



Sulfur Cycling in Salt Marshes of Jamaica Bay, Gateway National Recreation Area

Possible Links to Marsh Loss

Natural Resource Technical Report NPS/NER/NRTR—2013/730



ON THE COVER

Deteriorating *Spartina alterniflora* marsh at Jamaica Bay, NY.
Photo courtesy of Charles Roman (NPS).

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Abstract

The salt marshes within Jamaica Bay display high levels of pore water sulfide, a phytotoxin that can cause toxicity in *Spartina sp.* The pattern of pore water sulfide in the different marshes is consistent with the pattern of marsh loss, with JoCo (a stable marsh) displaying lower pore water sulfide concentrations (generally <5 mM) than seen at the highly degraded Elders East (up to 19 mM) or Big Egg (up to 8 mM) prior to restoration projects at those sites. There are both seasonal and interannual variations in the pore water sulfide concentrations to which marsh plants are exposed. Values were generally higher in 2004-2006 than 2007 (at sites where interannual comparison was possible), possibly due to temporal variation in organic loading onto the marsh surface.

Solid phase sulfur and Fe data complement the perspective gained from the pore water sulfide data. They suggest that JoCo may display lower pore water sulfide because a greater fraction of the pore water sulfide produced by sulfate reduction is associated with solid phase sulfide phases, principally pyrite (FeS_2), that precipitate from pore water. In part this reflects the amount of total reactive Fe present in the fine-grained sediment at JoCo. However, JoCo also shows a very high “Degree of Pyritization”, indicating that most of the reactive Fe is associated with pyrite and unavailable to react with newly produced pore water sulfide to precipitate fresh pyrite. This may be interpreted as a cautionary sign that JoCo is near the biogeochemical “limit” of its ability to deal with pore water sulfide. In contrast, the restoration effort at Elders East re-set the sediment biogeochemical system to lower degrees of pyritization, providing more flexibility for future biogeochemical regulation of pore water sulfide through iron sulfide precipitation.

This study provides circumstantial support for a “sulfur-logging” positive feedback model of marsh loss in Jamaica Bay, however further testing of this model is needed. We recommend 1) establishing reference sites in key marshes (stable, degrading and restored) that can be sampled seasonally for pore water sulfide, nutrients and pH and 2) collection of cores in conjunction with each pore water sampling to be analyzed for solid phase leachable iron, carbon and nitrogen, and sulfur phases

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Introduction

Salt marsh plants are subject to numerous stresses including keeping pace with sea level rise and dealing with potential high concentrations of phytotoxins such as hydrogen sulfide in marsh peat pore water. Jamaica Bay, NY, is an example of a salt marsh system located within a major urban area (New York City) which has displayed increasing loss of marsh area over the past ~50 years (Hartig et al., 2002). The Bay receives most of its freshwater input from treated sewage wastewater and the bay bottom has been modified heavily by dredging activities (Benotti et al., 2006). Increasing urbanization and development of the Jamaica Bay “sewershed” have lead to eutrophication of the Bay waters (NYCDEP, 2003a). The present study was designed to test a positive-feedback model of salt marsh loss Jamaica Bay in which the proximate driver of loss is sulfide stress and the ultimate driver is organic carbon loading and eutrophication (Fig. 1). These drivers lead to an overabundance of non-living organic matter (reductant) in the marsh peat that causes the bacterial community to utilize the available oxidants: O_2 , NO_3^- , MnO_2 , Fe_2O_3 , and SO_4^{2-} in turn (Froelich et al., 1979). This leads to excessive pore water concentrations of the phytotoxic hydrogen sulfide molecule, H_2S (or HS^-), resulting in plant die-offs and the degradation of salt marsh peat. High concentrations of H_2S decrease the inherent ability of a salt marsh to take up nitrogen, thus aggravating the problems caused by eutrophication (e.g., Koch et al., 1990).

Central to this model is the long-held understanding that sulfides are toxic to salt marsh plants in high concentrations. Goodman and Williams (1961) reported that *Spartina townsendii* could be killed by adding a solution of 0.94 mM NaS to plants grown in greenhouses. Excessive sulfide concentrations have been shown to cause marsh loss in rapidly subsiding salt marshes in the Mississippi Delta. DeLaune et al. (1994) demonstrated that H_2S accumulates under heavily flooded conditions and leads to plant mortality. When *S. alterniflora* dies, its roots collapse, causing a sudden and unrecoverable loss in marsh elevation, and subsequently marsh loss (DeLaune et al., 1994). This idea of sulfide driven marsh loss, via phyto-toxicity, can be extended to anthropogenically-altered eutrophic environments.

We envision two possible pathways that lead to excessive concentrations of labile organic matter in the marsh (Fig. 1). One is eutrophication, in which an overabundance of nutrients supplied via wastewater discharges or submarine groundwater discharge causes phytoplankton blooms. The second pathway is the direct input of organic matter, which may come from untreated sewage, for example, supplied to the system during a Combined Sewer Overflow (CSO) event. Both phytoplankton and untreated sewage are rich in labile organic carbon and have a high biological oxygen demand (Parker and O'Reilley, 1991; Richards and Redfield, 1954). This labile organic carbon can be delivered tidally to salt marshes, leading to increased rates of sulfate reduction (Westrich and Berner, 1984). Long-term exposure to the resulting elevated pore water sulfide concentrations hinders the growth of marsh plants (King et al., 1982; Koch and Mendelssohn, 1989), or causes mortality (Koch et al., 1990; Seliskar et al., 2004). Deterioration of the *S. alterniflora* community leads to roots that are less supportive of the marsh peat structure, and less efficient at detoxifying sulfides by transporting oxygen (Lee et al., 1999). In turn, the marsh elevations drops, and the plants experience water-logged conditions in which sulfides are not readily removed by drainage (DeLaune et al., 1994; Redfield, 1972; Turner, 1997). Ultimately, large scale plant die-offs occur (DeLaune et al., 1994; Koch and Mendelssohn, 1989). This process could be called "sulfur-logging," to indicate that the pool of reactive Fe has become

saturated with sulfide, and its ameliorating potential is reduced (e.g. Howarth, 1984). Thus the marsh becomes increasingly exposed to high sulfide concentrations and decreasingly able to cope with such conditions. This positive feedback results in a downward spiral of marsh loss, such that a new ecosystem, such as a mudflat or sand bar, eventually replaces the marsh.

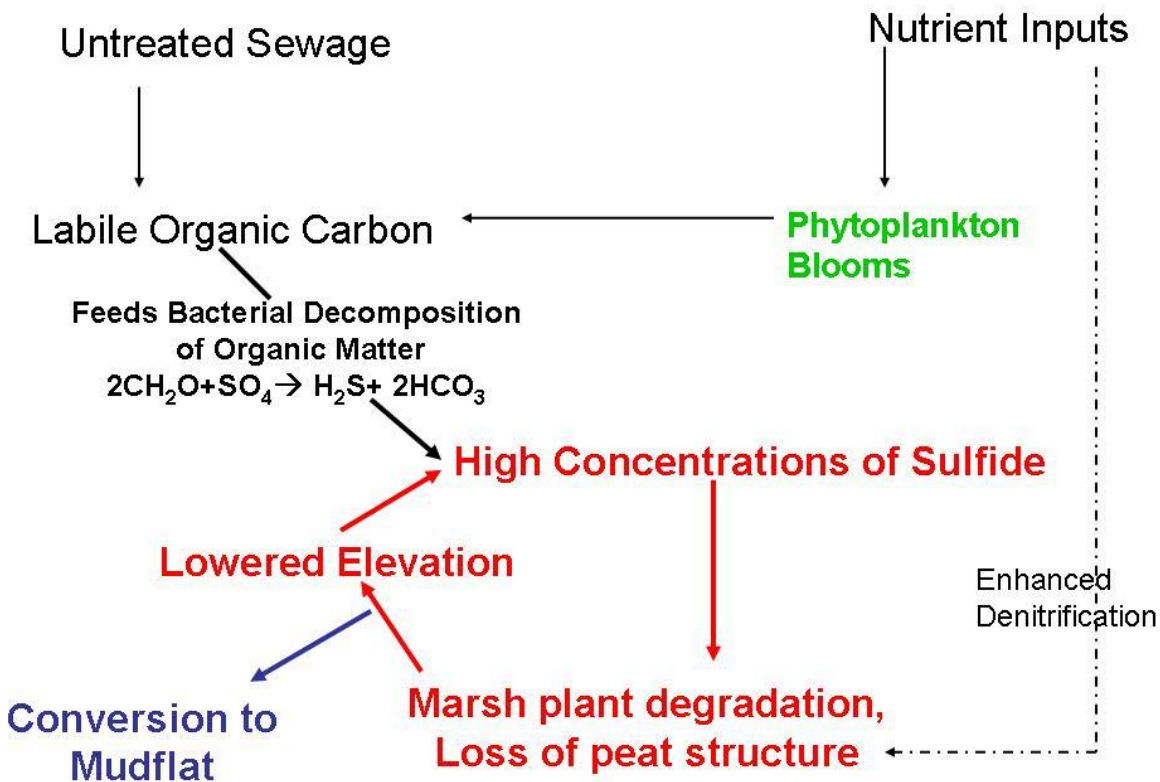


Figure 1. “Sulfur-logging” model of salt marsh loss. Model involves a positive feedback loop in which labile organic carbon is added to the marsh surface. Bacterial oxidation of this material via sulfate reduction produces elevated levels of sulfide in pore water, leading to stress to plants, peat collapse, increased frequency of flooding and supply of labile organic carbon to the marsh surface.

This model provides a mechanism to explain why marsh loss accelerated in Jamaica Bay in the mid- to late-1990s (Hartig et al., 2002). In the early 1990s, nitrogen loads and chlorophyll a in Jamaica Bay increased by almost a factor of 2 (NYCDEP, 2003a). Daily inputs of nitrogen from water pollution control plants (WPCP) to Jamaica Bay, measured only during dry weather, increased from about 1.4×10^4 kg/day in 1992 to 2.3×10^4 kg/day in 1995 (Swanson and Tonges, 2001). Concomitantly, there was a substantial increase in summer chlorophyll a concentrations in Jamaica Bay, from about 10-30 $\mu\text{g/L}$ in the late 1980s and early 1990s to 30-50 $\mu\text{g/L}$ starting in mid-1990s and continuing to the early 2000s (NYCDEP, 2003b). These changes in nitrogen and chlorophyll may have led to an increase in sulfide production that caused the plant die-offs and the acceleration in marsh loss.

The study described in this report was designed to evaluate important aspects of the sulfur cycle in Jamaica Bay marshes, notably measurements of the concentrations of pore water hydrogen sulfide and the solid phase sulfur and iron reservoirs. The marshes selected for characterization include JoCo (as an example of a stable marsh) and Big Egg and Elders Point as examples of deteriorated marsh systems. Additionally, Elders Point East was sampled before and after restoration work there in 2006.

The Sulfur Cycle in Salt Marshes

A generalized description of sulfur cycling is presented in Fig. 2. Sulfur enters salt marshes as SO_4^{2-} , one of the major conservative anions in oxic seawater. In anoxic environments, sulfate is reduced by bacteria that use it to oxidize organic matter and produce bicarbonate and hydrogen sulfide. This reaction follows the generalized stoichiometry (Berner, 1980):



Rates of SO_4^{2-} reduction typically range between 1- 4 $\mu\text{mol S/cm}^3/\text{day}$. In seawater and marine sediments, the limiting reactant in this reaction is the supply of organic matter rather than SO_4^{2-} (Goldhaber and Kaplan, 1974). In general, fresh pulses of organic matter accelerate SO_4^{2-} reduction rates (Westrich and Berner, 1984). SO_4^{2-} reduction rates are temperature dependent, and are greatest in salt marshes during the late summer and fall (Howarth and Teal, 1979; King, 1988; Morse et al., 1987).

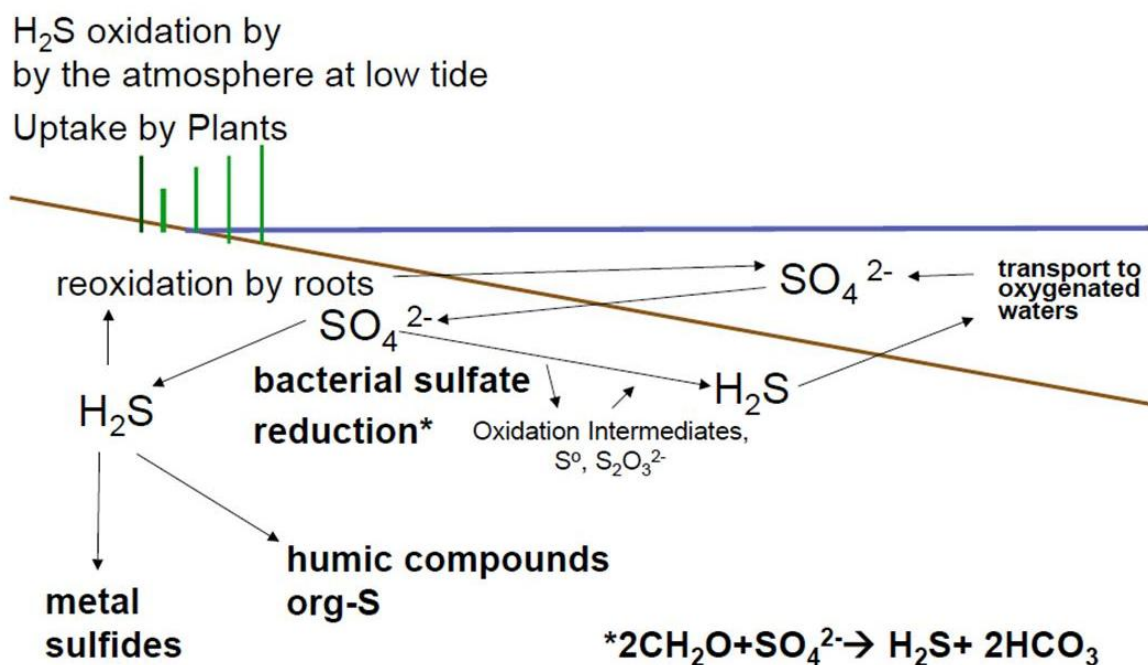


Figure 2. The biogeochemical cycle of sulfur in marine sediments.

While it is generally assumed that bacteria release H_2S to the environment, the compound is not always found in that form. In seawater, H_2S speciates as a diprotic acid (Morse et al., 1987). The speciation is dependent on pH and temperature, and in seawater with pH= 8.1 and $T= 25^\circ\text{C}$, 97% of hydrogen sulfide is present as HS^- (Morse et al., 1987). In salt marshes, the temperature and pH can vary widely, affecting reaction pathways such as mineral formation (Morse et al., 1987). While the speciation of H_2S is important, here we are concerned only with the major forms of reduced sulfur marsh sediment and pore water. All H_2S species (H_2S , HS^- , S^{2-}) will be assumed to function similarly with respect to phytotoxicity and will be referred to as dissolved sulfide. Additionally, we consider only the major classes of solid phase iron sulfide compounds, FeS and FeS_2 .

Iron Cycling in Salt Marshes

Once formed, pore water sulfide can undergo chemical reactions, including its precipitation as iron sulfides (Berner, 1980; Goldhaber and Kaplan, 1974). Iron is one of the most abundant elements in the Earth's crust (Turekian and Wedepohl, 1961), and is abundant in salt marshes. As such, iron sulfides are a large potential sink for pore water sulfide that is produced from sulfate reduction. This sink may be particularly important when sulfide reaches toxic values (Howarth, 1984). However, only a fraction of the total Fe pool in sediments is diagenetically mobilized and available for chemical reactions; some Fe is inaccessibly bound in the inner-matrices of sedimentary minerals (Berner, 1984; Raiswell and Canfield, 1998). For example, in a Delaware salt marsh, Koska and Luther (1995) found that 23 –85% of the total sedimentary Fe pool was "reactive," defined as that fraction which dissolved in a dithionite solution.

In salt marshes, the most common reduced metal-sulfide compounds are iron-monosulfides (FeS), such as mackinawite and griegite, and pyrite (FeS_2) (Berner, 1984; Goldhaber and Kaplan, 1974; Howarth and Teal, 1979). Pyrite is probably a better indicator of Fe and S dynamics in salt marshes because this pool is typically 1 – 2 orders of magnitude larger than the iron monosulfide pool (Howarth and Merkel, 1984; Hsieh and Sheih, 1997; Koska and Luther, 1995). Though rates of iron monosulfide and pyrite formation reported in the literature vary, many studies suggest that they are formed on seasonal time scales or shorter, with iron monosulfides being formed and destroyed over shorter time scales than pyrite. Pyrite is generally considered to be a stable form of reduced sulfur, though iron monosulfides are often considered to be meta-stable (Morse et al., 1987). Iron monosulfides are rapidly destroyed in oxidizing or acidic conditions (Morse et al., 1987). They are also rapidly converted into pyrite in highly sulfidic settings. For example, Raiswell and Canfield (1998) state that in marine sediments, goethite and hematite are converted to pyrite on time scales of 11.5 and 31 days. Since pyrite pools typically change on seasonal time scales, their presence appears to reflect seasonal conditions of Fe and S in a salt marsh (Howarth, 1984; Howarth and Teal, 1979; Koska and Luther, 1995). Iron monosulfides are readily formed, destroyed or converted into pyrite (Morse et al., 1987), and their presence likely reflects sub-seasonal Fe and S dynamics that are closely related to the rate of sulfate reduction (Canfield et al., 1992; Howarth, 1984; Morse et al., 1987).

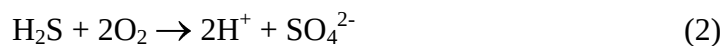
Organic Sulfur

Humic organo-sulfur compounds often form in salt marshes, typically when the supply of reactive iron is limited (Ferdelman et al., 1991). These compounds are long-lived (months to years) products of the sulfur system that are non-toxic to plants (Ferdelman et al., 1991). Organic sulfur compounds form in the upper centimeters of salt marshes and are more resistant to re-

oxidation than are iron sulfide minerals. In one Delaware salt marsh, these organic sulfur compounds sequester $10.6 \mu\text{mol S cm}^{-3} \text{ y}^{-1}$ (Ferdelman et al., 1991). This rate is less than 2% of the annual rate of sulfate reduction in that salt marsh (Ferdelman et al. 1991), and it suggests that organic sulfur formation is not an efficient mechanism for sequestering pore water sulfides in salt marshes. However, because these compounds are more resistant to re-oxidation than iron sulfides (Ferdelman et al., 1991), they may be regarded as a quasi-permanent sink for sulfides in salt marshes. Additionally, sulfide is used anabolically by *S. alterniflora*, and this plant comprises a living organic sink for sulfides (Carlson and Forrest, 1982).

Sediment Oxidation in Salt Marshes

Oxygen enters the salt marsh rhizosphere through three primary mechanisms. Air interacts with the surface of a marsh and may intrude through cracks and burrows (Howes et al., 1986; Lord and Church, 1983). Secondly, *S. alterniflora* can transport oxygen to its roots as a means of detoxifying sulfides (Lee et al., 1999; Teal and Kanwisher, 1961). Oxygen also enters marshes as a gas dissolved in seawater, and dissolved O_2 can be both diffused and advected through bioturbated and unbioturbated marsh sediments (Aller, 1982; Lord and Church, 1983). Sulfide oxidation typically proceeds according to the general reaction (Stumm and Morgan 1996):



The sulfuric acid produced by this reaction is often responsible for the low pH found in many salt marshes (King, 1988).

Solute Transport

Transport of dissolved chemical species is also a common pathway for sulfide removal from salt marshes. Sulfide can diffuse out of marsh sediments into creeks where it is advected away from the marsh by tidal and river currents. Sediment irrigation by tube-building worms or ribbed mussels enhances fluid movements and therefore sulfide removal from salt marshes. Similarly, pore waters can be advected through crab burrows or relict *S. alterniflora* stems (e.g. Aller, 1982).

The molecular diffusion coefficient of chloride, measured in a Delaware salt marsh, is $1.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, (Lord and Church, 1983) which is similar to its value in a typical marine sediment ($1.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$; Berner, 1980). The diffusion coefficient of sulfide, also measured in a Delaware salt marsh, is $1.1 \times 10^{-5} \text{ cm}^2/\text{sec}$, or very similar to that of chloride (Lord and Church, 1983).

Advection rates are typically orders of magnitude greater than diffusion rates. In a South Carolina salt marsh, pore water advection rates, determined from Ra inventories, were calculated to be $10 \text{ cm}^3 \text{ cm}^{-2} \text{ d}^{-1}$ (Rama and Moore, 1996). The average retention time of pore water in these marshes was estimated to be 10 days (Rama and Moore, 1996). In a Georgia salt marsh, sulfide fluxes out of pore waters, were estimated to be about $2.4 \text{ mmol m}^{-2} \text{ d}^{-1}$, which accounted for about 5% of total sulfide production in that marsh (Howarth, 1984). This estimation also leads to mean sulfide residence times of 1 week to 10 days. Based on this review, daily tidal exchange probably affects sulfide concentrations by less than 10%. However, tidal exchange over the course of a week to ten days may reduce sulfide concentrations by factor of 2 in many salt marshes.

Ecological Implications of Sulfur Cycling

Sulfur cycling plays an important role in the ecology of salt marshes. For example, the distribution of sulfide helps explain the border between *S. alterniflora* and *S. patens*. Bertness (1991a) concluded that *S. patens* is excluded from the low marsh by its inability to cope with a sulfidic environment. On the other hand, *S. alterniflora* possesses aerenchyma tissue that facilitates oxygen diffusion into sediments (Teal and Kanwisher, 1961), and an ability to ferment sugars (Mendelssohn et al., 1981), both of which allow it to live in sulfidic environments (Bertness, 1991a).

While *S. alterniflora* can cope with sulfidic conditions, its ability to do so is limited. A threshold exists beyond which *S. alterniflora* can no longer cope with high sulfide concentrations. At high concentrations, defined below, plants are either stunted in their growth or killed outright. Redfield (1972) understood the interaction between sediment water logging, anoxia (which is now known to correlate with sulfide concentrations) and *S. alterniflora* health when he wrote, "Teal and Kanwisher (1966) have shown that uninterrupted spaces in the leaves and roots of *S. alterniflora* permit the diffusion of oxygen to the roots during submergence. However, *S. alterniflora* apparently cannot survive continuous submergence of its roots in water. This characteristic accounts for the presence of unvegetated pannes at any level of the marsh where the surface is inadequately drained."

An idealized response of *S. alterniflora* to sulfide is shown in Fig. 3, in which biomass growth is depicted as decreasing in a quasi-stepwise fashion with increasing sulfide concentrations in the active root zone of *S. alterniflora*. Biomass is high at low sulfide concentrations (tall *S. alterniflora*), low at medium levels of sulfide (short *S. alterniflora*), and there is no growth at very high concentrations of sulfide (salt panne). The scientific literature supports the idea that *S. alterniflora* can effectively cope with sulfide concentrations less than 1–2 mM, while at concentrations of 2–4 mM growth is stunted and above 4–6 mM mortality occurs. These toxicity thresholds are supported by a series of greenhouse experiments that showed stunted growth of *S. alterniflora* at HS^- concentrations >2.0 mM (Koch and Mendelssohn, 1989; Koch et al., 1990). These experiments indicated that toxicity was due in part to the deleterious effects of sulfide on *S. alterniflora*'s metabolism and on its capacity to take up NH_4^+ . In a separate study, Seliskar et al. (2004) exposed *S. alterniflora* seedlings to various sulfide concentrations in the lab. Measuring various forms of plant growth (number of leaves, shoot length, root length and leaf length), they found no effect below 0.4 mM, stunted growth at concentration of 0.2–1.2 mM and severe impacts (*i.e.* mortality) after two weeks in the seedlings experiencing >3.0 mM. In another study, Pezeshki et al. (1988) exposed *S. alterniflora* to sulfide concentrations of 1.0 and 10.0 mM. In the 1.0 mM treatment, the net photosynthetic rate dropped by one third, while in the 10.0 mM treatment, it dropped to 0.

In field studies, sulfide has been correlated with the growth form (*i.e.* tall vs. short) of *S. alterniflora*. In a Georgia salt marsh, King et al. (1982) found the highest pore water sulfide concentrations in the regions of short form *S. alterniflora* in the marsh interiors (1–1.5 mM at 10 cm), and the lowest concentrations in the region of tall form *S. alterniflora* (<0.3 mM at 10 cm) at the levee banks. They reasoned that tidal currents advected sulfide away from the sediments in the creek bank settings, ameliorating the sediments and facilitating *S. alterniflora* growth. In an analysis of two decades worth of data from healthy salt marshes in Massachusetts, Teal and Howes (1996) found that sulfide values were about 1.0 mM in surface sediments of

short-form *S. alterniflora* stands and about 4.0 mM at 10 cm in these sites. This review of field studies reinforces the view that sulfide concentration should be considered normal when concentrations are below 1.0 –2.0 mM in the root zone, stressful if they are between 2.0 –4.0 mM and toxic if they are above 4.0 mM.

Plant growth appears to be linked not only to sulfide concentrations, but also to the presence of Fe and to Fe mineral formation. For example, Nyman et al. (1993) examined the mineral requirements of salt and fresh marshes in the Mississippi Delta. While fresh marshes needed only nutrients to accrete, salt marshes required a quantity of mineral sediments to do so. The mineral matter was considered necessary for sequestering sulfide, thereby facilitating plant growth (Nyman et al., 1993). The sequestration of sulfide in marshes depends not on the amount of mineral matter present, but on the amount of Fe that is available for reactions (Canfield et al., 1992; Raiswell and Canfield, 1998). Reactive Fe is typically present as Fe oxide mineral coatings that are dissolved under reducing conditions or iron monosulfides that are converted to pyrite under increasingly sulfidic conditions (Canfield et al., 1992; Raiswell and Canfield, 1998)

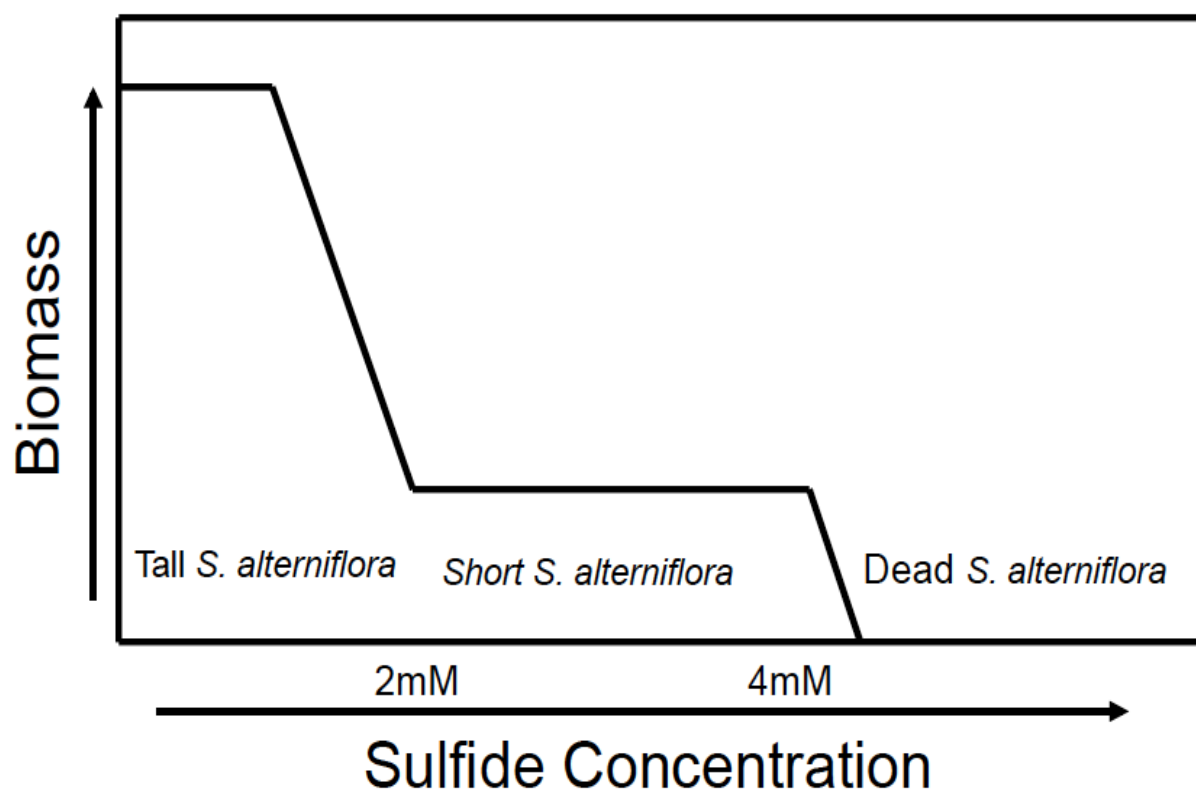


Figure 3. Schematic of the response of *S. alterniflora* to varying levels of pore water sulfide in the root zone of the plant.

Methods

Study Sites

Pore water and solid phase geochemistry were characterized in three salt marshes in Jamaica Bay- JoCo, Big Egg and Elders Point (East and West)- over the period 2004-2007 (Fig. 4). Sediment chronologies were determined from cores taken in JoCo, Big Egg and East High marshes. Sampling was carried out primarily in stands of *S. alterniflora*, although adjacent mud flat areas were sampled in some cases. Restoration projects were undertaken at Elders Point East and Big Egg marshes. The elevation at Elders East was increased by sediment application and marsh grass was planted in 2006-2007; our sampling at Elders East was carried out both before and after restoration. Big Egg marsh had been restored by sediment application and grass planting in 2003, and was sampled by us in 2004-05, but only in unrestored areas. Sampling in the early phases of this study (2004-2005) was carried out to document spatial variability in a given marsh, with less regard to temporal (seasonal) variation. In 2007, seasonal sampling was carried out at multiple sites within JoCo, Elders East and Elders West, with sampling in May (spring), August (summer) and October (fall). All samples were collected at or near low tide, both as a practical necessity and to reduce variability.



Figure 4. Map of Jamaica Bay, New York showing marshes sampled. Pore water sampling was conducted at Big Egg, JoCo and Elders Point. Cores for ^{210}Pb dating were taken at Big Egg, East High and JoCo.

Field Methods

Pore water was extracted in situ from the marsh sites by means of a pore water “sipper” as well as a multiport sampler (Figs. 5-6). Each sipper consisted of a hollow acrylic rod (lengths of about 5, 15, and 25, and 50 cm; GE Plastics) that terminated in a porous filter tip (Porex Products, "Nib" # 4059). Tygon tubing (2.7mm I.D) was run through the center of the acrylic rod and attached to the porous tip. The filter tips were pre-soaked in 30% ethanol for 30 minutes and rinsed in de-ionized water to remove residues (as recommended by K. Mylan, Porex Products) and kept moist until they were used in the field. The multiport sampler was constructed in a fashion similar to the sipper, but multiple porous entry points were placed along a hollow PVC pipe. Each of these was connected to the top of the pipe with Tygon tubing (Fig. 6).

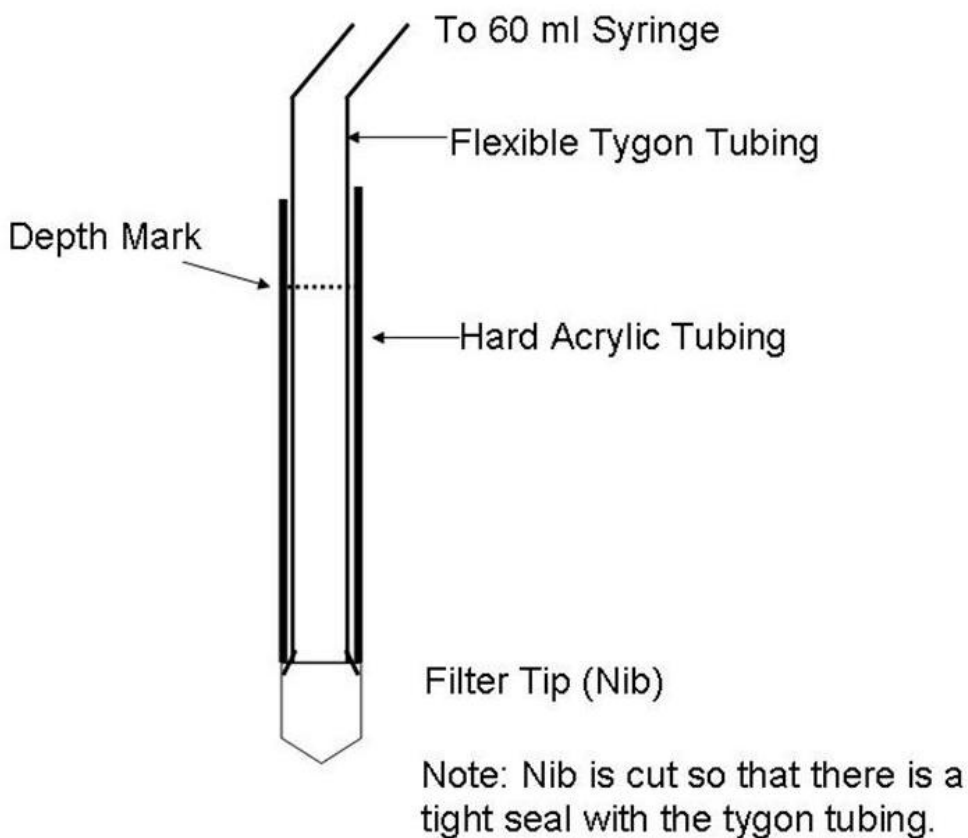


Figure 5. “Sipper” for pore water sampling. Each sipper is cut to the length desired for sampling (from Kolker, 2005).

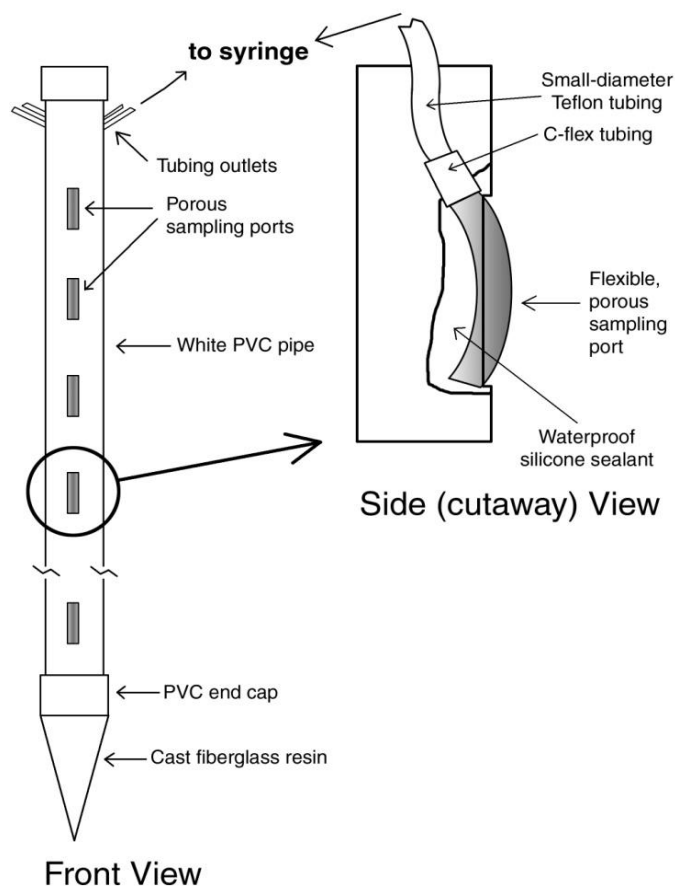


Figure 6. Multiport pore water sampler. Each sampler collects simultaneous samples from multiple depths in the marsh peat.

Once in the field, the sippers or multiport sampler were inserted to the desired depth in the marshy peat. The open end of the Tygon tube was connected to a 60 cc syringe. A vacuum was drawn by withdrawing the plunger and holding it in place with a wooden block. After the syringe was filled with 1-3 ml pore water, it was flushed to remove air and the water which had kept the tip moist. An additional 2- 5 ml of pore water were extracted, after which the sample was considered complete. Samples of ~5 – 45 ml were obtained. Aliquots were taken for dissolved sulfide (0.5 ml) and nutrients (~10 ml; NH_4^+ , $\text{NO}_2^- + \text{NO}_3^-$ and total dissolved PO_4). Samples collected in 2004-2006 were only filtered via the porous tip on the sampler before the sulfide and nutrient aliquots were taken, while those in 2007 were additionally filtered in the field through a Whatman Puradisc 1 μm GMF filter before taking the aliquots for sulfide and nutrients. A comparison of the pore water sulfide results from the two procedures was made at a marsh site on the north shore of Long Island (Table 1). The results show good agreement (generally within 15%) and no systematic offsets caused by one procedure relative to the other. For all samples, the sulfide aliquots were fixed by adding 0.5ml of 0.05 M $\text{Zn}(\text{C}_2\text{O}_2\text{H}_3)_2 \cdot 2\text{H}_2\text{O}$ to each sample. Nutrient aliquots were acidified with a drop of concentrated HCl. Also, in 2007, pH and Eh were determined using a YSI probe converted into a pH-Eh cell. This was possible only for samples that had >30 ml total sample volume.

Table 1. Comparison of samplers used in Jamaica Bay.

Marsh/Site	Sipper Type	Depth (cm)	HS ⁻ (mM)
West Pond 1	Kolker-filtered†	12	2.5
	"	20	5
	"	30	5
	Kolker- unfiltered‡	12	2.7
	"	20	4.6
	"	30	4.8
West Pond 2	Kolker-filtered†	12	-
	"	20	1.1
	Kolker- unfiltered‡	12	1.4
	"	20	0.8
West Pond 3	Kolker-filtered†	2	0.1
	"	12	4.2
	"	20	4.2
	Kolker- unfiltered‡	2	0.2
	"	12	3.7
	"	20	3.8

†Kolker-type sipper with nib; filtered in field through 1 μ m filter after sampling

‡Kolker-type sipper with nib; no filtration in field after sampling

Sediment cores were taken at some of the pore water sampling sites by inserting a 7.6 cm diameter aluminum pipe into the marsh, attaching a plumber's test plug, and extracting the core. Cores were then returned to the laboratory where they were frozen until analysis of solid phase Fe, sulfide and ²¹⁰Pb (single cores from JoCo, Big Egg and East High marshes).

Pore Water Sulfides

Pore water sulfide was analyzed colorimetrically using the method of Cline (1969). A diamine reagent solution was made from 1.6 g FeCl₃ and 4.0 g N,N-dimethyl-p-phenylene diamine dissolved in 100 ml of 6N HCl. This reagent was added to the sample, and 20 minutes later the sample was diluted with a known volume (3 to 5 ml) of deionized water (DI H₂O). The absorbance of the sample at 670nm was measured on a spectrophotometer. The concentration of HS⁻ was determined by comparing the sample absorbance to a standard curve and correcting for the volume of the sample and the volume of DI H₂O added. The standard curve was generated first by measuring the absorbance of samples of a known concentration, and second by fitting a quadratic curve through these points using the software program Origin 6.0 (Microcal Corporation). These standard curves typically had a precision of ± 1 -5%. Detailed comparison of multiple sampling types and replicate samples taken as part of a related project (funded by the New York State Dept. of Environmental Conservation) shows that pore water sulfide concentrations at any given depth generally agreed within 15-20%. This variation likely reflects real small-scale spatial variation in sulfide profiles within a marsh.

Pore Water N and P

Nutrient measurements were made using a Lachat Nutrient Autoanalyzer. The instrument separates the N and P into ammonia (NH₄⁺), nitrite + nitrate (NO₂⁻ + NO₃⁻) and total phosphate (PO₄³⁻) fractions. Analytical precision for these analyses is $\pm 5\%$.

Solid Phase Sulfides

Several fractions of solid phase sulfides were measured: acid volatile sulfides, chromium-reducible sulfur (CRS) and total sulfur. The AVS pool corresponds to iron monosulfides, and this fraction was measured by placing a small amount of sediment (0.05 g- 0.1 g) along with 5 ml DI H₂O in a 125 ml glass jar. Inside the jar were a 10 ml Pyrex beaker containing 4 ml buffered Zn(C₂O₂H₃)₂ · 2H₂O solution (made as 425 ml 2N NaOH, 75 ml 20% Zn(C₂O₂H₃)₂ · 2H₂O), 6 N HCl, 0.1 N C₆H₈O₆, and DI H₂O; Hsieh and Yang, 1989) that served as a trap for the evolved AVS and a small round bottom test tube containing 1 ml 6N HCl and 0.1 ml 0.1 N C₆H₈O₆. The jar was flushed with N₂ gas for 15 seconds and sealed tightly. It was shaken gently such that the test tube would fall over (thus releasing the acid to react with the sediment), but the trap would not be disturbed. The slurry was shaken on a rotary shaker for 4 hours to evolve the AVS, which was taken up in the Zn(C₂O₂H₃)₂ · 2H₂O solution. The jar was then opened and the trap removed (Hsieh and Sheih, 1997; Hsieh and Yang, 1989; van Griethuysen et al., 2002). The HS⁻ contained in the trap solution was determined colorimetrically (Cline, 1969), as described in section 2.3. To overcome the buffering capacity of the NaOH, and to adjust for the high mass of ZnS, it was necessary to use 200 µl diamine and 750 µl concentrated HCl for each sample. Generally, duplicate or triplicate measurements were made.

Chromium-reducible sulfur (CRS) is largely sulfur associated with pyrite (FeS₂) and this fraction was measured on samples collected in 2004-2006 using a similar set-up as for the AVS extraction. A solution of Cr(II) at room temperature was created by bubbling N₂ gas through a solution of acid cleaned mossy zinc in 1M 6 H₂O-CrCl₃ in 0.5 N HCl (Fossing and Jorgensen, 1989). When the solution turned bright blue, indicating that all Cr was reduced, it was drawn into 10 ml syringes (Fossing and Jorgensen, 1989). Wet sediment (0.1 g) was placed in a 125 ml glass jar that included a 10 ml Pyrex beaker containing 6 ml of NaOH-buffered Zn(C₂O₂H₃)₂ · 2H₂O. The jars were flushed with N₂ gas and 4 ml Cr(II) and 2 ml de-aerated 12N HCl were added to each jar in a glove bag with a continuous flow of N₂ gas. The reaction was run for ~48 hours (Fossing and Jorgensen, 1989). This technique measures neither elemental nor organic sulfur (Fossing and Jorgensen, 1989).

Some samples from the Big Egg Marsh turned green after time, suggesting that all Cr(II) had been oxidized. In such cases, additional Cr(II) was added, and a new trap placed in the vessel to determine if any additional CRS could be liberated. The total sulfur liberated by the CRS technique was trapped in the Zn(C₂O₂H₃)₂ · 2H₂O solution and determined colorimetrically using the method of Cline (1969). During this distillation procedure, a large quantity of ZnS was generated, due to the large amount of CRS present in these samples. Therefore, substantial dilutions needed to be made. To the trap solution were added 2-3 ml of DI H₂O, 500 µl diamine and 1125 µl concentrated HCl and the diluted solution was set aside for 15-20 minutes. Afterward, the solution was further diluted with 75 ml DI H₂O and 1ml of this solution was analyzed on the spectrophotometer. While the necessity of this procedure may have resulted in limited accuracy of the final values, their precision, and therefore their comparability, is probably high because 1) no remains of ZnS crystals could be seen in the sample, 2) triplicate samples taken from the same section had similar results and 3) downcore trends (see results) emerged that are generally consistent with prior studies (Berner, 1980, 1984; Goldhaber and Kaplan, 1974).

CRS was not determined on samples collected in 2007. Instead, total solid phase sulfur was measured using a Perkin Elmer CHNS Analyzer. Small aliquots (~0.1 g) of dried sediment were

combusted and the fractions containing C, N and S were quantified. The sulfur measured in this way includes both sulfide ($\text{FeS} + \text{FeS}_2$) and organic sulfur.

Solid Phase Reactive Iron

Reactive iron was measured by leaching 0.05 g of dried sediment with 1N HCl for 24 hours. Different authors have used a variety of reagents and procedures to leach out the residual reactive Fe pool, including a 2 minute boil in 12N HCl, a 6N leach for 15 minutes, a 1N HCl leach and a dithionite leach (Berner, 1984; Goldhaber and Kaplan, 1974; Koska and Luther, 1995). However, Leventhal and Taylor (1990) presented convincing empirical evidence that many of these procedures yield very similar results, particularly when the investigator is ultimately interested in measuring the degree of pyritization (DOP). They recommend a 1N HCl 24 hour leach, largely for its simplicity and safety. Therefore, this method was chosen. Total reactive Fe was measured colorimetrically using the ferrozine method (Stookey, 1970).

Solid Phase C-N-S

Dried sediment samples (~0.1 g) were analyzed for total C, N and S using a Perkin Elmer CHNS Analyzer. The C from this analysis (expressed as mg/g) can be converted into % organic matter in the sediment using a conversion factor of 0.4 – 0.6 g C/g organic matter (Craft et al., 1991). As noted by Craft et al. (1991), partial decomposition of organic matter in marshes over time leads to conversion factors near the higher end of the range, i.e. .55 - .60 g C/g organic matter. These values are more likely to typify marshes in Jamaica Bay.

Lead-210

Although not formally a part of this study, single cores were collected at Big Egg, East High and JoCo marshes for determination of the natural radionuclide ^{210}Pb (via the alpha activity of its granddaughter ^{210}Po). A mixture of HCl, HNO_3 and HF acids were added to aliquots of ~1g dried sediment and the samples were spiked with ^{209}Po tracer of known activity. The initial treatment used 10 ml of 12N HCl, 10ml of 16N HNO_3 , and 10 ml of 14N HF. This was followed by 5 ml of 16N HNO_3 and 5 ml of 12N HClO_4 , and finally 10 ml of 12N HCl. Following the third treatment, the dissolved sample was diluted to 50 ml using 1.5N HCl. Po was plated onto silver disks, as the sample was heated to 50~80°C for 3hrs (Flynn, 1968). ^{210}Po activities were calculated from the alpha spectra of ^{209}Po and ^{210}Po . ^{210}Pb activities were determined by assuming secular equilibrium with ^{210}Po .

Supported ^{210}Pb , or that amount produced by the decay of ^{226}Ra in the mineral matrices, was estimated based on a geometric regression of Al vs. the ^{210}Pb activity in depth intervals where all ^{210}Pb present could be assumed to be supported ^{210}Pb ; i.e. samples at a significant depth in the cores (Kolker, 2005). In the East High and Big Egg marsh cores, Al concentrations were estimated from the loss-on-ignition (LOI) values and a geometric regression of Al vs. 1-LOI in other Long Island cores (Kolker, 2005). The estimated Al concentrations were then used to derive supported ^{210}Pb .

Results

Pore Water Data

The pore water data are given in Tables 2-7. We have separated the data into two chronological groupings for samples taken in 2004-2006 and in 2007 because the nature of the sampling changed in 2007 and the sample handling technique was slightly different then, although as noted above (see Table 1), the sulfide data based on the slightly different field protocols are comparable. Pore water sulfide concentrations generally increased from near-zero concentrations at the marsh surface to elevated values at depth. Maximum $[\text{HS}^-]$ concentrations were greater at all sites in 2004 – 2006 than in 2007: 5.3 vs. 2.8 mM at JoCo, 19 vs. 2.9 mM at Elders East and 6 vs. 2.6 mM at Elders West. Concentrations of $[\text{NH}_4^+]$ were consistently greater than those of $[\text{NO}_2^- + \text{NO}_3^-]$ at all sites and times, except occasionally in the upper few cm of the marsh. Differences in the profiles were evident as well, with NH_4^+ generally increasing and $\text{NO}_2^- + \text{NO}_3^-$ decreasing with depth in the peat. These patterns are consistent with denitrification occurring in the upper few cm of the marsh and NH_4^+ accumulation in the pore water as organic matter is remineralized with depth (Berner, 1984). Chloride was measured systematically in the samples in 2007 as a check on pore water salinity. Bay water $[\text{Cl}^-]$ was ~440 mM (Tables 6 and 7) and pore water $[\text{Cl}^-]$ ranged from 390-620 mM at Elders East, 360-570 mM at Elders West and 320-530 mM at JoCo (Tables 4, 6 and 7). At JoCo and Elders West, $[\text{Cl}^-]$ in the spring was lower than in the summer/fall, suggesting the effect of hot weather on pore water $[\text{Cl}^-]$. The range of concentrations of the other pore water constituents exceeded that of $[\text{Cl}^-]$ at all sites, and thus evaporation played a minor role in affecting the concentrations of pore water $[\text{HS}^-]$, for example. Values of pH generally fell within the range of 7 – 8, although values as low as 4.6 were recorded at JoCo. These low pH values generally occur at depths with $E_h > 0$ (Table 4), and JoCo was the only marsh to display positive E_h values. Both Elders East and West show negative E_h values in the upper 2 cm of the peat (Tables 6 and 7). Redox potential values at depth in the marshes were commonly -300 to -400.

Solid Phase Data

Solid phase C-N-S and Fe data are given in Table 8 for Big Egg marsh (2005 sampling) and in Table 9 for JoCo and Elders Point marshes (2007 sampling). The % C was greatest at JoCo (~10-30%) and least at Elders West (0.2 - ~5%) and Elders East (0.1 - ~8%). The sediment characteristics at the three sites were fundamentally different as well- JoCo had water contents ranging from 71-88% while Elders displayed %_{water} as low as 13%. These differences are partly due to the changes in sediment characteristics at Elders following the restoration work at Elders East. The solid phase sulfur pools showed significant differences among the sites as well. Acid volatile sulfide (AVS, FeS) was lowest at JoCo and highest at Elders East. In contrast, total sulfur (largely pyrite, FeS_2) was highest at JoCo (and at Big Egg, Tables 8 and 9). Leachable Fe (that not associated with pyrite or tightly bound in the mineral structure) was generally higher at Elders Point than at JoCo or Big Egg.

²¹⁰Pb Profiles

The ²¹⁰Pb data are shown in Fig. 7. Maximum excess ²¹⁰Pb activities are ~17 dpm g⁻¹, seen at Big Egg marsh. The inventories of excess ²¹⁰Pb in the three marshes are 9.7 ± 0.1 dpm cm⁻² at East High, 51.1 ± 0.4 dpm cm⁻² at Big Egg, and 12.8 ± 0.2 dpm cm⁻² at JoCo. Figure 8 shows the accretion chronologies of the cores. These were calculated using a constant rate-of-supply or

constant flux model (see Kolker, 2005 for details). Average accretion rates for the period 1974-2000 are 0.35, 0.41 and 0.46 cm y⁻¹ for East High, Big Egg and JoCo marshes, respectively. In comparison, the rate of sea level rise is 0.30 cm y⁻¹ at the Battery (1900-2003) and 0.25 cm y⁻¹ at Montauk, NY (1948-2003; Kolker, 2005).

Table 2. Big Egg marsh pore water geochemistry (2004-2005).

Date	Location	Date	Profile ID	Depth (cm)	HS ⁻ (mM)
2004	Untreated, Interior (degrading)	7/29/2004	I	1	0.3
				2	0.6
				5	0.9
				10	2.0
				15	4.2
				20	3.5
		7/29/2004	-	0.5	0.0
				5	0.5
				10	2.7
				15	4.2
				20	6.5
		8/4/2004	K	0.5	0.0
				3	2.2
				6	3.7
				11	4.9
				16	4.6
				21	7.2
	Untreated, Creek bank	7/29/2004	J	2	2.0
				5	1.7
				10	1.9
				15	4.7
				20	2.3
		8/2/2004	L	2	1.9
				5	3.1
				10	3.4
				15	2.8
				20	2.7
		8/4/2004	M	0.5	4.3
				3	5.0
				6	5.0
				11	7.6
				16	5.0
				21	3.1

Table 2. Big Egg marsh pore water geochemistry (2004-2005) (continued).

Date	Location	Date	Profile ID	Depth (cm)	HS ⁻ (mM)
2005	Untreated, Interior (degrading)	4/18/2005	AF	2	0.3
				5	0.0
				7	1.1
				12	0.5
				20	1.0
		4/18/2005	AG	2	0.2
				5	0.6
				7	0.1
				12	0.6
				20	0.6
		5/2/2005	AL	2	0.4
				5	1.5
				7	1.0
				12	1.0
				20	2.1
		5/2/2005	AM	2	0.0
				5	0.0
				7	0.0
				12	0.5
				20	0.4
	Untreated, Creek bank (degrading)	5/2/2005		2	1.7
				5	3.5
				7	3.4
				12	1.3
				20	4.1

Table 3. JoCo marsh pore water geochemical data (2005-2006)

Location	Date	Latitude (N)	Longitude (W)	Profile	Depth (cm)	Cl ⁻ (mM)	HS ⁻ (mM)	PO ₄ ³⁺ (μM)	NH ₄ ⁺ (μM)	NO ₂ ⁻ + NO ₃ ⁻ (μM)
BL-100-024 (South side, <i>S. patens</i>)	2005									
	7/18/2005	40° 36.719'	73° 46.182'	AZ	2	-	-	8.7	113	13.6
					7	-	-	2.6	145	65.7
					12	-	-	2.6	144	14.3
	7/18/2005			AX	2	-	-	2.6	36	11.4
					7	-	-	40.0	31	5.7
					12	-	-	11.9	53	8.6
	7/18/2005			AY	2	-	-	5.8	116	8.6
					7	-	-	1.9	131	5.7
					12	-	0.1	2.6	198	8.6
					12	-	0.4	-	-	-
	7/18/2005			BA	12	-	-	45.2	82	11.4
	9/24/2005			BJ	7	-	2.6	-	-	-
					12	-	3.1	4.5	48	2.9
					20	-	5.8	4.2	77	2.9
	9/24/2005			BK	2	432	2.1	10.0	26	2.1
					7	494	4.0	11.0	41	5.7
					12	468	4.2	-	-	10.0
20					469	4.0	14.5	334	15.0	
2006										
BL-100-024	4/21/2006	40° 36.719'	73° 46.182'	CI	20	-	2.1	-	-	-
	4/21/2006			CJ	20	-	1.8	-	-	-

Table 3. JoCo marsh pore water geochemical data (2005-2006)(continued).

Location	Date	Latitude (N)	Longitude (W)	Profile	Depth (cm)	Cl ⁻ (mM)	HS ⁻ (mM)	PO ₄ ³⁺ (μM)	NH ₄ ⁺ (μM)	NO ₂ ⁻ + NO ₃ ⁻ (μM)
	8/3/2006			CM	2	323	0.02	1.9	76	20.0
					7	350	0.04	3.6	56	11.4
					12	314	-	5.2	32	5.7
					20	370	1.2	8.4	136	7.9
	8/3/2006			CN	2	-	0.04			
					7	344	0.5	0.3	118	20.7
					12	194	-	4.5	25	7.1
					20	245	1.2	11.3	116	6.4
	8/3/2006			CO	12	345	0.3	5.2	49	5.0
					20	368	0.9	9.7	136	2.9
										0.0
	8/3/2006			CP	12	258	1.3	4.5	41	26.4
					20	-	1.9	11.0	150	5.0
	8/3/2006			CQ	7	-	0.1	-	-	10.7
					12	382	0.8	2.9	59	3.6
					20	363	1.3	10.3	151	5.0
	8/3/2006			CR	12	206	1.3	4.5	46	4.3
					20	195	1.7	9.0	97	3.6
	8/3/2006			CS	7	264	0.01	3.6	44	3.6
					12	-	0.6	-	-	
					20	367	1.1	6.8	149	3.6
	8/3/2006			CT	7		0.1	<0.1	8	12.9
					12	291	1.3	10.3	126	5.0
					20	371	0.6	4.8	81	5.0
	8/10/2006			CU	2	446	0.5	23.2	308	30.7

Table 3. JoCo marsh pore water geochemical data (2005-2006)(continued).

Location	Date	Latitude (N)	Longitude (W)	Profile	Depth (cm)	Cl ⁻ (mM)	HS ⁻ (mM)	PO ₄ ³⁺ (μM)	NH ₄ ⁺ (μM)	NO ₂ ⁻ + NO ₃ ⁻ (μM)
BL-100-024 (dying patch nearby)					7	407	1.3	23.9	311	31.4
					12	366	0.7	3.2	381	8.6
					20	338	2.9	2.6	144	6.4
	9/7/2006			DB	2	355	2.0	51.0	21	3.6
					7	367	3.0	48.4	72	7.9
					12	430	2.8	24.5	169	5.7
					20	375	2.2	30.7	81	5.7
	9/7/2006			DC	2	407	3.8	32.9	318	20.0
					7	378	2.8	61.7	109	6.4
					12	350	2.3	58.8	121	9.3
	10/18/2006			DM	2	194	0.03	6.8	76	3.6
					7	-	0.9	-	-	-
					12	-	0.9	-	-	-
					20	-	1.5	-	-	-
	10/18/2006			DN	2	195	0.0	3.6	24	0.7
					7	-	1.9	-	-	-
					12	-	2.8	-	-	-
					20	-	3.3	-	-	-
	9/7/2006	40° 36.719'	73° 46.182'	DD	2	278	4.1	31.6	1054	5.0
					7	-	2.5	-	-	-
					12	381	2.3	85.2	750	5.0
					20	362	5.3	21.3	596	1.4
	9/7/2006			DE	2	381	2.8	104.0	1012	3.6
					7	333	1.6	61.0	1095	25.7
					12	316	3.3	55.5	1202	6.4
					20	352	4.0	-	-	10.0

Table 3. JoCo marsh pore water geochemical data (2005-2006)(continued).

Location	Date	Latitude (N)	Longitude (W)	Profile	Depth (cm)	Cl ⁻ (mM)	HS ⁻ (mM)	PO ₄ ³⁺ (μM)	NH ₄ ⁺ (μM)	NO ₂ ⁻ + NO ₃ ⁻ (μM)
					20	442	2.1	23.6	396	5.7
BL-100-084	8/10/2006	40° 36.701'	73° 47.219'	CV	2	442	2.1	40.4	21	12.9
					12	387	3.1	22.6	71	7.9
					20	305	4.7	312.6	-	7.1
	8/10/2006			CW	2	387	1.5	25.5	4	5.0
					12	442	1.1	87.2	14	5.0
					20	428	3.2	36.8	33	4.3
	9/7/2006			DF	2	399	4.8	43.6	1070	5.7
	9/7/2006			DG	2	-	2.2	-	-	-
					7	-	1.3	-	-	-
					12	-	4.5	42.0	161	5.0
					20	421	4.8	49.1	104	6.4
BL-100-144	9/7/2006	40° 36.690'	73° 47.237'	DH	7	389	-	111.4	460	18.6
					12	393	-	82.0	579	11.4
					20	395	-	93.0	479	12.1
BL-100-084	10/18/2006	40° 36.701'	73° 47.219'	DO	2	280	-	2.3	114	6.4
					7	-	0.8	-	-	-
					12	-	2.4	-	-	-
					20	-	2.7	-	-	-
	10/18/2006			DP	2	-	-	-	-	-
					7	242	-	2.3	79	5.0
					12	292	2.5	59.4	139	15.0
					20	-	-	48.4	161	32.1

Table 3. JoCo marsh pore water geochemical data (2005-2006)(continued).

Location	Date	Latitude (N)	Longitude (W)	Profile	Depth (cm)	Cl ⁻ (mM)	HS ⁻ (mM)	PO ₄ ³⁺ (μM)	NH ₄ ⁺ (μM)	NO ₂ ⁻ + NO ₃ ⁻ (μM)
BL-100-144	10/18/2006	40° 36.690'	73° 47.237'	DR	2	-	-	2.9	18	6.4
					7	273	-	10.0	34	4.3
					12	-	-	30.4	152	9.3
					20	390	-	22.6	130	5.7
	10/18/2006			DS	2	349	-	10.0	88	7.1
					7	-	0.7	34.9	51	5.0
					12	345	1.1	53.0	98	5.0
					20	368	2.0	64.3	73	4.3

Table 4. JoCo marsh pore water data- 2007.

Station ID	Sampling Date	Latitude (N)	Longitude (W)	Depth (cm)	pH	Eh	Cl ⁻ (mM)	HS ⁻ (mM)	PO ₄ ³⁻ (μM)	NH ₄ ⁺ (μM)	NO ₂ ⁻ + NO ₃ ⁻ (μM)
Spring											
JOCO 1	5/21/2007	40° 36.716'	73° 47.184'	2	5.2	222	420	0.0	1.7	<1.0	1.1
				6	5.8	190	400	0.0	4.5	76	1.5
				20	6.7	-235	460	1.3	44.9	591	2.8
				30	6.5	-316	380	1.8	27.1	534	0.7
JOCO 2	5/21/2007	40° 36.701'	73° 47.212'	2	5.9	-57	400	0.0	<0.3	<1.0	3.8
				7	4.7	60	390	0.0	1.7	<1.0	1.0
				20	5.9	-110	380	0.0	23.3	50	1.5
				25	-	-	420	0.0	2.7	20	<1.0
				30	6.3	-187		0.3	34.9	109	<1.0
JOCO 3	5/21/2007	40° 36.681'	73° 47.253'	2	-	-	370	0.0	2.4	9	8.4
				7	4.6	116	400	0.0	3.6	9	1.5
				10	5.5	45	340	0.0	4.9	1	0.8
				15	5.9	-75	400	0.0	14.8	24	0.9

Table 4. JoCo marsh pore water data- 2007 (continued).

	Sampling	Latitude	Longitude	Depth			Cl ⁻	HS ⁻	PO ₄ ³⁻	NH ₄ ⁺	NO ₂ ⁻ + NO ₃ ⁻
Station ID	Date	(N)	(W)	(cm)	pH	Eh	(mM)	(mM)	(μM)	(μM)	(μM)
JOCO 4	5/21/2007	No record	No record	2	6.8	-217	320	0.1	37.1	109	1.1
				7	7.0	-264	360	0.4	61.3	214	<1.0
				12	-	-	340	0.3	47.5	214	3.0
				20	-	-	350	0.2	54.9	120	1.4
Summer											
JOCO1	8/27/2007	40° 36.718'	73° 47.184'	2	-	-	434	0.0	39.4	19	27.6
				6	-	-	474	0.0	74.3	33	10.6
				12	7.3	-365	485	1.0	82.3	155	12.8
				20	-	-	477	1.2	125.6	424	22.2
				30	-	-	465	2.0	55.2	506	18.4
JOCO2	8/27/2007	40° 36.693'	73° 47.224'	2	7.6	-300	448	0.0	12.1	4	13.4
				15	-	-	485	0.0	19.4	78	40.1
				25	6.7	-226	491	0.0	43.9	27	10.3
				45	6.7	-326	454	0.3	40.7	32	10.1
JOCO5	8/27/2007	40° 36.764'	73° 47.212'	2	-	-	443	0.0	3.8	<1.0	<1.0
				7	-	-	415	0.0	8.0	<1.0	45.2
				12	-	-	457	0.2	80.7	70	11.3
				20	7.1	-130	468	0.9	75.9	53	5.7
				30	7.0	-357	460	0.9	36.2	36	3.9
JOCO6	8/2720/07	40° 36.742'	73° 47.202'	2	6.3	-330	403	0.0	5.0	6	3.9
				7	-	-	426	0.0	4.5	<1.0	4.8
				15	-	-	482	0.0	8.0	62	24.4
				25	-	-	482	0.0	9.3	42	10.5
				34	-	-	477	0.0	11.7	3	16.8
				45	-	-	480	0.0	20.5	88	23.8
				55	7.3	-275	451	0.5	49.4	48	9.1

Table 4. JoCo marsh pore water data- 2007 (continued).

Station ID	Sampling Date	Latitude (N)	Longitude (W)	Depth (cm)	pH	Eh	Cl ⁻ (mM)	HS ⁻ (mM)	PO ₄ ³⁻ (μM)	NH ₄ ⁺ (μM)	NO ₂ ⁻ + NO ₃ ⁻ (μM)
Fall											
JOCO 1	10/24/2007	40° 36.719'	73° 47.184'	2	-	-	443	0.0	3.2	<1.0	9.0
JB Coordinates RBL 100W024				6	-	-	460	0.0	8.4	1	20.1
				12	-	-	525	0.2	38.7	3	20.9
				20	6.7	-338	530	1.7	40.7	98	8.4
				30	6.9	-291	522	2.0	56.8	239	8.9
				40	6.7	-414	499	2.4	48.1	351	6.4
				50	6.9	-311	491	2.8	57.8	376	5.2
JOCO 2	10/24/2007	40° 36.704'	73° 47.216'	6	-	-	516	0.0	36.8	15	6.2
JB Coordinates RBL 100 W084				20	-	-	505	0.3	63.0	45	8.2
				50	-	-	451	1.9	40.4	116	<1.0
				60	-	-	448	1.6	39.7	121	<1.0
JOCO 5	10/24/2007	40° 36.766'	73° 47.211'	2	-	-	465	0.0	8.3	31	<1.0
JB Coordinates RBL 200W 02211				6	-	-	465	0.0	11.1	6	3.7
				12	-	-	474	0.1	28.5	34	4.8
				20	6.2	-277	485	0.2	27.0	36	<1.0
				30	-	-	480	0.4	39.1	70	<1.0
				40	-	-	465	0.8	40.4	92	<1.0
				50	-	-	448	1.0	35.5	79	<1.0
JOCO 6	10/24/2007	40° 36.744'	73° 47.197'	6	-	-	477	0.0	15.2	13	<1.0
JB Coordinates RBL 150W016				12	-	-	513	0.0	28.9	6	<1.0
				20	-	-	516	0.3	39.4	1	<1.0
				30	-	-	496	0.7	35.2	18	<1.0
				40	6.3	-363	463	0.6	30.7	53	4.6
				50	-	-	457	1.1	21.6	79	2.3

Table 5. Elders Point East and West pore water geochemical data (2005-2006).

Marsh	Location*	Date	Profile	Depth (cm)	Cl ⁻ (mM)	HS ⁻ (mM)	PO ₄ ³⁻ (μM)	NH ₄ ⁺ (μM)	NO ₂ ⁻ + NO ₃ ⁻ (μM)
2005									
Elders West (summer)	Sandy area	6/17/2005	AP	2	-	0.7	78.8	345	8.6
				7	-	0.8	106.9	591	8.6
				12	-	6.3	22.0	225	5.7
				20	-	3.3			
		6/17/2005	AQ	2	-	-	27.1	106	117.1
				7	-	5.9	43.3	840	14.3
				12	-	5.1	0.3	-	-
				20	-	4.3	60.1	820	17.1
		6/17/2005	AR	2	-	0.0	28.7	146	8.6
				7	-	0.1	18.1	149	
				12	-	0.2	15.5	187	5.7
				20	-	0.3	19.7	206	5.7
		6/17/2005	AS	2	-	-	17.8	111	5.7
				7	-	-	-	-	-
				12	-	-	17.8	105	5.7
				20	-	0.2	19.4	231	-
Elders East (summer)	Sandy area (subtidal)	6/30/2005	AT	2	-	0.6	31.6	227	116.4
				7	-	0.5	27.1	165	34.3
				12	-	0.5	13.9	242	19.3
				20	-	0.2	21.3	96	21.4
		6/30/2005	AU	2	-	0.1	11.6	58	11.4
				7	-	0.1	3.9	18	11.4
		6/30/2005	AV	2	-	0.1	20.7	288	14.3
				7	-	0.9	0.3	-	-
				12	-	1.3	24.9	133	17.1

Table 5. Elders Point East and West pore water geochemical data (2005-2006) (continued).

Marsh	Location*	Date	Profile	Depth (cm)	Cl ⁻ (mM)	HS ⁻ (mM)	PO ₄ ³⁻ (μM)	NH ₄ ⁺ (μM)	NO ₂ ⁻ + NO ₃ ⁻ (μM)
Elders East (fall)	BL 600 5 m (marsh interior)	9/25/2005	BL	2	-	9.9	70.4	1245	5.7
				7	-	10.6	41.3	1245	8.6
				12	-	16.9	39.1	2175	5.7
				20	-	17.9	34.2	2149	5.7
		9/25/2005	BM	2	-	10.1	55.5	1214	8.6
				7	-	17.8	47.1	2354	2.9
				12	-	15.4	92.3	2418	5.7
				20	-	19.2	91.1	1929	5.7
		9/25/2005	BN	2	-	12.8	33.6	1414	5.7
				7	-	10.3	52.3	1137	5.7
				12	-	17.9	63.6	1471	120.0
				20	-	14.1	33.6	936	10.0
		11/19/2005	BW	2	-	10.6			
				7	-	9.3	56.8	1524	16.4
				12	-	11.2	29.4	1185	2.1
				20	-	7.3	24.2	1666	49.3
		11/19/2005	BY	2	-	0.2	-	-	-
				7	-	7.8	-	-	-
				12	-		-	-	-
				20	-	7.1	-	-	-
	BL 600 200m (marsh exterior)	11/19/2005	BO	2	392	4.5	87.2	841	34.3
				7	369	1.9	34.2	573	10.0
				12	313	3.7	32.0	628	10.7
				20	324	5.1	36.8	622	5.7
		11/19/2005	BP	2	325	2.1	53.6	642	8.6
				7	317	2.2	42.0	504	5.7
				12	337	2.9	19.1	524	5.7
				20	-	5.2			

Table 5. Elders Point East and West pore water geochemical data (2005-2006) (continued)..

Marsh	Location*	Date	Profile	Depth (cm)	Cl ⁻ (mM)	HS ⁻ (mM)	PO ₄ ³⁻ (μM)	NH ₄ ⁺ (μM)	NO ₂ ⁻ + NO ₃ ⁻ (μM)
2006 Elders West (summer)		11/19/2005	BZ	2	-	0.4	-	-	-
				7	-	4.4	-	-	-
				12	-	7.4	-	-	-
				20	-	3.9	-	-	-
	BL 300 0m Muddy Interior	8/11/2006	CX	2	362	6.1	68.5	1717	7.1
				7	399	1.9	25.8	753	57.9
				12	257	0.1	9.0	113	8.6
				20	359	0.1	120.8	353	5.7
		8/11/2006	CY	2	337	3.5	65.5	1552	5.0
				7	342	4.6	65.2	1615	3.6
				12	371	10.9	69.1	2021	3.6
				20	-	10.9	-	-	-
	BL 300 200m Sandy Edge	8/11/2006	CZ	2	376	0.2	18.4	220	4.3
				7	-	0.3	-	-	-
				12	-	0.6	20.0	218	4.3
				20	272	0.6	22.0	319	4.3
		8/11/2006	DA	2	302	0.1	5.5	136	5.7
				7	254	0.0	2.6	108	4.3
				12	144	0.0	4.8	60	2.9
				20	366	0.1	15.8	171	28.6
Elders East (fall)	Select fill	10/17/2006	DK	2	-	0.0	593	116	5.7
				7	-	3.8	-	466	2.9
				12	-	-	1315	-	-
				20	-	3.9	234	646	10.7

Table 5. Elders Point East and West pore water geochemical data (2005-2006) (continued).

Marsh	Location*	Date	Profile	Depth (cm)	Cl ⁻ (mM)	HS ⁻ (mM)	PO ₄ ³⁻ (μM)	NH ₄ ⁺ (μM)	NO ₂ ⁻ + NO ₃ ⁻ (μM)
		10/17/2006	DL	2	-	-	550	164	3.6
				7	-	-	-	76	4.3
				12	-	-	377	257	4.3
				20	-	-	888	-	-

*Site designations according to A. Kolker; lat/long not recorded

Table 6. Elders Point East pore water geochemical data- 2007.

Station ID	Sampling Date	Latitude (N)	Longitude (W)	Depth (cm)	pH	Eh	Cl ⁻ (mM)	HS ⁻ (mM)	PO ₄ ³⁻ (μM)	NH ₄ ⁺ (μM)	NO ₂ ⁻ + NO ₃ ⁻ (μM)
Spring											
ELDERS E-1	5/22/2007	40° 38.055'	73° 50.883'	2	7.2	-318	500	0.8	94	361	2
				7	7.2	-304	450	0.5	98	368	<1.0
				12	-	-	380	1.2	78	524	<1.0
				20	-	-	400	1.6	86	497	<1.0
ELDERS E-2	5/22/2004	40° 38.060'	73° 50.892'	2	7.2	-60	440	0.0	41	116	<1.0
				7	7.1	-142	410	0.0	103	349	<1.0
				12	7.0	-303	390	0.8	116	743	<1.0
				20	-	-	440	2.0	139	1200	2
ELDERS E-3	5/22/2007	40° 38.082'	73° 50.881'	2	-	-	500	0.0	112	376	2
Samples taken outside of hummock				6	7.3	-161	440	0.0	73	636	2
"				10	7.2	-117	420	0.0	15	655	2
"				15	7.1	-128	450	0.0	20	641	1
Samples taken in hummock				20	-	-	420	0.6	<0.3	<1.0	<1.0
"				30	-	-	360	1.1	<0.3	<1.0	<1.0
ELDERS E-4	5/22/2007	40° 38.110'	73° 50.873'	2	7.6	-198	410	0.0	162	490	2
Samples taken between hummocks				6	7.4	-282	400	0.3	180	786	<1.0
"				20	7.1	-365	470	1.5	142	1129	<1.0
"				30	-	-	490	1.6	214	1314	2

Table 6. Elders Point East pore water geochemical data- 2007 (continued).

	Sampling	Latitude	Longitude	Depth			Cl ⁻	HS ⁻	PO ₄ ³⁻	NH ₄ ⁺	NO ₂ ⁻ + NO ₃ ⁻
Station ID	Date	(N)	(W)	(cm)	pH	Eh	(mM)	(mM)	(μM)	(μM)	(μM)
ELDERS E-5	5/22/2007	40° 38.126'	73° 50.866'	2	7.9	-281	510	0.1	55	139	2
				6	7.5	-333	420	0.2	49	121	2
				10	7.2	-358	600	0.9	102	424	2
				15	7.3	-350	630	1.1	130	634	<1.0
ELDERS E-6	5/22/2007	40° 38.158'	73° 50.874'	2	7.8	-251	590	0.0	138	239	3
				6	7.6	-216	510	0.0	112	266	<1.0
				20	7.0	-321	530	0.3	96	419	<1.0
				30	-	-	640	1.8	176	1143	2
ELDERS E-7	5/22/2007	40° 38.156'	73° 50.719'	2	-	-	620	0.1	88	333	2
				6	-	-	420	1.0	195	986	2
				10	7.0	-350	470	0.9	141	661	2
ELDERS E-8	5/22/2007	40° 38.225'	73° 50.718'	2	8.0	-156	370	0.0	7	24	79
				6	7.8	-119	630	0.0	8	5	208
				20	7.3	-133	310	0.0	15	9	31
				30	7.2	-128	530	0.0	15	<1.0	59
ELDERS E-9	5/22/2007	40° 38.208'	73° 50.712'	10	7.6	-138	620	0.0	16	44	2
				20	7.6	-139	500	0.0	16	25	1
				Overlying Water	8.2	-84	390	0.0	4	12	16
Summer											
ELDERS E-1	8/28/2007	40° 38.055'	73° 50.880'	2	7.5	-213	448	0.1	48	229	3
				7	7.7	-190	451	0.3	67	316	<1.0
ELDERS E-2	8/28/2007	40° 38.062'	73° 50.892'	2	7.6	-153	465	0.0	29	296	3
				7	7.8	-161	471	0.0	39	385	5
				12	7.8	-187	516	0.2	192	1386	3
				20	-	-	547	2.5	307	2386	6

Table 6. Elders Point East pore water geochemical data- 2007 (continued).

Station ID	Sampling Date	Latitude (N)	Longitude (W)	Depth (cm)	pH	Eh	Cl ⁻ (mM)	HS ⁻ (mM)	PO ₄ ³⁻ (μM)	NH ₄ ⁺ (μM)	NO ₂ ⁻ + NO ₃ ⁻ (μM)
ELDERS E-3	8/28/2007	40° 38.085'	73° 50.883'	2	-	-	533	0.0	113	893	<1.0
				7	-	-	519	0.3	106	551	5
				12	-	-	564	0.0	78	1543	3
				20	-	-	601	0.3	190	1629	4
ELDERS E-4	8/28/2007	40° 38.108'	73° 50.874'	2	7.3	-224	516	1.9	208	1664	<1.0
				7	-	-	511	0.0	351	2086	5
				12	-	-	542	2.4	202	1736	<1.0
				20	7.0	-303	533	2.9	241	2014	<1.0
ELDERS E-5	8/28/2007	40° 38.120'	73° 50.873'	2	-	-	547	0.0	53	93	3
				7	-	-	539	1.8	196	1071	27
				12	7.4	-138	553	0.1	92	151	<1.0
				20	-	-	564	0.1	101	272	5
ELDERS E-6	8/28/2007	40° 38.160'	73° 50.872'	2	7.4	-191	513	1.5	77	750	4
				7	-	-	474	0.4	107	456	2
				12	-	-	465	0.2	111	471	3
				20	7.6	-277	491	0.7	111	647	<1.0
ELDERS E-8	8/28/2007	40° 38.231'	73° 50.712'	2	7.7	-155	522	0.0	51	245	5
				7	-	-	499	0.0	1	340	4
				12	7.9	-103	485	0.0	19	334	3
				20	7.8	-97	477	0.0	59	200	3
ELDERS E-9	8/28/2007	40° 38.269'	73° 50.758'	2	7.8	-38	451	0.0	38	103	3
				7	7.8	-59	454	0.0	62	248	5
				12	7.7	-72	437	0.0	85	341	2
				20	7.7	-84	460	0.0	87	291	3

Table 6. Elders Point East pore water geochemical data- 2007 (continued).

Station ID	Sampling Date	Latitude (N)	Longitude (W)	Depth (cm)	pH	Eh	Cl ⁻ (mM)	HS ⁻ (mM)	PO ₄ ³⁻ (μM)	NH ₄ ⁺ (μM)	NO ₂ ⁻ + NO ₃ ⁻ (μM)
Fall											
BAY WATER	10/22/2007				-	-	437	0.0	10	17	54
ELDERS E-1	10/22/2007	40° 38.057'	73° 50.876'	2	-	-	477	0.0	102	45	18
Select fill area				15	7.1	-125	477	0.9	129	401	16
				35	-	-	482	0.7	708	2486	55
				45	-	-	468	2.3	261	1186	20
ELDERS E-2	10/22/07	40° 38.058'	73° 50.890'	6	7.4	-107	457	0.1	68	168	14
Select fill area				2	7.6	110	460	0.1	54	124	15
				20	7.4	-203	477	1.5	106	786	17
				12	7.5	-231	468	0.2	99	395	13
ELDERS E-3	10/22/2007	40° 38.085'	73° 50.883'	2	7.5	31	480	0.0	37	70	14
Open area, between <i>Spartina</i> stands				6	7.1	-79	499	0.0	66	58	13
				12	-	-	516	0.0	116	183	14
				20	7.1	-145	556	0.0	275	1029	14
				50	-	-	604	1.3	148	1250	13
ELDERS E-4	10/22/2007	40° 38.108'	73° 50.876'	2	-	-	499	0.0	160	394	<1.0
<i>Ulva</i> -covered area, near <i>Spartina</i> stand				15	-	-	530	0.5	181	907	13
				35	7.0	7	542	2.3	180	1093	12
				45	-	-	530	2.2	205	1379	6
ELDERS E-5	10/22/2007	40° 38.124'	73° 50.872'	2	-	-	474	0.0	53	115	12
Site 50% <i>ASpartina</i> covered				6	7.4	-52	480	0.0	70	21	8
				12	7.0	-45	499	0.0	57	17	8
				20	6.8	-200	485	0.9	75	274	8
				50	-	-	508	2.5	224	1243	14

Table 6. Elders Point East pore water geochemical data- 2007 (continued).

Station ID	Sampling Date	Latitude (N)	Longitude (W)	Depth (cm)	pH	Eh	Cl ⁻ (mM)	HS ⁻ (mM)	PO ₄ ³⁻ (μM)	NH ₄ ⁺ (μM)	NO ₂ ⁻ + NO ₃ ⁻ (μM)
ELDERS E-6 Site 40% <i>Spartina</i> covered, <i>Ulva</i> present	10/22/2007	40° 38.146'	73° 50.869'	2	-	-	477	0.4	96	329	8
				6	6.7	-221	480	1.5	78	422	13
				12	6.8	-212	494	2.1	294	1050	13
				20	-	-	471	2.1	260	1121	17
ELDERS E-7 At edge of tidal creek near <i>Spartina</i> JB Coordinates EEBL 300W 043	10/22/2007	40° 38.165'	73° 50.834'	2	7.8	-209	485	0.0	51	44	15
				6	7.3	-184	471	0.0	33	16	13
				12	-	-	471	0.0	26	21	14
				20	7.3	-172	488	0.0	50	116	15
				30	7.3	-168	488	0.0	23	17	13
				Overlying water	8.8	-280	454	0.0	14	29	24
ELDERS E-8 Sandy nearshore area	10/22/2007	40° 38.228'	73° 50.713'	6	7.3	-162	525	0.0	79	366	14
				12	7.4	-241	556	0.0	139	589	14
				20	7.4	-241	556	0.0	179	671	15
				30	7.4	-64	556	0.0	203	771	15
ELDERS E-9 Sandy nearshore low area	10/22/2007	40° 38.262'	73° 50.755'	2	7.4	141	471	0.0	35	141	14
				6	7.7	-91	494	0.0	79	379	17
				12	7.7	-220	516	0.0	145	656	17
				20	7.3	-136	522	0.0	152	680	16
				30	7.3	-200	525	0.0	136	721	17

Table 7. Elders Point West pore water geochemical data- 2007.

Station ID	Sampling Date	Latitude (N)	Longitude (W)	Depth (cm)	pH	Eh	Cl ⁻ (mM)	HS ⁻ (mM)	PO ₄ ³⁻ (μM)	NH ₄ ⁺ (μM)	NO ₂ ⁻ + NO ₃ ⁻ (μM)
Spring											
ELDERS W-1	5/24/2007	40° 37.932'	73° 51.293'	2	-	-	490	0.0	9	159	3.7
				6	-	-	510	0.0	10	251	4.1
				12	7.5	-116	460	0.0	24	236	4.5
				20	-	-	360	1.4	136	886	1.6
				30	-	-	430	1.1	191	736	<1.0
ELDERS W-2	5/24/2007	40° 37.945'	73° 51.255'	2	7.5	-192	460	0.1	12	106	1.2
				15	7.2	-312	490	1.3	50	574	<1.0
				25	7.0	-367	460	2.0	-	-	-
ELDERS W-3	5/24/2007	40° 37.927'	73° 51.221'	2	6.8	-251	310	0.0	25	155	2.5
				7	-	-	490	0.3	79	394	2.5
				12	-	-	430	0.7	93	101	0.8
				20	-	-	460	1.2	170	557	4.1
ELDERS W-4	5/24/2007	40° 37.845'	73° 51.257'	2	7.3	-191	480	0.0	9	89	<1.0
				7	7.2	-247	390	0.1	13	111	3.0
				12	-	-	490	0.1	48	272	3.0
				20	-	-	480	0.8	94	633	3.7
ELDERS W-5	5/24/2007	40° 37.846'	73° 51.326'	2	-	-	480	0.0	19	311	7.3
				12	7.5	-259	440	0.1	35	229	1.6
				20	7.3	-321	500	0.2	46	271	2.8
				30	-	-	410	0.0	48	289	<1.0
ELDERS W-6	5/24/2007	40° 37.827'	73° 51.392'	2	-	-	450	0.0	11	280	2.7
				12	7.7	-163	520	0.0	23	101	0.7
				20	-	-	370	0.0	20	239	<1.0
				30	-	-	420	0.0	30	250	3.3

Table 7. Elders Point West pore water geochemical data- 2007 (continued).

	Sampling	Latitude	Longitude	Depth			Cl ⁻	HS ⁻	PO ₄ ³⁻	NH ₄ ⁺	NO ₂ ⁻ + NO ₃ ⁻
Station ID	Date	(N)	(W)	(cm)	pH	Eh	(mM)	(mM)	(μM)	(μM)	(μM)
Summer											
NEARSHORE BAY WATER					-	-	434	0.0	9	47	18.1
ELDERS W-2	8/29/2007	40° 37.940'	73° 51.292'	2	-	-	451	1.0	101	729	7.1
				6	-	-	454	1.1	109	514	7.2
				12	7.5	-525	454	2.0	67	764	2.6
				20	-	-	474	1.7	77	779	4.8
				30	-	-	482	2.3	74	843	8.3
ELDERS W-4	8/29/2007	40° 37.917'	73° 51.125'	2	-	-	474	0.2	230	1029	7.5
				15	-	-	474	1.1	155	764	<1.0
				25	-	-	463	1.2	103	936	5.0
ELDERS W-5	8/29/2007	40° 37.855'	73° 51.317'	2	-	-	465	0.0	33	244	2.6
				6	-	-	465	0.0	0	0	0.0
				12	7.7	-304	448	0.8	41	786	3.4
				20	-	-	451	2.3	62	1479	5.0
				30	-	-	468	1.4	103	1350	20.1
ELDERS W-6	8/29/2007	40° 37.827'	73° 51.390'	2	8.0	-185	465	0.0	35	191	3.0
				15	-	-	477	0.0	62	344	3.6
				25	7.9	-161	448	0.4	51	254	5.3
				55	7.8	-266	440	0.4	35	194	3.6
ELDERS W-7	8/29/2007	40° 37.936'	73° 51.275'	2	-	-	448	0.0	11	55	18.1
				7	-	-	454	0.0	22	177	11.0
				12	-	-	437	0.1	45	308	4.2
				20	-	-	423	0.1	46	206	5.7
				30	-	-	468	0.7	99	295	5.5

Table 7. Elders Point West pore water geochemical data- 2007 (continued).

	Sampling	Latitude	Longitude	Depth			Cl ⁻	HS ⁻	PO ₄ ³⁻	NH ₄ ⁺	NO ₂ ⁻ + NO ₃ ⁻
Station ID	Date	(N)	(W)	(cm)	pH	Eh	(mM)	(mM)	(μM)	(μM)	(μM)
ELDERS W-8	8/29/2007	40° 37.877'	73° 51.347'	2	7.6	-135	474	0.0	20	155	4.6
				15	7.5	-147	505	0.0	23	170	5.0
				25	7.3	-131	522	0.0	12	134	3.2
				35	-	-	468	0.0	10	89	33.2
Fall											
NEARSHORE BAY WATER					-	-	437	0.0	10	17	53.7
10/22/2007											
ELDERS W-1 Open mud flat	10/23/2007	40° 37.947'	73° 51.296'	2	-	-	488	0.6	66	410	7.4
				6	7.0	-316	465	2.4	54	692	8.1
				12	7.4	-339	465	2.5	72	626	13.1
				20	7.5	-276	474	2.5	85	508	11.4
ELDERS W-2 Sandy area, near shoreline	10/23/2007	40° 37.937'	73° 51.292'	2	-	-	471	0.0	22	179	12.8
				6	7.7	-282	485	1.1	46	368	13.6
				20	7.8	-341	480	1.9	88	516	12.2
ELDERS W-4 Mud flat near isolated <i>Spartina</i> hummock	10/23/2007	40° 37.847'	73° 51.255'	2	7.4	-203	471	2.2	85	921	12.3
				12	-	-	457	2.6	356	2014	20.0
ELDERS W-5 Transitional area between tall-form <i>Spartina</i> and short form, <i>Ulva</i> -covered, 50% <i>Spartina</i> coverage	10/23/2007	40° 37.847'	73° 51.328'	6	7.5	-304	465	1.7	93	414	8.1
				20	-	-	463	1.0	144	476	13.4
				50	-	-	463	1.6	130	524	<1.0
ELDERS W-6 Transitional area between mud flat and <i>Spartina</i> stand, <i>Ulva</i> -covered	10/23/2007	40° 37.826'	73° 51.386'	2	8.0	-233	446	0.1	74	160	12.6
				6	7.8	-311	465	0.8	129	330	12.3
				12	-	-	471	1.3	102	486	12.6
				20	-	-	463	1.8	92	501	12.6
				50	7.1	-303	448	1.8	54	448	<1.0

Table 7. Elders Point West pore water geochemical data- 2007 (continued).

Station ID	Sampling Date	Latitude (N)	Longitude (W)	Depth (cm)	pH	Eh	Cl ⁻ (mM)	HS ⁻ (mM)	PO ₄ ³⁻ (μM)	NH ₄ ⁺ (μM)	NO ₂ ⁻ + NO ₃ ⁻ (μM)
ELDERS W-8 Open sandy area, <i>Ulva</i> -covered.	10/23/2007	40° 37.877'	73° 51.347'	2	–	–	480	0.0	57	163	<1.0
				6	7.7	-329	474	0.1	34	197	<1.0
				12	7.7	-366	494	0.2	29	184	<1.0
				20	7.6	-383	502	0.1	24	154	<1.0
				30	7.5	-401	494	0.2	15	121	<1.0
				40	7.3	-300	488	0.3	12	111	<1.0
				50	7.3	-322	494	0.0	22	143	<1.0

Table 8. Big Egg marsh solid phase geochemical data (2005; 40° 35.772'N, 73° 49.571'W).

Depth (cm)	N (wt. %)	C (wt. %)	S (wt. %)	Total S (mmol/g)	C/S (mol/mol)	C/N (mol/mol)	CRS ¹ (mmol/g)	AVS ² (mmol/g)	Leachable Fe (mmol/g)	Pyrite Fe ³ (mmol/g)	Pyrite Fe ⁴ (mmol/g)	Degree of Pyritization ³	Degree of Pyritization ⁴
0-3	1.00	13.0	1.71	1219	8.9	15.2	760	0.9	126	380	609	0.75	0.83
3-6	0.61	7.3	0.68	485	13	14.1	660	20.1	125	320	232	0.72	0.65
6-9	0.88	13.2	0.74	525	21	17.6	740	32	99	354	247	0.78	0.71
9-12	0.77	11.0	0.86	613	14.9	16.5	1140	23.3	99	558	295	0.85	0.75
12-16	0.65	9.1	1.43	1024	7.4	16.3	820	17.9	100	401	503	0.80	0.83
16-20	0.74	9.5	1.01	722	11	15.0	860	25	113	418	349	0.79	0.76
20-25	0.67	8.6	1.03	737	9.7	15.1	890	96.7	175	397	320	0.69	0.65
25-30	0.99	18.9	0.79	561	28	22.3	690	11.7	110	339	275	0.76	0.71

¹ Chromium-reducible sulfur (FeS + FeS₂)

² Acid volatile sulfide (FeS)

³ Pyrite Fe (FeS₂) calculated from CRS and AVS

⁴ Pyrite Fe (FeS₂) calculated from total S and AVS

Table 9. JoCo and Elders Point solid phase geochemical data.

Location	Sampling date	Latitude (N)	Longitude (W)	Depth in core (cm)	H ₂ O (%)	N (wt. %)	C (wt. %)	S (wt. %)	Total S (mmol/g)	Acid Volatile Sulfide (mmol/g)	Leachable Fe (mmol/g)	Pyrite Fe (mmol/g)	Acid Volatile Sulfide (wt. %)	Degree of Pyritization
JoCo														
JoCo 1	5/21/2007	40° 36.715'	73° 47.184'	0-5	87.7	1.81	22.2	1.40	438	0.0	62.3	219	0.0	0.78
				5-10	85.0	1.14	31.3	2.24	700	0.0	27.4	350	0.0	0.93
				10-15	80.0	1.61	22.3	3.06	955	0.0	20.4	478	0.0	0.96
				15-20	77.3	1.38	18.6	4.42	1383	0.0	49.1	691	0.0	0.93
				20-25	87.4	1.07	30.4	3.49	1091	0.3	52.3	545	0.0	0.91
JoCo 2	5/21/2007	40° 36.701'	73° 47.212'	0-5	74.5	1.32	14.8	1.16	362	0.0	75.4	181	0.0	0.71
				5-10	70.5	1.13	13.5	1.81	565	0.0	81.1	283	0.0	0.78
				10-15	77.6	1.18	13.7	1.85	579	0.0	89.1	289	0.0	0.76
				15-20	80.3	0.95	21.0	4.61	1441	0.0	67.8	720	0.0	0.91
				20-25	87.7	0.89	14.6	4.46	1394	0.5	86.3	697	0.0	0.89
				25-30	80.8	0.72	10.3	3.31	1033	0.1	94.9	517	0.0	0.84
JoCo 1 100% <i>Spartina</i> Coverage JB Coordinates RBL 100W024	10/24/2007	40° 36.719'	73° 47.184'	0-5	81.2	1.89	23.2	1.65	515	0.0	58.1	258	0.0	0.82
				5-10	82.0	1.84	25.1	3.82	1192	0.0	6.8	596	0.0	0.99
				10-15	83.4	1.53	23.3	2.88	899	1.6	20.1	449	0.2	0.96
				15-20	79.1	1.39	18.0	2.54	793	1.4	58.2	396	0.2	0.87
				20-25	83.7	1.40	22.6	2.73	855	0.4	24.0	427	0.0	0.95
Elders West														
Elders West 2 Sand between tussocks	5/24/2007	40° 37.945'	73° 51.255'	0-5	23.8	0.04	0.3	0.18	55	17.7	26.0	19	32.0	0.42
				5-10	24.3	0.02	0.3	0.19	60	10.4	18.4	25	17.5	0.57
				10-15	22.0	0.04	1.2	0.26	80	7.1	21.7	37	8.9	0.63
				15-20	23.5					4.1	22.2			
				20-25	29.4	0.04	0.5	0.35	109	3.2	32.6	53	2.9	0.62
				25-30	42.5	0.12	1.6	0.74	232	4.0	73.1	114	1.7	0.61

Table 9. JoCo and Elders Point solid phase geochemical data (continued).

Location	Sampling date	Latitude (N)	Longitude (W)	Depth in core (cm)	H ₂ O (%)	N (wt. %)	C (wt. %)	S (wt. %)	Total S (mmol/g)	Acid Volatile Sulfide (mmol/g)	Leachable Fe (mmol/g)	Pyrite Fe (mmol/g)	Acid Volatile Sulfide (wt. %)	Degree of Pyritization
Elders West 4	5/24/2007	40° 37.845'	73° 51.257'	0-5	20.1	0.04	0.3	0.14	42	0.2	17.8	21	0.4	0.54
Near tussock				5-10	27.9	0.03	0.5	0.17	55	5.5	27.1	25	10.1	0.48
				10-15	39.0	0.10	1.1	0.91	286	0.1	95.3	143	0.0	0.60
				15-20	40.6	0.15	1.5	1.24	389	0.0	113.4	194	0.0	0.63
				20-25	41.6	0.15	1.5	1.35	423	0.3	192.1	211	0.1	0.52
Elders West 5	0920 5/24/07	40° 37.846'	73° 51.326'	0-5	16.1	0.04	0.3	0.18	56	9.2	15.3	23	16.5	0.61
Mud flat between tussocks				5-10	16.5	0.02	0.3	0.14	44	7.4	23.9	18	16.7	0.43
				10-15	20.6	0.02	0.2	0.13	42	6.4	14.9	18	15.2	0.54
				15-20	52.8	0.21	3.0	1.11	346	3.0	33.1	171	0.9	0.84
				20-25	47.2	0.38	4.7	2.67	834	2.5	110.5	416	0.3	0.79
				25-30	55.2	0.29	3.4	1.79	559	2.6	118.3	278	0.5	0.70
Elders West 6	5/24/2007	40° 37.827'	73° 51.392'	0-5	21.3	0.01	0.2	0.13	40	0.6	18.9	20	1.6	0.51
				5-10	22.7	0.00	0.6	0.11	33	1.2	13.3	16	3.7	0.55
				10-15	17.2	0.00	0.0	0.10	30	14.4	14.6	8	47.4	0.35
				15-20	17.8	0.01	0.0	0.10	30	23.8	81.7	3	80.2	0.03
October, 2007 Elders West 1	10/23/2007	40° 37.947'	73° 51.296'	0-5	17.9	0.02	0.2	0.16	49	5.8	11.7	21	11.9	0.65
Open mud flat				5-10	24.0	0.03	0.3	0.16	49	3.3	15.1	23	6.6	0.60
				10-15	45.5	0.21	2.8	1.48	462	3.6	91.2	229	0.8	0.72
				15-20	49.1	0.14	2.5	1.71	534	2.0	66.6	266	0.4	0.80
				20-25	53.4	0.25	4.6	1.68	525	2.0	85.9	261	0.4	0.75
				25-30	44.0	0.18	1.9	1.48	463	2.4	112.1	230	0.5	0.67

Table 9. JoCo and Elders Point solid phase geochemical data (continued).

Location	Sampling date	Latitude (N)	Longitude (W)	Depth in core (cm)	H ₂ O (%)	N (wt. %)	C (wt. %)	S (wt. %)	Total S (mmol/g)	Acid Volatile Sulfide (mmol/g)	Leachable Fe (mmol/g)	Pyrite Fe (mmol/g)	Acid Volatile Sulfide (wt. %)	Degree of Pyritization
Elders East														
Elders East	2005			0-3	-	-	-	-	344*	36.5	60.0	344	-	0.72
Pre-restoration; site BL-6009				3-6	-	-	-	-	601	26.9	73.0	601	-	0.80
				6-9	-	-	-	-	376	18.8	75.0	376	-	0.70
				9-12	-	-	-	-	373	10.9	70.0	373	-	0.72
				12-16	-	-	-	-	567	12.0	98.0	567	-	0.74
				16-20	-	-	-	-	639	22.8	131.0	639	-	0.70
				20-25	-	-	-	-	486	33.3	129.0	486	-	0.64
Elders East 1														
	5/22/2007	40° 38.055'	73° 50.883'	0-5	59.3	0.37	3.6	1.56	487	11.4	139.4	238	2.3	0.63
				5-10	58.3	0.21	2.8	1.27	397	2.5	75.7	197	0.6	0.72
				10-15	78.9	0.62	7.8	3.27	1022	7.6	180.9	507	0.7	0.74
				15-20	59.8	0.62	7.8	3.13	979	11.0	207.3	484	1.1	0.70
				20-25	70.0	0.56	6.9	3.46	1080	7.5	168.3	536	0.7	0.76
				25-30	69.2	0.50	6.2	3.04	951	3.8	269.6	474	0.4	0.64
Elders East 2														
	5/22/2007	40° 38.060'	73° 50.892'	0-5	16.7	0.01	0.1	0.06	18	0.0	29.3	9	0.1	0.24
				5-10	18.6	0.00	0.0	0.05	16	26.1	29.7	-5	~100	0.00
				10-15	25.3	0.11	1.0	0.43	135	20.2	57.9	57	15.0	0.50
				15-20	62.8	0.50	6.4	3.29	1028	2.3	114.5	513	0.2	0.82
				20-25	72.9	0.61	7.7	2.89	905	3.5	167.2	451	0.4	0.73
				25-30	68.2	0.55	6.8	4.17	1302	2.8	165.9	649	0.2	0.80
Elders East 3														
	5/22/2007	40° 38.082'	73° 50.881'	0-5	36.1	0.23	2.7	1.95	610	1.5	17.7	304	0.2	0.95
				5-10	15.5	0.01	0.2	0.04	13	5.3	27.1	4	39.2	0.13
				10-15	13.5	0.02	1.2	0.03	9	2.0	39.7	4	21.3	0.09
				15-20	13.2	0.00	0.0	0.00	1	13.0	21.0	-6	~100	0.00

Table 9. JoCo and Elders Point solid phase geochemical data (continued).

Location	Sampling date	Latitude (N)	Longitude (W)	Depth in core (cm)	H ₂ O (%)	N (wt. %)	C (wt. %)	S (wt. %)	Total S (mmol/g)	Acid Volatile Sulfide (mmol/g)	Leachable Fe (mmol/g)	Pyrite Fe (mmol/g)	Acid Volatile Sulfide (wt. %)	Degree of Pyritization
Elders East 6	5/22/2007	40° 38.158'	73° 50.874'	0-5	23.0	0.04	0.3	0.00	0.2	39.9	36.5	-20	~100	0.00
North end of select fill				5-10	22.1	0.00	0.1	0.05	16	14.7	16.5	1	93.0	0.03
				10-15	18.4	0.02	0.6	0.05	15	11.8	23.8	2	76.2	0.07
				15-20	19.1	0.01	0.1	0.08	26	23.1	15.1	1	90.1	0.08
				20-25	20.7	0.00	0.1	0.00	1	21.8	14.5	-10	~100	0.00
Elders East 2	10/22/2007	40° 38.058'	73° 50.890'	0-5	30.1	0.16	1.0	0.38	119	30.3	34.6	44	25.4	0.56
Select fill area, near <i>Spartina</i> hummock.				5-10	17.4	0.00	0.1	0.18	55	34.7	32.8	10	62.7	0.24
				10-15	19.6	0.03	0.2	0.19	60	41.8	40.2	9	69.3	0.19
				15-20	57.1	0.39	5.2	1.36	426	22.7	147.4	202	5.3	0.58
				20-25	52.3	0.35	5.5	1.69	528	10.5	106.4	259	2.0	0.71
				25-30	63.3	0.50	6.6	3.23	1009	6.0	168.1	502	0.6	0.75

* Measured as chromium-reducible sulfur

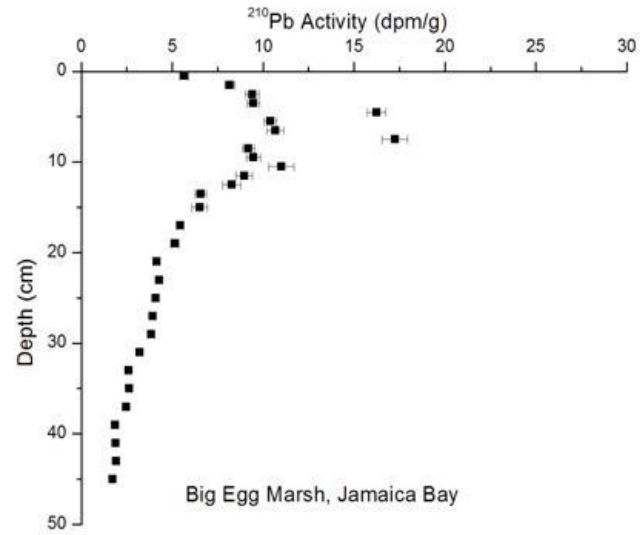
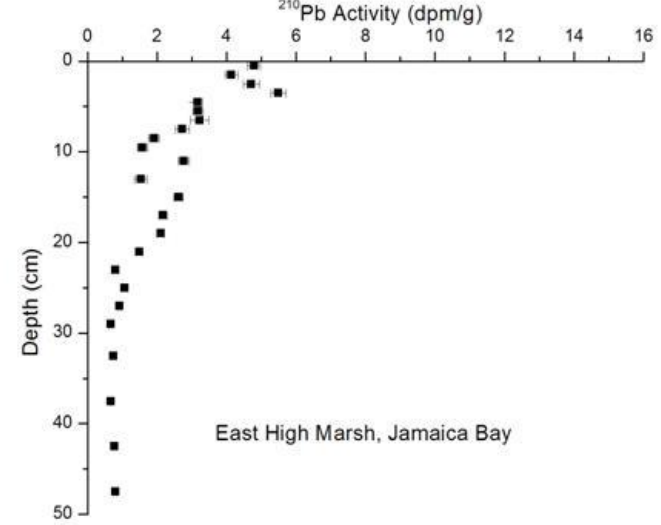
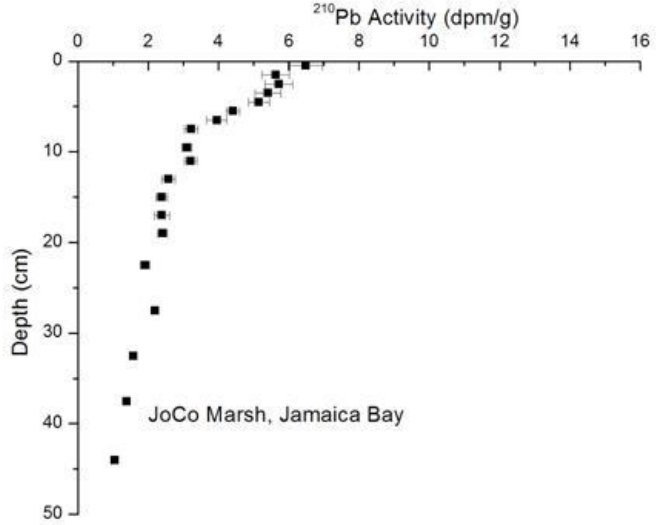


Figure 7. Profiles of ^{210}Pb in salt marsh cores.

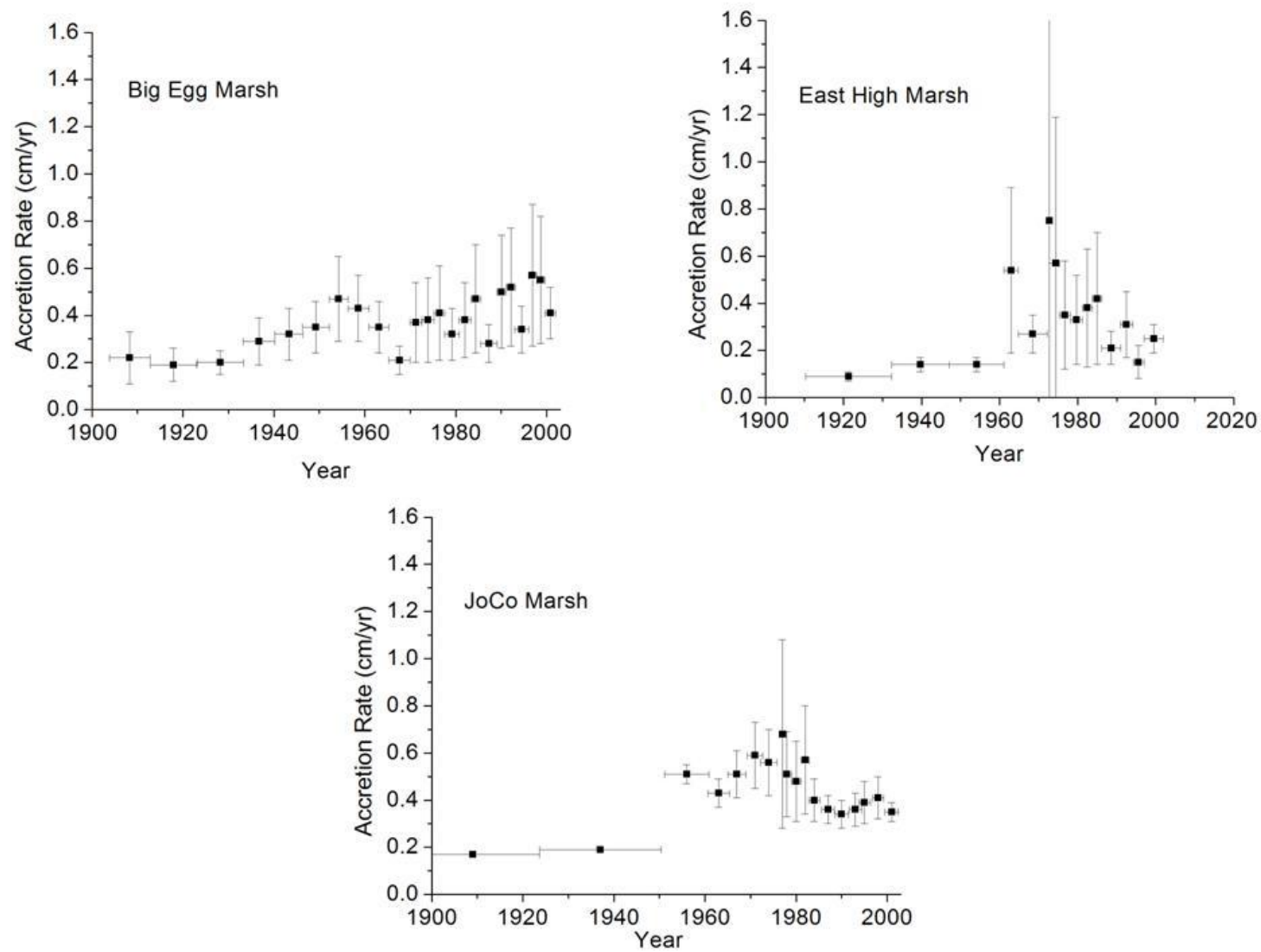


Figure 8. Accretion rate chronologies of Jamaica Bay marsh cores derived from ^{210}Pb (from Kolker, 2005).

Discussion

Pore Water Sulfides

The Jamaica Bay marshes are highly sulfidic systems. All the sites examined generally show increases in pore water sulfide with depth in the marsh peat. This pattern is reasonable based on the importance of sulfate reduction as a mechanism for the oxidation of organic matter in marine deposits. There also appear to be important differences in the spatial and temporal patterns of pore water and solid phase sulfur among the sites studied and we consider each in turn.

Big Egg Marsh

Big Egg marsh was sampled only in the period 2004-2005 (Table 2). Although restoration efforts were undertaken in 2003, the sites sampled were in still-degraded portions of the marsh interior and along the bank of a creek draining the marsh. The root zone of *S. alterniflora* varies among marshes from the upper 10 to 20 cm of the marsh, as shown by Davey et al. (2011) using computed tomography (CT) imaging. Their results for two marshes in Jamaica Bay (JoCo and Black Bank) show that the root zone extended to 20 cm and that 55-63% of the coarse and fine roots and rhizomes occurred in the upper 10 cm of the marsh. Pore water hydrogen sulfide concentrations generally increase with depth in the marsh (Tables 2-7; Figs. 9-12). We use the sulfide concentrations at ~10 cm to compare sites, recognizing that root zones that extend to 20 cm may experience greater sulfide concentrations than observed at 10 cm. At Big Egg, marsh plants at the creek bank site were generally exposed to higher pore water sulfide concentrations than in the interior (~1.3 – 7.6 mM vs. 0.5 – 4.9 mM). At times, both sites experienced concentrations that would be considered stressful to *Spartina*, and the creek bank site had concentrations sufficient to cause mortality if the plants were exposed for extended periods. The higher concentrations at the creek bank are noteworthy because such sites are thought to have lower sulfide concentrations than interior regions of a marsh due to their enhanced ability to drain (King et al. 1982). Instead, the higher sulfide concentrations near the creek margin may indicate enhanced tidal loading of organic matter on the marsh surface there relative to the interior. Concentrations in the root zone of the interior site reached toxic levels, ~5mM at 11 cm (but were as high as 7.2 mM at 21 cm; Table 2) on August 4, 2004, and were consistently high (4.3 – 7.6 mM) in the upper 20 cm at the creek bank site on the same date, indicating that sulfide concentrations in Big Egg Marsh were very high during the summer of 2004.

There is also a suggestion of seasonal (if not interannual) variability in the Big Egg data. Concentrations of pore water sulfide were greater in summer, 2004 than in spring 2005 at both the interior and creek bank sites (Table 2). Air temperatures were 22-25°C during sample collection in 2004 and 10-16°C in 2005. Microbial sulfate reduction is temperature-dependent, and it is likely that the 2005 sampling represented seasonally lower rates of sulfide production. Detailed seasonal sampling elsewhere in Jamaica Bay in 2007 was designed to test this possibility.

JoCo Marsh

JoCo marsh represents a stable marsh in Jamaica Bay, and sampling was carried out in 2005, 2006 and 2007 (Tables 3, 4). Using a sampling depth of ~10 cm to represent the mid-depth of the *Spartina* root zone, pore water sulfide at all sites sampled in 2005-2006 in JoCo varied from 3.1 – 4.2 mM in September, 2005, 0.3 – 3.1 in August, 2006, 2.3 – 4.5 in September, 2006 and 0.9 – 2.5 in October, 2006 (Table 3). These data represent snapshots in time and principally reflect

summer-early fall conditions, a time when sulfide production would likely be highest. The sampling in 2007 was done in May, August and October and was designed to bracket the seasons (Table 4). Concentrations of pore water sulfide in 2007 were systematically lower than in 2005-2006 (Tables 3 and 4). Fig. 9 is a composite of the 2007 profiles, plotting averages for a given depth and sampling time. The general increase in sulfide with depth is seen, but mean concentrations do not exceed 2 mM in the upper ~50 cm. There is also no strong seasonal dependence (Fig. 9), although mean values at 30 cm are highest in the summer sampling. The difference between the 2005-2006 and 2007 data may reflect interannual differences in organic loading to the marsh surface (and consequent different rates of sulfide production as the organic matter is oxidized by sulfate reduction). These data suggest that *Spartina* in JoCo marsh may be subject to stressful levels of [HS⁻] at some times, but that this is not a permanent situation. Indeed, the levels seen in 2007 are consistently below or at the lower limit of [HS⁻] that is stressful (Fig. 3). Another noteworthy aspect of sulfur cycling at JoCo is the presence of low pH, positive Eh and low pore water [HS⁻] in the upper few cm (Table 4). This suggests active oxidation of solid phase sulfides (eqn. 2), either via transport of O₂ by the roots, bioirrigation or effective drainage.

Elders Point Marsh

Elders Point marsh was sampled before and after the restoration of the Elders East site. Samples were also collected at Elders West, an unrestored area, for comparison. There is considerable spatial variation in pore water solute profiles at Elders, particularly after the restoration. In part this is because the sites sampled range from open mud flat to sandy, vegetated areas. Even the latter have spatial variability, with incomplete marsh grass coverage in 2007. Nevertheless, the patterns in pore water [HS⁻] seen at Elders East represent a striking contrast before and after restoration. Sulfide concentrations at 12 cm ranged from 15.4 – 17.9 mM in the interior of the marsh September, 2005, and from 3.7 – 7.4 mM in the exterior in November, 2005 (Table 5). These levels are clearly in the toxic range and would cause mortality if *Spartina* were exposed to them for long periods of time. Values at ~10 cm were markedly lower after restoration in 2007: 0 – 1.2 mM in May, 0 – 2.4 in August and 0 – 2.1 in October (Table 6; Fig. 10). As with JoCo marsh there seems relatively little seasonal variation in pore water [HS⁻] with depth in the peat in 2007, although average values are higher in the upper few centimeters of the peat in summer (Fig. 10). The difference between the fall pre- and post-restoration conditions at Elders East is shown in Fig. 11. There are significantly lower concentrations at all depths post-restoration.

At Elders West, pore water sulfide at 12 cm ranged from 0.2 – 6.3 mM in June, 2005 and 0 – 10.9 mM in August, 2006 (Table 5). The seasonal sampling in 2007 showed that HS⁻ values at 12-15 cm were ~0 – 1.3 mM in May, ~0 – 2 mM in August and 0.15 – 2.6 mM in October (Table 7; Fig. 10). Some of the spatial and even interannual variation in the data may be due to the fact that the different sampling sites at Elders West, especially, had very different sediment characteristics. In particular, the grain size (as seen in water content) and organic matter content differed considerably among the sites (Table 9). Because stations were re-occupied three times in 2007, the data from that year are more intercomparable.

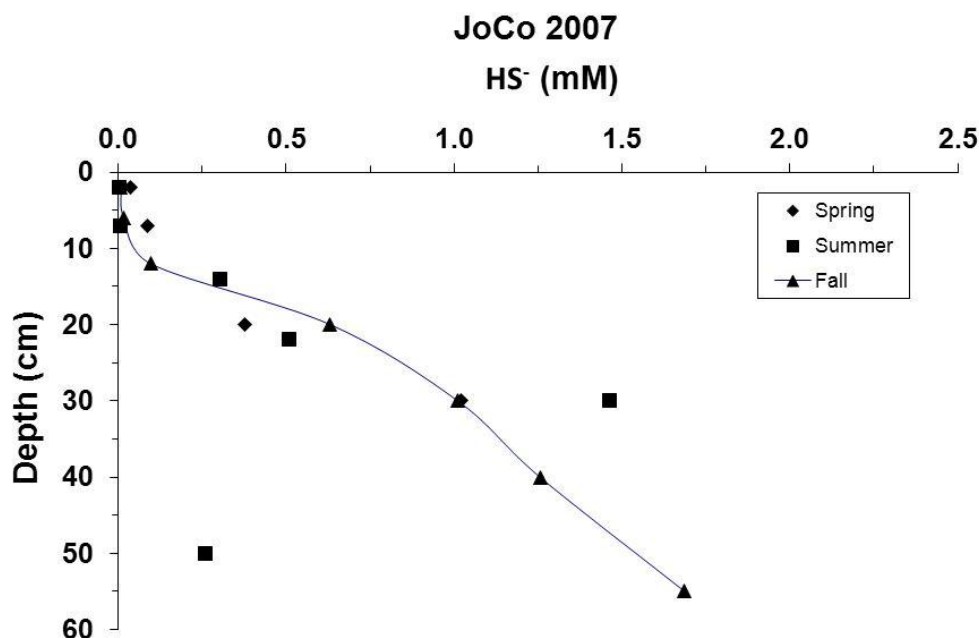


Figure 9. Pore water hydrogen sulfide concentrations at JoCo marsh (sample collected in 2007). Values at each depth represent averages of multiple samples taken at the indicated sampling time. Line connects data from the fall sampling.

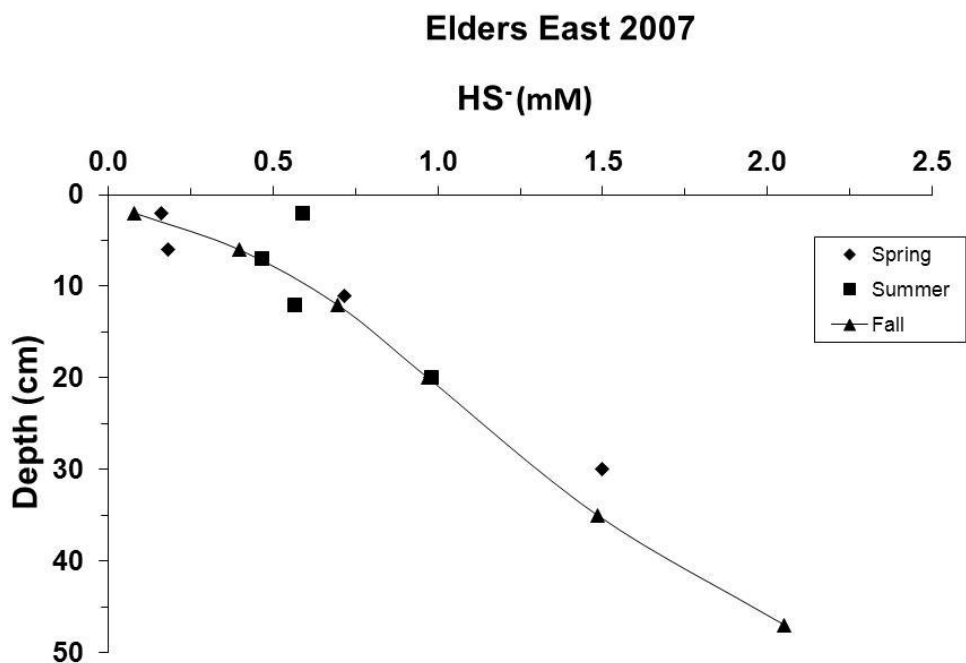


Figure 10. Pore water hydrogen sulfide concentrations at Elders Point East marsh (samples taken in 2007). Values at each depth represent averages of multiple samples taken at the indicated sampling time. Line connects data from the fall sampling.

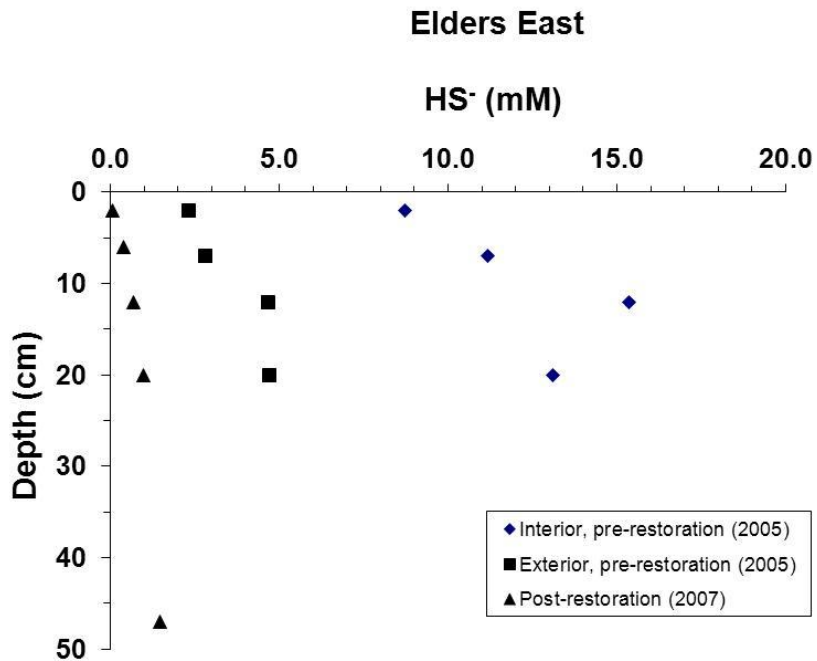


Figure 11. Pore water hydrogen sulfide concentrations at Elders Point East marsh taken before and after the restoration of the marsh. Values at each depth represent averages of multiple samples taken at each site.

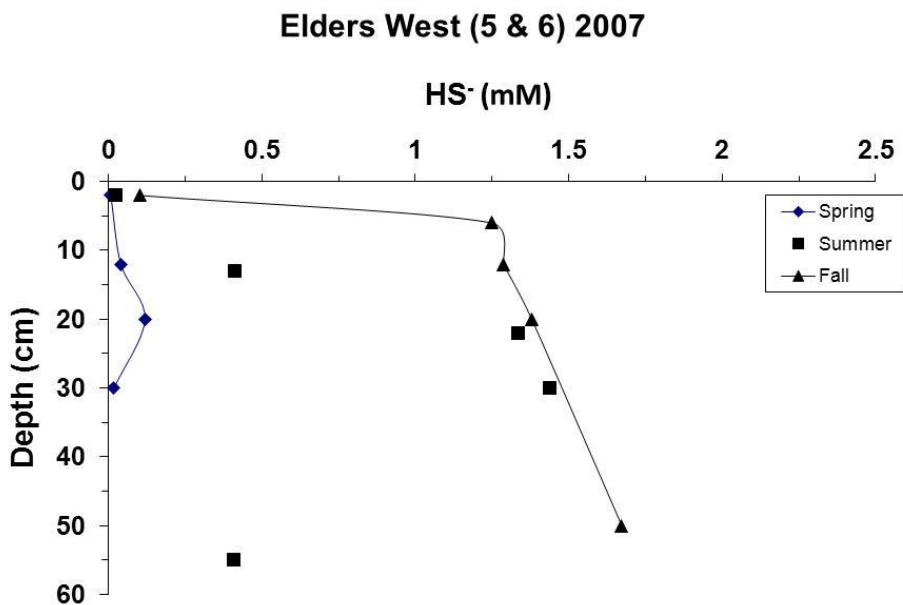
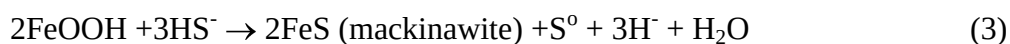


Figure 12. Pore water hydrogen sulfide concentrations at Elders Point West marsh (samples taken in 2007). Values at each depth represent average of multiple samples taken at the indicated sampling time. Lines connect data from the fall and spring samplings. Sampling sites 5 and 6 have been chosen as representative of the marsh.

Solid Phase Sulfur

Solid phase sulfur is a particularly useful measure of sulfur dynamics because it effectively integrates sulfide concentrations over longer time periods. In this study, the AVS pool is assumed to be iron monosulfides (FeS), which are readily formed in salt marsh sediments (Koska and Luther, 1995). The remaining sulfur reservoirs in the solid phase are organic sulfur and pyrite (FeS₂). Chromium-reducible sulfur, measured in 2005, is considered to be largely pyrite (FeS₂), which is generally formed and destroyed over longer time scales than the AVS pool (Ferdeman et al., 1991; Goldhaber and Kaplan, 1974; Howarth, 1984; Howarth and Teal, 1979). The CRS fraction also includes acid volatile sulfur. In contrast, total sulfur, as measured but a CHNS analyzer, includes all the sulfur reservoirs (FeS, FeS₂ and organic). All three sulfur reservoirs were measured in the Big Egg samples collected in 2005 (Table 8) and the data show that the total S and CRS pools are larger than the AVS pool. In general the CRS and total S concentrations are comparable, indicating that most of the total sulfur is bound as pyrite, and that the organic sulfur fraction is minimal. In some of the samples, the CRS sulfur is greater than the total sulfur, suggesting that one of these methods is more accurate than the other. Additionally, this discrepancy may stem from sample heterogeneity related to the very small sample sizes (0.05-0.1g) used in both procedures. Nevertheless the overall pattern suggests that most of the total sulfur is bound as pyrite in both settings.

The formation of iron sulfides is highly complex and involves numerous intermediate stages (Burdige, 1993; Morse et al., 1987). However, a simplified version of AVS formation is as follows:



Pyrite may be formed according by (Goldhaber and Kaplan, 1974):



or



The AVS concentrations in the marshes studied vary as: Big Egg $\geq$ Elders East > Elders West > JoCo (Tables 8 and 9). Total S (largely pyrite) varies less among the sites, although Elders West has lower concentrations on average than Elders East, Big Egg or JoCo. If Fe is assumed not to be limiting in these settings, higher concentrations of iron sulfides suggest higher long-term exposure to pore water sulfide in a given marsh environment.

Another way of comparing the sulfur pools at the different sites is to take into consideration the fraction of reactive Fe associated with pyrite at each site. This “degree of pyritization” (DOP) expresses the extent to which Fe in the sediment is unavailable to react further with pore water sulfide as it is produced. As the sediment Fe pool becomes “saturated” with sulfides, the sediment loses its ability to buffer or “titrate” pore water sulfide, which can then build up to levels toxic to *Spartina* (Berner, 1984; Leventhal and Taylor, 1990; Raiswell and Canfield, 1998). The degree of pyritization is expressed as:

$$DOP = \frac{Fe_{Pyrite}}{Fe_{Pyrite} + Fe_{Leach}} \quad (6)$$

where

$$Fe_{Pyrite} = \frac{CRS(or S_{total}) - AVS}{2} \quad (7)$$

and Fe_{Leach} is amount of Fe leached in 1N HCl for 24 hrs. Note that it does not make a large difference whether CRS sulfur or total sulfur is used to calculate the DOP. Table 8 compares the two possibilities for Big Egg and the values agree within 10%. For discussion, we use the values calculated using S_{total} in eqn. 7.

In terms of degree of pyritization, the marshes rank as: JoCo > Big Egg $\geq$ Elders East (pre-restoration) > Elders West. Absolute values in these unrestored sites range from 0.35 to 0.96. Figure 13 shows the comparison for JoCo, Elders East (restored) and Elders West in May, 2007. Both Elders West and East (restored) have lower DOP values than JoCo. The restoration of Elder East served to “reset” the DOP (Fig. 14), such that DOP values in the upper 15 cm of the sediment are lower after restoration. This is likely related to the fresh sediment emplaced during the restoration process. With time, the DOP values will increase as pore water sulfide reacts with available Fe to form pyrite.

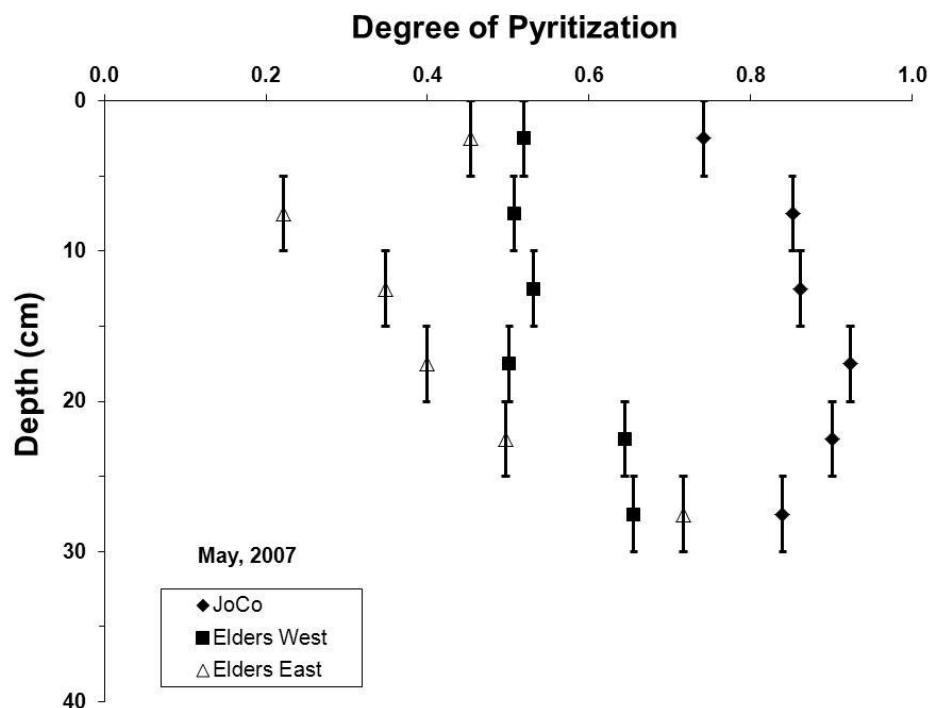


Figure 13. “Degree of Pyritization” (DOP) as a function of depth at JoCo, Elders Point East and West marshes. The DOP indicates the extent to which reactive Fe in the solid phase in each marsh is associated with pyrite (FeS_2). Profile at Elders East represents post-restoration conditions.

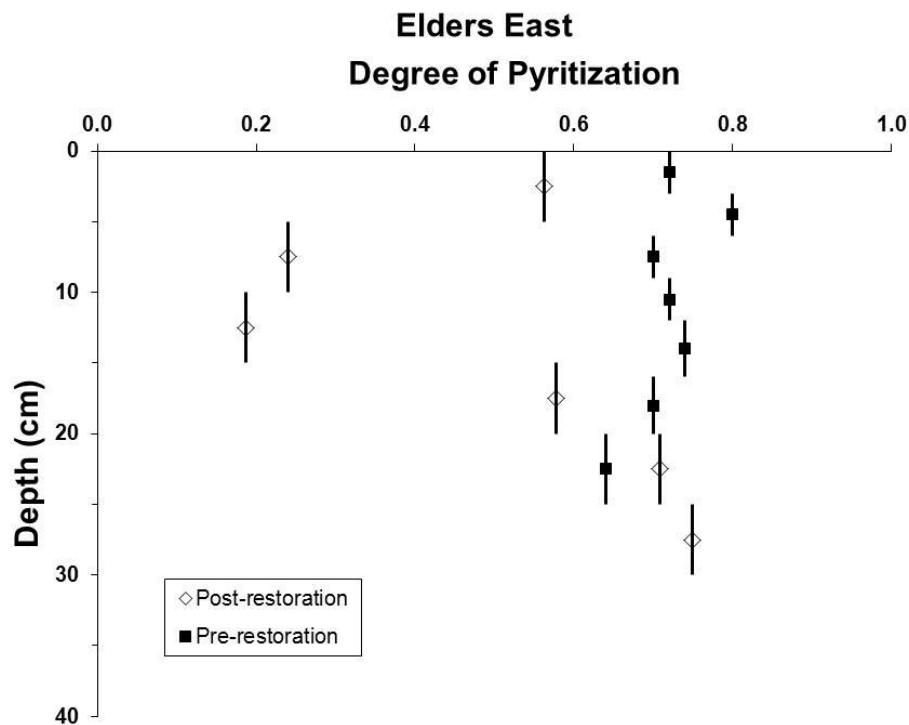


Figure 14. “Degree of Pyritization” (DOP) as a function of depth at Elders Point East marsh before and after restoration.

The DOP values observed in Jamaica Bay marshes can be placed in context by comparing them with other marine sediments (subtidal). For example, DOP values of 0.63 – 0.72 are found in dysaerobic settings such as the Santa Barbara Basin and the Gulf of California, while values of 0.7 – 0.86 are typical of organic rich, euxinic sediments in the Black Sea (Raiswell and Canfield, 1998). The high DOP values observed in most of the Jamaica Bay sites indicate that reactive Fe in the marsh sediments is heavily saturated with sulfide. These findings have implications for salt marsh loss: as the total reactive Fe pool becomes more saturated with solid phase sulfide (FeS_2) the marsh has a decreased ability to sequester pore water sulfide and it can increase, possibly to toxic levels, in the pore water of the root zone. This DOP “saturation” could lead to a positive feedback loop: persistent high pore water sulfide concentrations lead to high degree of solid phase sulfide saturation of reactive Fe, allowing high sulfide concentrations to persist. This “sulfur logging” would have deleterious effects on the plant community such as reduced plant growth (Howarth, 1984; Howes et al., 1986), increased mortality (Koch and Mendelssohn, 1989; Koch et al., 1990), a decreased ability to uptake nitrogen (Bradley and Morris, 1990) and a decreased ability to detoxify sulfides via gas exchange (Lee et al., 1999; Teal and Kanwisher, 1961). Additionally, pyrite oxidation, which produces H_2SO_4 , leads to a low pH that could also be destructive to marsh plants (Howarth and Merkel, 1984; Stumm and Morgan, 1996). Indeed, JoCo marsh has the highest concentrations of pyrite (as seen in pyrite Fe, Table 9) and some of the lowest pore water pH values observed in the study (Table 4).

Marsh Accretion

In addition to the marsh plants coping with exposure to elevated pore water sulfide concentrations, marsh surface elevation must increase to keep pace with sea level rise. The rate of change of the marsh surface with respect to sea level is a complicated function of accretion of organic and inorganic material, subsidence, storage of pore water and other factors. These contribute to elevation changes in the marsh surface, and are best measured through long-term emplacements of Sediment Elevation Tables (SETs; Cahoon and Reid, 1995). We have measured accretion rates from ^{210}Pb chronologies at three sites (Big Egg, East High and JoCo). As noted above these measurements were not formally a part of the present project. However, as seen in Fig. 8, the accretion rates in three marshes have varied with time but all are accreting at rates that correspond to the long-term rates of sea level rise at the Battery, NY (0.30 cm y^{-1} , 1900-2003) and Montauk, NY (0.25 cm y^{-1} , 1948-2003). It would be useful to obtain additional ^{210}Pb chronologies on Jamaica Bay marshes and compare the results with SET measurements of accretion and elevation change.

Summary and Recommendations

Our data suggest that the *Spartina* community within Jamaica Bay marshes is subject to levels of pore water sulfide that have been shown to be stressful and even toxic to plants in laboratory studies. The pattern in the different marshes is consistent with the pattern of marsh loss, with JoCo (a stable marsh) displaying lower pore water sulfide concentrations than seen at the highly degraded Elders East or Big Egg prior to restoration projects at those sites. We observed significant interannual variations in the pore water sulfide concentrations to which marsh plants are exposed, with generally higher values in 2004-2006 than 2007 (at sites where interannual comparison was possible). In part the difference may be related to temporal variation in organic loading onto the marsh surface. For example the July 29 – August 4, 2004 sampling in Big Egg marsh occurred directly after a large rainstorm in which 6.37 cm fell at JFK Airport on July 27 (www.noaa.gov). This precipitation was well in excess of the amount needed for a Combined Sewer Overflow (CSO) event to inject untreated sewage into Jamaica Bay. During this sampling, the marsh smelled unusually foul, and the mud consistency was fluid, suggesting that untreated sewage had settled onto Big Egg marsh. The surficial sediments in a core from the interior site in Big Egg marsh collected during this period were rich in both nitrogen and carbon. This pulse of labile organic matter may have stimulated the bacterial community, enhancing sulfate reduction rates, which probably led to the increase in sulfide concentrations from ~ 2 to $\sim 4 \text{ mM}$ in the upper 2 cm of the creek bank site (Table 2).

The solid phase sulfur and Fe data complement the perspective gained from the pore water sulfide data. They suggest that JoCo may display lower pore water sulfide because a greater fraction of the HS^- produced by sulfate reduction there is associated with solid phase sulfide phases, principally pyrite (FeS_2). In part this reflects the amount of total reactive Fe present in the fine-grained sediment there. However, JoCo also shows a very high “Degree of Pyritization”, indicating that most of the reactive Fe is associated with pyrite and unavailable to react with newly produced pore water sulfide to precipitate fresh pyrite. This may be interpreted as a cautionary sign that JoCo is near the biogeochemical “limit” of its ability to deal with pore water sulfide. In contrast, the restoration effort at Elders East re-set the sediment biogeochemical system to lower degrees of pyritization, providing more flexibility for future biogeochemical regulation of pore water sulfide through iron sulfide precipitation. Elders and other restored

marshes in Jamaica Bay should be periodically monitored for pore water sulfide concentrations and other biogeochemical parameters.

Accretion chronologies for East High, Big Egg and JoCo marshes suggest that these marshes are able to accrete at a pace that has kept up with long-term sea level rise. Although this suggests that accretion is not a factor in marsh loss in Jamaica Bay, more detailed measurements of short-term accretion and elevation rates obtained with SETs are necessary, and these should be compared more systematically with ^{210}Pb chronologies.

Although there is circumstantial support for the “sulfur-logging” positive feedback model of marsh loss in Jamaica Bay, further testing of this model is needed. We recommend the following:

- Establish reference sites in key marshes (stable, degrading and restored) which will be sampled seasonally. This should be done by permanent installation of multiport samplers (Fig. 6) from which pore water samples can be drawn as needed. Candidate sites include those at which SETs are currently in place and restored marshes. Analyses: pore water sulfide, N, P, pH, Cl.
- Collect cores in conjunction with each pore water sampling. Analyses: Leachable iron, total sulfur, carbon and nitrogen, acid-volatile sulfide.
- Collect cores at SET emplacements for detailed accretion chronologies based on ^{210}Pb dating.

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