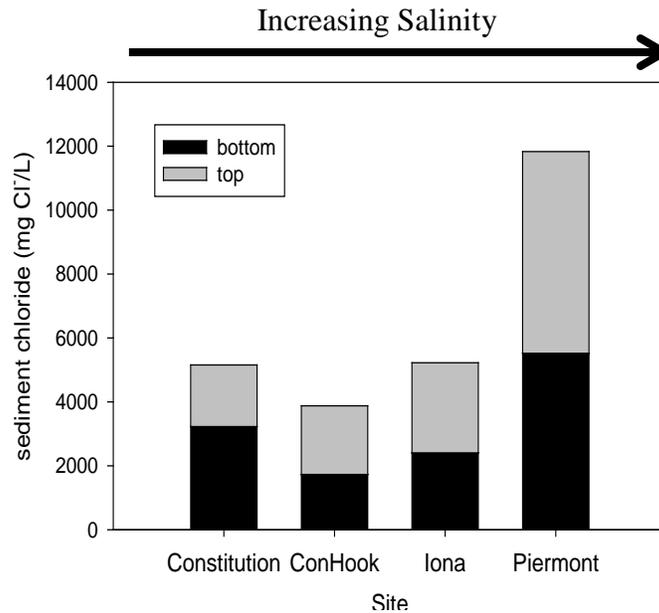


Figure 2. Sediment chloride concentrations in field study sites along salinity axis. Sites are arranged from left to right in order of increasing surface water salinity. Stacked bars are mean chloride concentrations (mg Cl⁻/L) in the top 2 cm and bottom 3 cm of 5 cm sediment cores extracted from each site. N = 6 for each bar.

Sulfate concentrations followed this trend, with Piermont Marsh having higher concentrations (mean = 717 mg SO₄³⁻/L; p<0.01). Constitution Marsh had mean sulfate

concentrations of 320 mg $\text{SO}_4^{3-}/\text{L}$, while Iona and Con Hook Marshes had pore-water sulfate concentrations of 248 mg $\text{SO}_4^{3-}/\text{L}$ and 143 mg $\text{SO}_4^{3-}/\text{L}$, respectively (Figure 3). Nitrate concentrations were also highest in Piermont Marsh, which had maximum concentrations of 12 mg NO_3^-/L . In Constitution and Iona Marshes, sediment pore-water nitrate concentrations were 4.5 mg NO_3^-/L and Con Hook Marsh had mean concentrations of 2 mg NO_3^-/L (Figure 4). In contrast, Constitution, Con Hook, and Piermont Marsh sediments all had lower sulfide concentrations, ranging from 0.12 to 0.18 mg $\text{H}_2\text{S}/\text{L}$, whereas Iona Marsh had a significantly higher H_2S concentration (mean = 0.5 mg $\text{H}_2\text{S}/\text{L}$; $p < 0.01$; Figure 5).

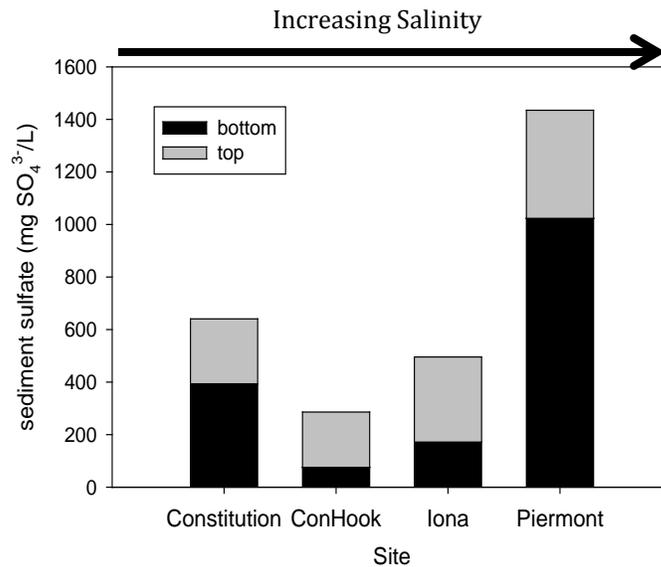


Figure 3. Sediment sulfate concentrations in field study sites along salinity axis. Sites are arranged from left to right in order of increasing salinity. Stacked bars are mean sulfate concentrations (mg $\text{SO}_4^{3-}/\text{L}$) in the top 2 cm and bottom 3 cm of 5 cm cores extracted from each site. $N = 6$ for each bar.

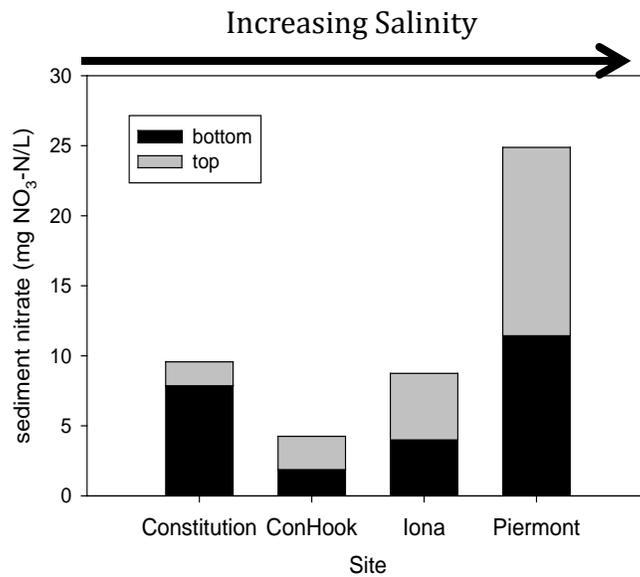


Figure 4. Sediment nitrate concentrations in field study sites along salinity axis. Sites are arranged from left to right in order of increasing salinity. Stacked bars are mean nitrate concentrations (mg NO₃⁻-N/L) in the top 2 cm and bottom 3 cm of 5 cm cores extracted from each site. N = 6 for each bar.

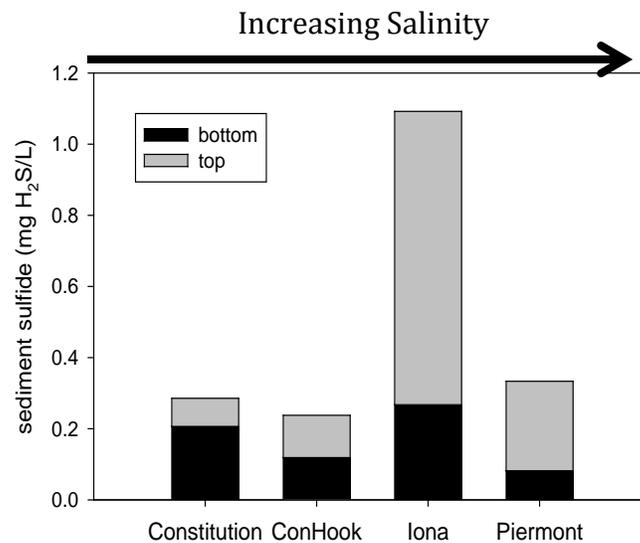


Figure 5. Sediment sulfide concentrations in field study sites along salinity axis. Sites are arranged from left to right in order of increasing salinity. Stacked bars are mean sulfide concentration (mg H₂S/L) in the top 2 cm and bottom 3 cm of 5 cm cores extracted from each site. N = 6 for each bar.

In situ descriptive sampling: Sediment oxygen dynamics

Maximum and mean oxygen concentrations had distinct temporal and spatial variation across the study sites. Although maximum oxygen concentrations did not vary among sites within a sampling period ($p > 0.1$), maximum oxygen concentrations were significantly different between the June and August sampling events ($p < 0.01$). Mean maximum oxygen concentration in June was 12 mg/L for all four sites, whereas, in August the mean maximum oxygen concentration was 8 mg/L across sites (Figure 6). Mean oxygen concentrations exhibited spatial, north to south, variation with higher mean sediment concentrations at the northernmost site, Constitution Marsh (mean = 4 mg O₂/L; $p < 0.01$). Con Hook and Piermont had the lowest mean oxygen concentrations in August both being <3 mg O₂/L. During the August sampling event, mean oxygen concentrations in sediments dropped below 2 mg O₂/L at all sites except Constitution Marsh. Piermont Marsh exhibited the lowest mean O₂ levels during both sampling events (Figure 7).

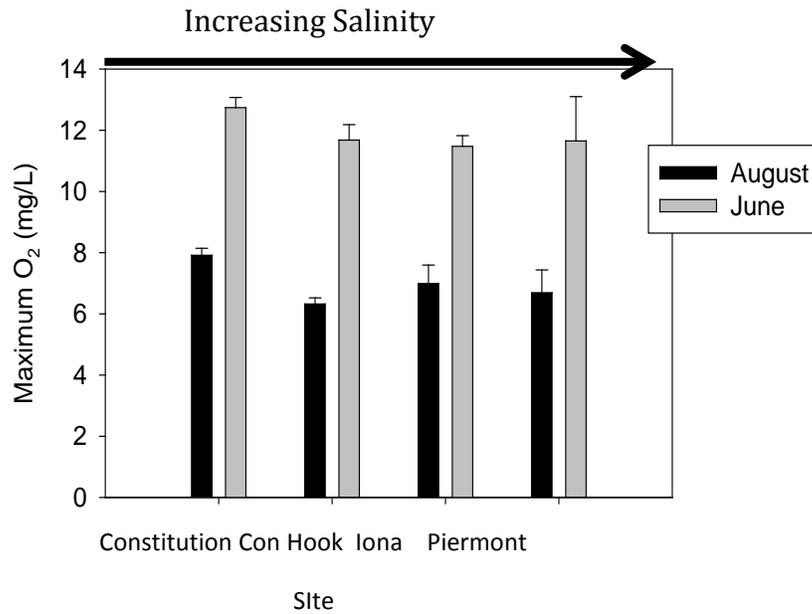


Figure 6. Variation in maximum oxygen concentrations of wetland sediments at study sites in June and August 2011. Sites are arranged from left to right in order of increasing salinity. N = 3 for each bar.

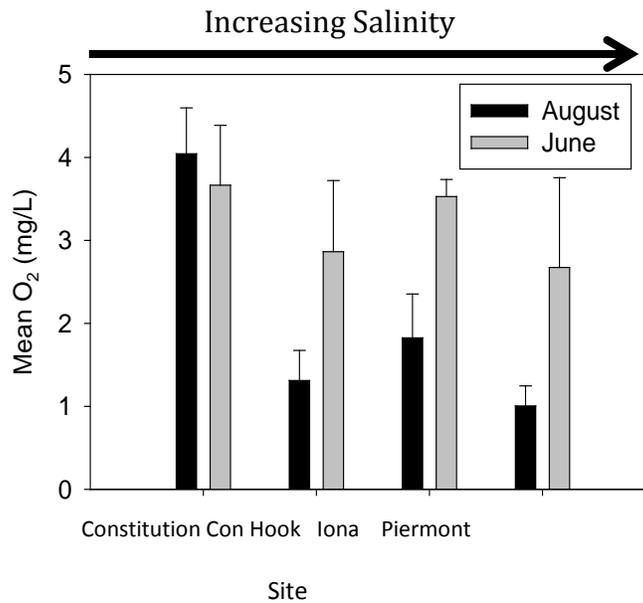


Figure 7. Variation in mean oxygen concentrations of wetland sediments at study sites in June and August 2011. Sites are arranged from left to right in order of increasing salinity. N = 3 for each bar.

In situ descriptive sampling: Sediment sulfide dynamics

In August, mean sulfide concentrations were highest in Con Hook and Iona Marshes, >10 mg H₂S/L in sediments. Piermont Marsh had mean sediment sulfide concentration of 9 mg/L while Constitution Marsh had the lowest mean sulfide concentrations of 5 mg/L (Figure 8). The maximum sulfide concentration in Con Hook Marsh was 60 mg H₂S /L. Iona Marsh had maximum sulfide concentrations of 20 mg H₂S /L; whereas, at Constitution and Piermont maximum sulfide concentrations were <20 mg H₂S/L (Figure 9). Piermont Marsh was the only site where sulfide concentrations were always above detection (≥ 4 mg/L). Constitution, Iona, and Con Hook Marshes all had minimum sediment sulfide concentrations below the detection limit of 0.01 mg H₂S/L (Figure 10).

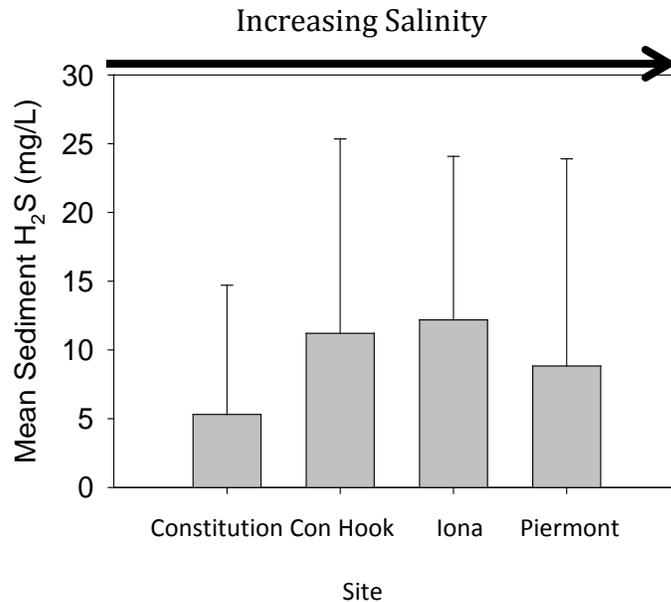


Figure 8. Mean sediment sulfide concentrations of wetland sediments at study sites in August 2011. Sites are arranged from left to right in order of increasing salinity. N = 3 for each bar.

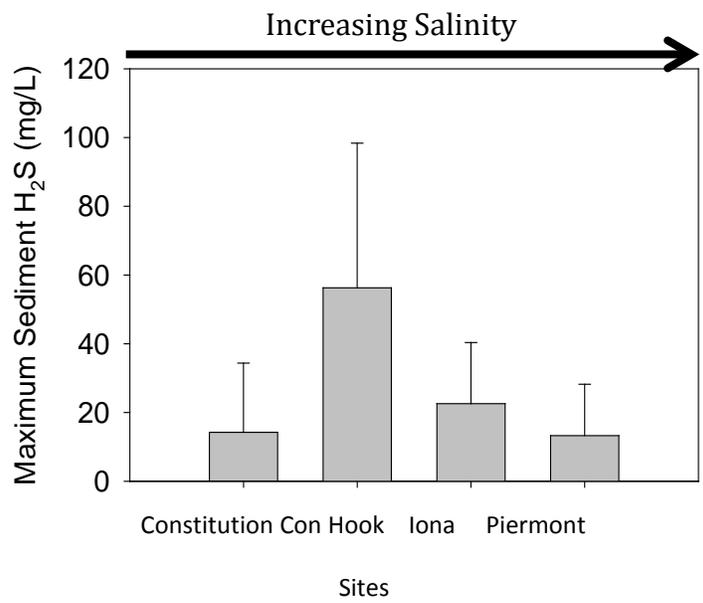


Figure 9. Maximum sediment sulfide concentrations of wetland sediments at study sites. Sites are arranged from left to right in order of increasing salinity. N = 3 for each bar.

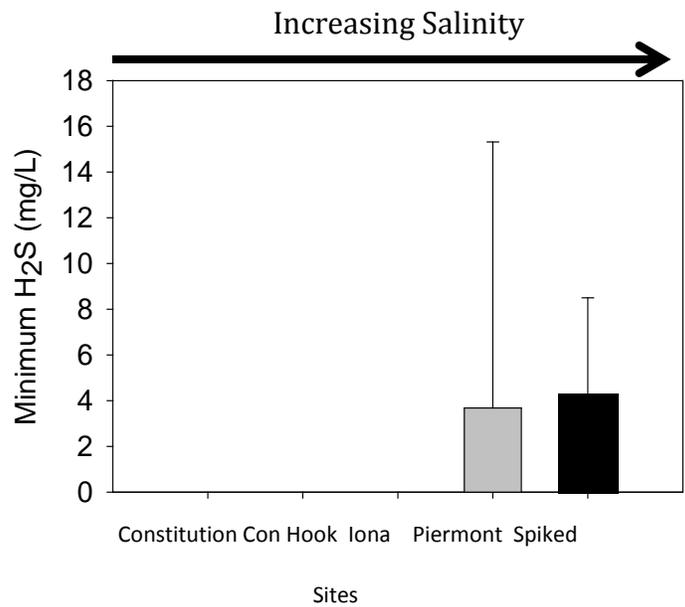


Figure 10. Minimum sediment sulfide concentrations in sediment of pulsed salinity cores in the laboratory experiment and field study sites. N = 3 for each bar.

In vitro sediment core experiments

Water chemistry analysis revealed average chloride concentrations of 5300 mg Cl⁻/L in sediments undergoing pulsed treatments. Sulfate concentrations averaged 400 mg SO₄²⁻/L and nitrate was found at average concentrations of 16 mg NO₃⁻-N/L in these sediments. Mean maximum oxygen concentration was 6 mg O₂/L in these cores and mean oxygen concentrations were 1 mg O₂/L.

Mean sediment sulfide concentrations in pulsed salinity cores ranged from 10-15 mg H₂S/L. A maximum sulfide concentration of 20 mg H₂S/L and a minimum concentration of around 4 mg H₂S/L were also recorded in these experimental cores (Figure 10).

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 O₂ 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 H₂S 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, 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, pulsed salinity cores became anoxic at greater sediment depths relative to Piermont Marsh sediment (Figure 11). 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).

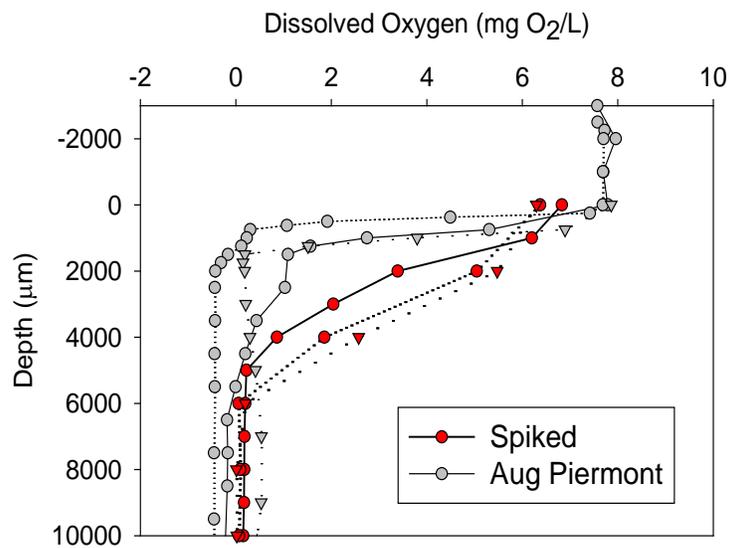


Figure 11. Sediment oxygen concentration profiles with sediment depth in pulsed salinity sediments in the laboratory experiment and Piermont Marsh sediments (high salinity site).

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 10). Further, sulfide levels in these sediments mimic those reported by previous research. DeLaune et al. (1982) reported sulfide concentrations of 6 mg H²S/L in brackish water sediments (0.5-18 psu) and 20 mgH₂S/L in sediments regularly exposed to seawater (18-30 psu). Additionally, Baldwin and Mendelssohn (1998) have shown average hydrogen sulfide concentrations of 6.7 mg H₂S/L corresponding to a salinity of 6 psu. Salinities at Piermont Marsh rarely exceeded these levels, as this was an unusually wet year in regard to rainfall.

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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REFERENCES

- Arrigoni, A., S. Findlay, D. Fischer, and K. Tockner. 2008. Predicting carbon and nutrient transformations in tidal freshwater wetlands of the Hudson River. *Ecosystems* 11:790-802.
- Baldwin, A.H. and I.A. Mendelsohn. 1998. Effects of salinity and water level on coastal marshes: an experimental test of disturbance as a catalyst for vegetation change. *Aquatic Botany* 61:255-268.
- Barbier, E.B., E.W. Koch, B.R. Silliman, S.D. Hacker, E. Wolanski, J. Primavera, E.F. Granek, S. Polasky, S. Aswani, L.A. Cramer, D.M. Stoms, C.J. Kennedy, D. Bael, C.V. Kappel, G.M.E. Perillo, and D.J. Reed. 2008. Coastal Ecosystem-Based Management with Nonlinear Ecological Functions and Values. *Science* 319:321-323.
- Brunet, R.C., and L.J. Garcia-Gil. 1996. Sulfide-induced dissimilatory nitrate reduction to ammonia in anaerobic freshwater sediments. *FEMS Microbial Ecology* 21:131-138.
- Cai, W., W.J. Wiebe, Y. Wang, and J.E. Sheldon. 2000. Intertidal marsh as a source of dissolved inorganic carbon and a sink of NO_3^- in the Satilla River-estuarine complex in southeastern U.S. *Limnology and Oceanography* 45:1743-1752.
- Capone, D.G. and R.P. Kiene. 1988. Comparison of microbial dynamics in marine and freshwater sediments – contrasts in anaerobic carbon catabolism. *Limnology and Oceanography* 33:725-749.
- Carpenter, J.H. 1966. New measurements of oxygen solubility in pure and natural water. *Limnology and Oceanography* 12:264-277.
- DeLaune, R.D., C.J. Smith., and W.H. Patrick. 1982. Methane release from Gulf Coast wetlands. *Tellus B* 35B:8-15.
- Giblin, A.E., N.B. Weston, G.T. Banta, J. Tucker, and C.S. Hopkinson. 2010. The effects of salinity on nitrogen losses from an oligohaline estuarine sediment. *Estuaries and Coasts* 33:1054-1068.
- Greene, S.E. 2005. Nutrient removal by tidal fresh and oligohaline marshes in a Chesapeake Bay tributary. MS Thesis. University of Maryland Solomons, MD, 149pp.
- Gribsholt, B., H.T.S. Boschker, E. Struyf, M. Andersson, A. Tramper, L. De Brabandere, S. van Damme, N. Brion, P. Meire, F. Dehairs, J.J. Middelburg, and C.H.R. Heip. 2005. Nitrogen processing in a tidal freshwater marsh: A whole-ecosystem ^{15}N labeling study. *Limnology and Oceanography*. 50:1945-1959.

- Hamilton, P. 1990. Modelling salinity and circulation for the Columbia River Estuary. *Progress in Oceanography* 25:113-156.
- Jeroschewski, P., C. Steuckart, and M. Kahl. 1996. An amperometric microsensor for the determination of H₂S in aquatic environments. *Analytical Chemistry* 68:4351-4357.
- Joye, S.B. and J.T. Holibaugh. 1995. Influence of sulfide inhibition of nitrification on nitrogen regeneration in sediments. *Science* 270:623-625.
- Kelley, C.A., C.S. Martens, and J.P. Chanton. 1990. Variations in sedimentary carbon remineralization rates in the White Oak River estuary, North Carolina. *Limnology and Oceanography* 35:372-383.
- Kemp, M. and W. Dodds. 2001. Centimeter-scale patterns in dissolved oxygen and nitrification rates in a prairie stream. *Journal of the North American Benthological Society* 20:347-357.
- Kiviat, E., S.E.G. Findlay, S., and W. C. Nieder. 2006. Tidal Wetlands of the Hudson River Estuary. pp. 279-310. in: J.S. Levinton and J.R. Waldman (Eds). *The Hudson River Estuary*. New York. Cambridge University Press.
- Knowles, N. 2002. Natural and management influences on freshwater inflows and salinity in the San Francisco Estuary at monthly to interannual scales. *Water Resources Research* 38:1289-1299.
- Magalhães, C.M., S.B. Joye,, R.M. Moreira, W.J. Wiebe, and A.A. Bordalo. 1980. Effect of salinity and inorganic nitrogen concentrations on nitrification and denitrification rates in intertidal sediments and rocky biofilms of the Douro River estuary, Portugal. *Water Research* 39:1783-1794.
- Megonigal, J.P. and S.C. Neubauer. 2009. Biogeochemistry of tidal freshwater wetlands. pp. 535-562. in: G.M.E. Perillo, E. Wolanski, D.R. Cahoon, and M.M. Brinson (Eds). *Coastal Wetlands: An Integrated Ecosystem Approach*. Elsevier.
- Milly, P.C.D., K.A. Dunne, and A.V. Vecchia. 2005. Global pattern of trends in streamflow and water availability in a changing climate. *Nature* 438:347-350.
- Mitsch, W.J. and J.G. Gosselink. 1993. *Wetlands*, 2nd Ed. New York. John Wiley & Sons, p. 722.
- Morris, J.T., P.V. Sundareshwar, C.T. Nietch, B. Kjerfve, and D.R. Cahoon. 2002. Responses of coastal wetlands to rising sea level. *Ecology* 83:2869-2877.

- Neubauer, S.C., K. Givier, S.K. Valentine, and J.P. Megonigal. 2005. Seasonal patterns and plant-mediated controls of subsurface wetland biogeochemistry. *Ecology* 86:3334-3344.
- Redfield, A.C. 1965. Ontogeny of a salt marsh estuary. *Science* 147: 50-55.
- Revsbech, N. and B. Jørgensen. 1986. Microelectrodes: their use in microbial ecology. *Advances in Microbial Ecology* 9:293-352.
- Seitzinger, S.P. 1988. Denitrification in freshwater and coastal marine ecosystems: Ecological and geochemical significance. *Limnology and Oceanography* 33:702-724.
- Seitzinger, S.P. and R.W. Sanders. 2002. Bioavailability of DON from natural and anthropogenic sources to estuarine plankton. *Limnology and Oceanography* 47:353-366.
- Smith, T.M., T.C. Peterson, J.H. Lawrimore, and R.W. Reynolds. 2005. New surface temperature analyses for climate monitoring. *Geophysical Research Letters* 32:L14712, 4 pp.
- Weston, N.B., M.A. Vile, S.C. Nebauer, and D.J. Velinsky. 2010. Accelerated microbial organic matter mineralization following salt-water intrusion into tidal freshwater marsh soils. *Biogeochemistry* 102:135-151.