Constraints on oxidation-reduction chemistry in estuarine salt marsh sediments of the Hackensack Meadowlands, NJ

Joanne Bacchus[*] and Victoria C. Hover
Department of Earth and Environmental Sciences, Rutgers University,
Newark, New Jersey, 07102-1814

[*]Rutgers Undergraduate Research Fellow

Abstract

The anaerobic decomposition of organic matter in anoxic estuarine sediments is governed by a series of oxidation-reduction (redox) reactions, which regulate the cycling of sulfur, carbon, iron, and phosphorus in sediments and sediment porewaters. The objective of this study is to document the co-variation of pH, dissolved SO_4^{2-}, ΣH_2S (total dissolved sulfide), ΣCO_2 (total dissolved inorganic carbon), Fe, Mn, and PO_4^{3-} in a series of porewaters extracted from estuarine sediments from the Hackensack Meadowlands, NJ, in order to constrain the redox conditions in the sediments. The oxidation of organic matter via microbially mediated sulfate reduction is the dominant decay process in these salt-marsh sediments. The decomposition of organic matter results in a decrease in SO_4^{2-}, and a concomitant increase in ΣCO_2 and ΣH_2S with depth in the sediment porewaters. Under these conditions, reactive Fe- and Mn-oxyhydroxides are unstable, and their reductive breakdown results in the releases of dissolved Fe and Mn to the porewaters. In addition, PO_4^{3-} adsorbed to the Fe- and Mn- oxyhydroxides is also released. When ΣH_2S is in excess, sulfides react with the dissolved Fe to form relatively unstable Fe-sulfides (acid volatile sulfides) and pyrite. The precipitation of these Fe-sulfides depletes the concentration of Fe in the porewaters. In older sediments, in which the supply of dissolved Fe is exhausted, ΣH_2S accumulates in the porewaters up to ~160 µmol/L. In younger sediments, Fe concentrations are higher (up to ~200 µmol/l) and ΣH_2S are lower (up to ~35 µmol/l), and their cocentrations are inversely correlated. Mn-sulfides are rarely formed under these conditions so dissolved Mn accumulates in porewaters and may diffuse into overlying surface waters. The PO_4^{3-} concentrations are influenced by both organic matter decay and desorption from Fe-oxyhydroxides during the breakdown Fe-P adsorption complexes.

Introduction

The Hackensack Meadowlands District covers approximately 83 sq. miles (3,400 hectares) and is the largest remaining brackish wetland region in the NY-NJ Harbor Estuary. The complex includes a variety of wetland systems: intertidal marshes dominated by common reed (*Phragmites australis*), low salt marsh with *Spartina alterniflora*, high salt marsh with *Spartina patens*, mudflats, brackish enclosures, and freshwater enclosures (U.S. Fish & Wildlife). All of this vegetation creates an

abundance of organic detritus that undergoes decomposition in the estuarine sediments.

The decomposition of organic matter in sediments is generally governed by a series of bacterially mediated oxidation-reduction (redox) reactions, which proceed according to their thermodynamic stability (Luther, 1995). The principal reactions are listed in Table 1, using the average composition of marine plankton (Redfield, 1958) to describe the organic matter component.

Table 1: Sequence of redox reactions for the decomposition of organic matter from Luther (1995). Organic matter ($C_{106}H_{263}O_{110}N_{16}P$) is represented by average marine plankton composition (Redfield, 1958).

			Gibbs Free Energy(kJ/mol)
<u>1</u>	Oxygen (O_2)reduction	$138\ \mathbf{O_2} + C_{106}H_{263}O_{110}N_{16}P =$ $106\ CO_2 + 16\ HNO_3 + H_3PO_4 + 122\ H_2O$	-3190
<u>2</u>	Nitrate reduction	$94.4\ \mathbf{HNO_3} + C_{106}H_{263}O_{110}N_{16}P =$ $106\ CO_2 + 55.2\ N_2 + H_3PO_4 + 177.3\ H_2O$	-3030
<u>3</u>	MnO_2 reduction	$236\ \mathbf{MnO_2} + C_{106}H_{263}O_{110}N_{16}P + 472\ H^+ =$ $8\ N_2 + 106\ CO_2 + H_3PO_4 + 236\ Mn^{2+} + 366\ H_2O$	-3000
<u>4</u>	Fe_2O_3 reduction	$212\ \mathbf{Fe_2O_3} + C_{106}H_{263}O_{110}N_{16}P + 848\ H^+ =$ $106\ CO_2 + 16\ NH_3 + H_3PO_4 + 424\ Fe^{2+} + 530\ H_2O$	-1410
<u>5</u>	Sulfate (SO_4^{2-}) reduction	$53\ \mathbf{SO_4^{2-}} + C_{106}H_{263}O_{110}N_{16}P =$ $106\ CO_2 + 16\ NH_3 + H_3PO_4 + 53\ S^{2-} + 106\ H_2O$	-380
<u>6</u>	Methanogenesis	$C_{106}H_{263}O_{110}N_{16}P =$ $53\ CO_2 + 53\ \mathbf{CH_4} + 16\ NH_3 + H_3PO_4$	-350

In salt marsh environments, like the Meadowlands, the redox chemistry is under several constraints. Aerobic decay (Reaction 1) is limited because the carbon content from the organic matter exceeds the levels of oxygen in the sediment porewater. Therefore, the conditions become anoxic very near the sediment-water interface. The limited extent of O_2-oxidation of organic matter results in limited nitrate formation (Reaction 2) and subsequent reduction to NH_4^+ (Berner, 1981).

The reduction of Mn^{4+}- and Fe^{3+}-oxides (Reactions 3 and 4) may result in increased levels of dissolved Mn^{2+} and Fe^{2+} in porewater relative to overlying waters. However, the concentration of dissolved Mn^{2+} and Fe^{2+} is also controlled by the reaction with other dissolved products of organic matter decay, as described below. The seawater component of waters in estuarine marsh systems contains high concentrations of dissolved sulfate relative to other potential oxidants. As a result, sulfate reduction (Reaction 5) is the dominant degradation process in salt marsh environments, such as the Meadowlands (Howarth and Giblin, 1984). Due to the high sulfate concentrations, conditions favoring methanogenesis (Reaction 6) are not encountered.

The reduction of sulfate to sulfide can be demonstrated by the simplified reaction:

Reaction 7: $2 \, CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$ (CH_2O = sucrose)

The dissolved H_2S and HCO_3^- produced by the sulfate reduction is available to react with dissolved Mn^{2+} and Fe^{2+} to form authigenic minerals, such as Fe-sulfides and Mn-carbonates (Berner 1981). In iron rich sediments, such as the Meadowlands, poorly crystalline Fe-sulfides, e.g., amorphous FeS, mackinawite (FeS), and griegite (Fe_3S_4), are readily formed. These metastable sulfides are known as acid volatile sulfides (AVS) (Morse et al., 1987). These AVS then react with other dissolved sulfur species to form pyrite (FeS_2), the dominant and most stable form of reduced Fe-sulfide (Berner, 1984; Henneke et al., 1996).

Reaction 8: $FeS + S^0 \rightarrow FeS_2$

The PO_4^{3-}content in the sediment pore waters may be derived from several sources, including the decomposition of organic matter (Table 1) and the breakdown of Fe-P adsorption complexes associated with Fe-oxyhydroxide minerals. Under oxygenated conditions, iron is in its oxidized state (Fe^{3+}) and Fe-oxyhydroxides maintain a net positive surface charge that allows the phosphate ion (PO_4^{3-}) to be adsorbed, forming Fe-P complexes (Sundareshwar and Morris 1999). Under anoxic conditions, these Fe-oxyhydroxides are reduced, resulting in the release of Fe^{2+} and desorption of phosphate ions. The free Fe^{2+} readily reacts with sulfide species to form AVS and pyrite. Thus, the high sulfide content of the salt marsh waters limits the potential for the formation of ferrous phosphates since the sulfides compete with PO_4^{3-} for adsorption sites. Under these conditions, PO_4^{3-} levels in the surface and porewaters may be higher than predicted from simply the decomposition of organic matter (Caraco et al., 1989).

The primary objective of this study is to constrain the geochemical redox environment as preserved in sediment porewaters obtained from a series of cores collected in the Hackensack Meadowlands. The study focuses on the covariation of pH, SO_4^{2-}, ΣH_2S (total dissolved sulfide), ΣCO_2 (total dissolved inorganic carbon), dissolved Fe, Mn, and PO_4^{3-} in order to evaluate the extent of organic matter decay via sulfate reduction, the concomitant release of Fe, Mn, and PO_4^{3-}, and the precipitation of Fe sulfides in this environment.

This report combines results from previously obtained analyses (pH, SO_4^{2-}, ΣCO_2, Cl^-, Fe, Mn; V.C. Hover) with new analyses of ΣH_2S and PO_4^{3-} obtained by UV-Visible spectrophotometric analysis. The results of this study demonstrate that processes including the bacterially mediated sulfate reduction of organic matter, the breakdown of Fe and Mn-oxyhydroxides, the release of phosphate, and the formation of Fe-sulfides are occurring within the sediments under anoxic conditions. The results of this study provide important constraints on the geochemical redox environment, which ultimately controls the geochemistry of potentially toxic trace metal contaminants in these salt marsh sediments.

Materials and methods

During the summer and fall of 1998, Dr. Hover collected sediments and overlying water samples from the Mill Creek marsh of the Hackensack Meadowlands area (Fig. 1).

Figure 1. Map showing the location of sampling sites in the Hackensack Meadowlands District, NJ.
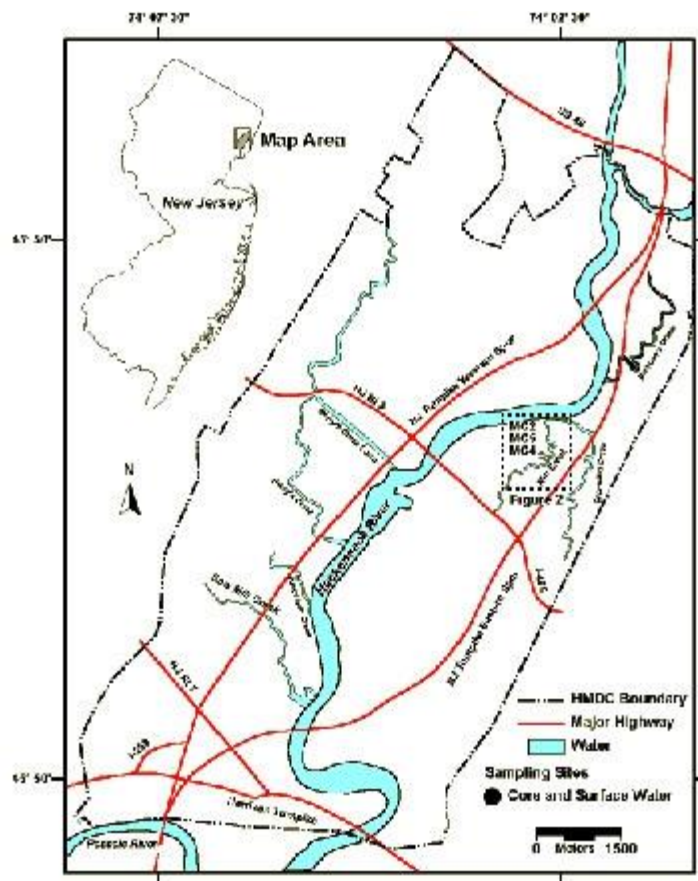
The Mill Creek marsh is located downstream from a wastewater treatment plant. The downstream portion of the creek underwent restoration in 1987 (Hartz Mountain Restoration; Fig. 2). Samples from Sites MC-2 and MC-5 were collected in the tidal flats adjacent to a restored *Spartina alterniflora* marsh in the restored area. Site MC-4 was situated in an area undergoing restoration by the Hackensack Meadowlands Development Commission (HMDC Restoration; Fig. 2). Prior to sampling, approximately 1 meter of overlying sediment had been removed from this site in preparation for *Spartina alterniflora* replanting.

Figure 2. Map showing the location of sampling sites in the Mill Creek area, Hackensack Meadowlands, NJ.
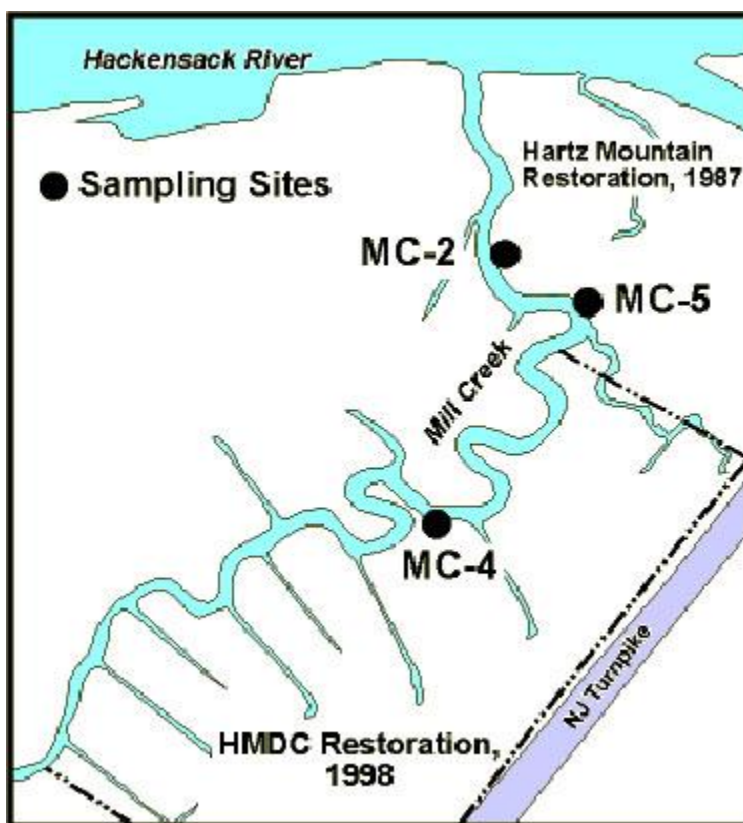
The uppermost intervals at MC-2 and all of MC-5 consist of very soupy organic-rich material, containing 6-10 wt% total organic carbon. Based on sedimentation rates determined by ^{210}Pb dating, these sediments have been deposited since the restoration in 1987 (Bopp, personal communication). The lowermost intervals of MC-2 (24-26 cm) and all of MC-4 from the recently scraped site consist of denser, gray, clay-rich sediment with only 3-4 wt % total inorganic carbon. The ^{210}Pb data obtained from these intervals suggest that they were deposited more than 100 years ago (Bopp, personal communication). Thus, these latter sediment intervals reflect pre-industrial conditions.

Surface waters with suspended sediment were collected at each site. A portion was filtered (0.45 µm) and aliquots separated for cation, anion, and ΣCO_2 analyses. Sediments were collected using 20 x 30-cm box cores to a depth of 25 cm. Within six hours of collection, sediment box cores were processed at room temperature in a glove bag filled with N_2 atmosphere to prevent oxidation. Sediment from 2-cm intervals was combined and placed into centrifuge tubes for extraction of porewater. Porewater pH was determined by insertion of a pH electrode into one of the centrifuge tubes. Remaining tubes were spun at 4500 rpm for 30 minutes and returned to the N_2-filled glove bag. Porewaters were then extracted via syringe,

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filtered (0.45 µm), and dispensed as aliquots for cation, anion, ΣH_2S, and ΣCO_2 analyses. Cation aliquots were preserved with ~1 vol.% trace-metal grade HNO_3. Phosphate aliquots were preserved with ~1 vol.% H_2SO_4. Anion and ΣH_2S aliquots were treated with Zn-acetate (1 mmol/L) to immediately trap H_2S and prevent oxidation artifacts for sulfate and sulfide determinations.

Total dissolved H_2S was determined in approximately 50 pore water samples, using UV-Visible spectrophotometric methods adapted from Cline (1969). All analyses were performed with a Perkin-Elmer 330 spectrophotometer. Duplicate samples were analyzed with accuracy better than ±15% for 56% of samples expressed as a coefficient of variation (standard deviation/mean x 100). The precision of analyses based on replicate runs was better than ±2%.

Dissolved phosphate was determined for 50 pore-water samples and 20 surface water samples acidified with H_2SO_4 (10 mmol/L), using UV-Visible spectrophotometric methods adapted from Standard Methods (Eaton et al., 1995). Accuracy of duplicate samples was ±10% while replicate samples resulted in precision better than ±2% for 94% of the samples.

The analytical data for SO_4^{2-}, ΣCO_2, Cl^-, Fe, and Mn were obtained by Dr. Hover. These data are part of a larger study investigating the behavior of trace metal elements in these same pore water sediment samples. Briefly, the analytical procedures are as follows. The Fe and Mn concentrations were determine by Inductively Coupled Plasma-Mass Spectrophotometric (ICP-MS) methods (Finnigan Mat Element) in the laboratory of Dr. Sherrell at the Institute of Marine and Coastal Sciences, Rutgers-New Brunswick. The Cl^- and SO_4^{2-} concentrations were determined by ion chromatographic methods (Dionex 4000I series) in the laboratory of Dr. Walter at the University of Michigan. ΣCO_2 levels were determined with coulometric methods (IUC Coulometrics CO_2 instrument) in Dr. Walter's laboratory.

Results

The concentration of Cl^-, pH, SO_4^{2-}, ΣCO_2, ΣH_2S, PO_4^{3-}, Fe^{2+}, and Mn^{2+} are plotted versus depth for each site's core in Figures 3-5. Figure 3 shows the depth plot for MC-2, where sediment samples were collected in May 1998. The samples for MC-5 (Fig. 4) and MC-4 (Fig. 5) were collected in September 1998. The results for the MC-2 and MC-5 sites are presented first, because both sites are in the previously restored area of the marsh, and contain relatively young sediments. The results from MC-4 are presented last because this site sampled the older pre-industrial sediments in the recently scrapped area of the Marsh.

Chloride is commonly considered to be a conservative element during the mixing of fresh and saline waters in estuaries (e.g., Chester 1990) and gains or losses of other components are thus commonly referenced to Cl^- in order to quantify the extent of sediment-pore water interactions. The first panels (A) in Figures 3-5 show the variation of Cl^- with depth at each site. The results from all sites will be described

collectively. The Cl⁻ concentrations in the surface water at all sites are more dilute than pore waters because sampling was conducted at low tide and the results reflect a reduced seawater component. The Cl⁻ concentrations range from 25 mmol/L (MC-2) for samples collected in the spring to 85 mmol/L and 105 mmol/L for samples collected in the fall (MC-4 and MC-5 respectively). This data corresponds to salinities of 1.6‰ for surface water collected at MC-2 to a high of 7‰ for surface water collected at MC-5 after a particularly hot and dry spell (normal salinity of seawater = 35‰; Millero, 1996). The variations of Cl⁻ composition with depth at each site are due to both seasonal and tidal fluctuations in surface water salinity. The concentration at depth reflects the approximate average salinity at each site. The variation with depth for pH, SO_4^{2-}, ΣCO_2, ΣH_2S, PO_4^{3-}, Fe^{2+}, and Mn^{2+} shown in Fig. 3-5 is greater than expected due to the variations in salinity, and thus record sediment-porewater interactions. The variations of these components will be described site by site.

MC-2: May 1998

Samples were collected at the MC-2 site during early May, 1998, when there was a large freshwater component in the estuary and biological activity in sediment was relatively low.

Figure 3. Porewater data from Mill Creek Site 2. Data labeled in cyan blue indicate surface water compositions.
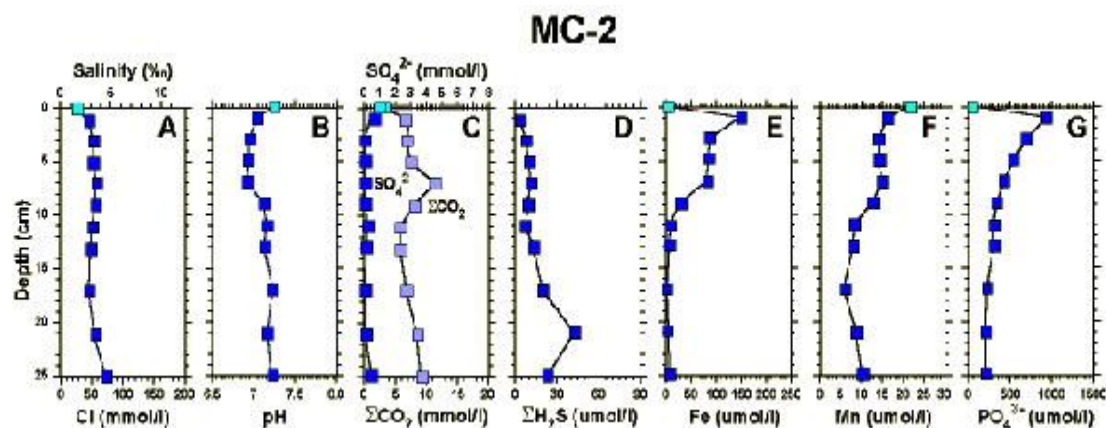
- pH (Fig. 3B): The pH decreases from a value of 7.24 at the surface to 6.90 at a depth of ~7 cm. Below ~7 cm, the pH is relatively constant at 7.1-7.2.
- SO_4^{2-} (Fig. 3C): The sulfate concentration declines from a surface value of 1.4 mmol/L to less than 0.1 mmol/L below ~3 cm.
- ΣCO_2 (Fig. 3C): Concurrent with SO_4^{2-} depletion, the concentrations of ΣCO_2 increased from 2.6 mmol/L in the surface water to 9.6 mmol/L at ~25 cm. A spike in concentration to 11.6 mmol/L was measured at a depth of ~7 cm.
- ΣH_2S (Fig. 3D): ΣH_2S was not sampled in the surface water of any site. The ΣH_2S concentration in the uppermost sediment interval (0-2 cm) is 3

mmol/L. The ΣH_2S concentration increases to a maximum concentration of 42 mmol/L at ~21 cm

- Fe (Fig. 3E): The dissolved Fe concentration in the surface water is 2 mmol/L. The maximum Fe concentration of 148 mmol/L occurs in the uppermost sediment interval (0-2 cm). From this maximum, the Fe concentration decreases somewhat gradually to ~25 mmol/L at the 8-10 cm interval, and declines sharply to a minimum of ~3 mmol/L at ~17 cm.
- Mn (Fig. 3F): Dissolved Mn concentrations are highest in uppermost interval (22 mmol/L) and decrease to ~6 mmol/L at 17 cm. The last two intervals show a slight increase in Mn concentration to ~10 mmol/L).
- PO_4^{3-} (Fig. 3G): The concentration of PO_4^{3-} in the surface water (34 mmol/L) is less than any concentrations observed in the sediment porewaters. The PO_4^{3-} concentrations increase sharply in the uppermost sediment interval (0-2 cm) to 923 mmol/L. This maximum in PO_4^{3-} concentration in the surface interval parallels the behavior of Fe. The PO_4^{3-} concentration steadily declines with depth to 202 mmol/L.

MC-5: September 1998

Samples were collected following a hot, dry summer. Salinity was greater than usual because of the greater incursion of seawater. The biological activity in sediments was relatively high.

Figure 4. Porewater data from Mill Creek Site 5. Data labeled in cyan blue indicate surface water compositions.
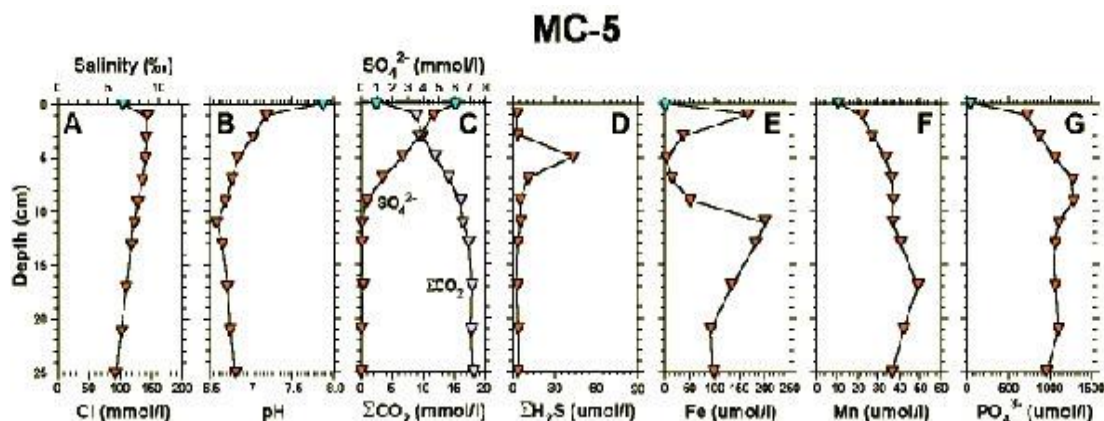

- pH (Fig. 4B): Surface waters show a maximum pH of 7.87, which steadily declines to 6.58 by ~11 cm. The pH levels then gradually increase to 6.81 at ~25 cm.
- SO_4^{2-} (Fig. 4C): The SO_4^{2-} concentration decreases from a surface maximum of 6 mmol/L to less than 0.1 mmol/L at ~7 cm. The SO_4^{2-} concentration remains low to the bottom of the core.
- ΣCO_2 (Fig. 4C): The ΣCO_2 concentration of the surface water is 2.5 mmol/L. The concentration increases immediately to 9 mmol/L at the

uppermost (0-2 cm) sediment interval and then gradually increases to ~18 mmol/L at ~9 cm and remains constant from this point downward.

- o ΣH_2S (Fig. 4D): The uppermost sediment interval has a sulfide concentration of ~3 mmol/L. The ΣH_2S concentration reaches a maximum of 43 mmol/L at a depth of ~5 cm. Below this depth, the ΣH_2S concentration decreases to ~3-4 mmol/L.
- o Fe (Fig. 4E): The surface water sample contains ~4 mmol/L Fe. The Fe concentration increases dramatically to 168 mmol/L in the uppermost sediment interval. The Fe concentration declines rapidly to a minimum of ~ 5 mmol/L at 5 cm (the same interval with the maximum concentration of ΣH_2S). The Fe concentration increases to 203 mmol/L at ~11 cm before declining to 100 mmol/L at ~25 cm.
- o Mn (Fig. 4F): The dissolved Mn concentration is lowest in the surface water sample (11 mmol/L). The Mn concentrations in the sediment porewaters gradually increase to 49 mmol/L at ~17 cm. Note that the concentration of Mn in this core are about four times greater than that of MC-2 or MC-4.
- o PO_4^{3-} (Fig. 4G): The surface water sample has the lowest PO_4^{3-} concentration of 37 mmol/L. The PO_4^{3-} concentration increases sharply to ~710 mmol/L in the uppermost sediment interval. The PO_4^{3-} levels increases with depth to a maximum of 1274 mmol/L at ~11 cm. Below ~11 cm, the level decreases to ~1000 mmol/L.

MC-4: September 1998

Samples were collected under similar conditions as described for the MC-5 site.

Figure 5. Porewater data from Mill Creek Site 4. Data labeled in cyan blue indicate surface water compositions.
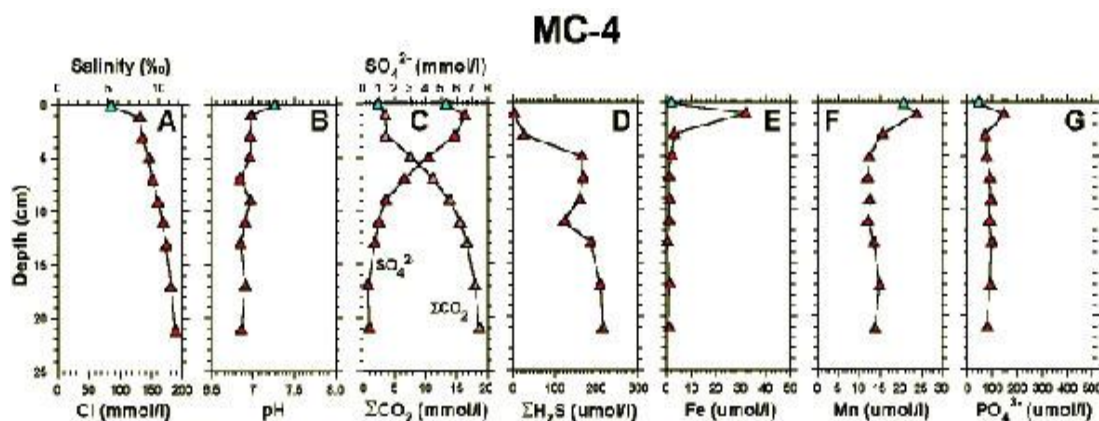
- pH (Fig. 5B): The pH of the surface water is 7.26. The pH decreases to a near constant value of between 6.86-6.96 in the sediment column.
- SO_4^{2-} (Fig. 5C): The surface waters contain ~5 mmol/L of dissolved SO_4^{2-}. The uppermost sediment interval (0-2 cm) contains the maximum

SO_4^{2-}.concentration of 6.5 mmol/L. The SO_4^{2-}.concentration then declines with depth to ~0.3 mmol/L.

- ΣCO_2 (Fig. 5C): The surface water sample has a ΣCO_2 concentration of 2.4 mmol/L. The ΣCO_2 concentration gradually increases with depth to 18 mmol/L in the lowermost sediment interval (20-22 cm).
- ΣH_2S (Fig. 5D): The uppermost sediment interval contains the lowest ΣH_2S concentration (~1.7 mmol/L). The ΣH_2S concentration increases rapidly to 162 mmol/L at a depth of ~5 cm, decreases to 121 mmol/L at 11 cm, and increases to 215 mmol/L at ~23 cm.
- Fe (Fig. 5E): The surface water sample at MC-4 contains a very low concentration of dissolved Fe (2 mmol/L). The Fe concentration increases to 32 mmol/L in the uppermost sediment interval and then immediately decreases until dissolved iron is barely detectable at (~0.6 mmol/L at ~13 cm). The maximum dissolved Fe at this site is about seven times lower than the maximum concentration observed at the MC-5 site and about four times lower than at the MC-2 site.
- Mn (Fig. 5F): The surface water sample contains a dissolved Mn concentration of 21 mmol/L. The maximum dissolved Mn concentration of ~24 mmol/L occurs in the uppermost sediment interval. The concentration decreases to a minimum of ~12 mmol/L at ~5 cm.
- PO_4^{3-} (Fig. 5G): The surface water sample contains ~42 mmol/L of PO_4^{3-}. The PO_4^{3-} concentration increases to a maximum of ~146 mmol/L in the uppermost sediment interval. Below 2 cm, the concentration decreases to a constant value ~70 mmol/L.

Discussion

With the exception of phosphate and iron, MC-2 samples appear to contain very low concentrations of chemical species analyzed in this study relative to the other two sites (MC-4 and MC-5). This lowering may be the result of seasonal difference in salinity of the overlying water and degree of microbial activity in the sediment. The MC-2 samples were collected during the spring when the surface waters of the estuary were more dilute and when microbial activity in the marsh sediments was probably lower than later in the season when the samples from MC-4 and MC-5 sites were collected. The surface water salinity was five to six times higher when samples from sites MC-4 and MC-5 were collected and microbial activity was probably at its peak.

Estuarine salt marshes, like the Hackensack Meadowlands, contain a great deal of organic detritus that is buried and subjected to organic degradation. Furthermore, location of the Mill Creek sites downstream from a wastewater treatment plant may result in additional input of organic carbon and phosphate. As discussed previously, the high levels of organic matter and the lack of available O_2 create anoxic conditions, which facilitate anaerobic decay of organic matter (Berner, 1981). Under such conditions, sulfate reduction is the primary organic matter oxidation process in

salt marsh systems (Howarth and Giblin, 1984). At each site, the SO_4^{2-} concentrations decrease with depth (Figs. 3-5) consistent with sulfate-reduction by Reactions 5 and 7. There is concomitant increase in ΣCO_2 (Figs. 3-5) resulting from the organic matter decay and release of dissolved carbonate species to the porewaters. Furthermore, the amount SO_4^{2-}-depletion and ΣCO_2-enrichment relative to surface water concentrations are consistent with the expected 1:2 proportions predicted by the reaction stoichiometry (e.g., Reaction 7). These data suggest that the conditions for anoxia are present and that sulfate reduction is occurring. The relatively low concentration of both SO_4^{2-} and ΣCO_2 in the porewaters of MC-2 relative to MC-4 and MC-5 are most likely the result of the overall lower salinity of surface water and the reduced microbial activity expected at the time of collection of MC-2 in early spring. The higher concentration SO_4^{2-} in surface water at the MC-4 and MC-5 sites collected in the late summer, and a higher degree of microbial activity results in greater extents of sulfate reduction and production of ΣCO_2 (Caraco et al., 1989).

With the reduction of SO_4^{2-}, reduced sulfide species ($\Sigma H_2 S$) are produced (Reactions 5 and 7). Upon comparison of the sulfate versus sulfide concentrations at each site, there is evidence to indicate an inverse relationship (i.e., as SO_4^{2-} concentrations decrease, $\Sigma H_2 S$ concentrations generally increase). This relationship is demonstrated best in MC-4 site (Fig. 5). The MC-4 porewaters contain the highest concentrations of $\Sigma H_2 S$, indicating an accumulation of reduced sulfide in the sediments. The $\Sigma H_2 S$ concentrations in porewaters at MC-5, however, are much lower for similar extents of sulfate reduction. Also, the variation of $\Sigma H_2 S$ with depth does not follow a smooth curve like that of the SO_4^{2-} variations. These observations indicate that additional processes influence the $\Sigma H_2 S$ concentrations at the MC-5 site.

The most likely factor influencing the $\Sigma H_2 S$ concentration in porewaters at each site is the presence of dissolved Fe(II). At each site, the Fe concentration in surface water is extremely low ($< \sim 5$ µmol/L). This is due to the fact that most Fe is associated with relatively insoluble oxy-hydroxides and most Fe is in the Fe(III) state. At each site, there is a dramatic increase in the dissolved Fe concentration in the uppermost (0-2 cm) porewater interval. This increase in dissolved Fe may be attributed to the breakdown of Fe-oxyhydroxides, which releases Fe^{2+} into the porewaters (e.g., Reaction 3). The dissolved Fe concentrations in this interval at the MC-2 and MC-5 sites are approximately four times higher than at the MC-4 site suggesting that more reactive Fe-oxyhydroxides may be present in the sediments at the MC-2 and MC-5 sites. At all sites, however, the dissolved Fe concentrations decrease substantially by the next sediment interval (2-4 cm) and continue to decrease with depth at sites MC-2 and MC-4 (Figs. 3D and 5D). The variation of dissolved Fe with depth at the MC-5 site is more complicated; rapidly declining between ~ 3 and 7 cm, and then increasing substantially at ~ 11 cm (Fig. 4D). However, at all sites, when $\Sigma H_2 S$ is the greatest, the Fe concentrations are the most depleted. These data are consistent with the reaction between dissolved Fe and dissolved sulfides, which can form AVS Fe-sulfides and precipitate pyrite (Reaction 8; Morse et al.,

1987). There is abundant evidence that authigenic pyrite does form in these salt marsh sediments (Fig. 6).

Figure 6. Several pyrite framboids enclosed in organic material. This pyrite habit is consistent with authigenic formation. (MC-5; 0-2 cm).
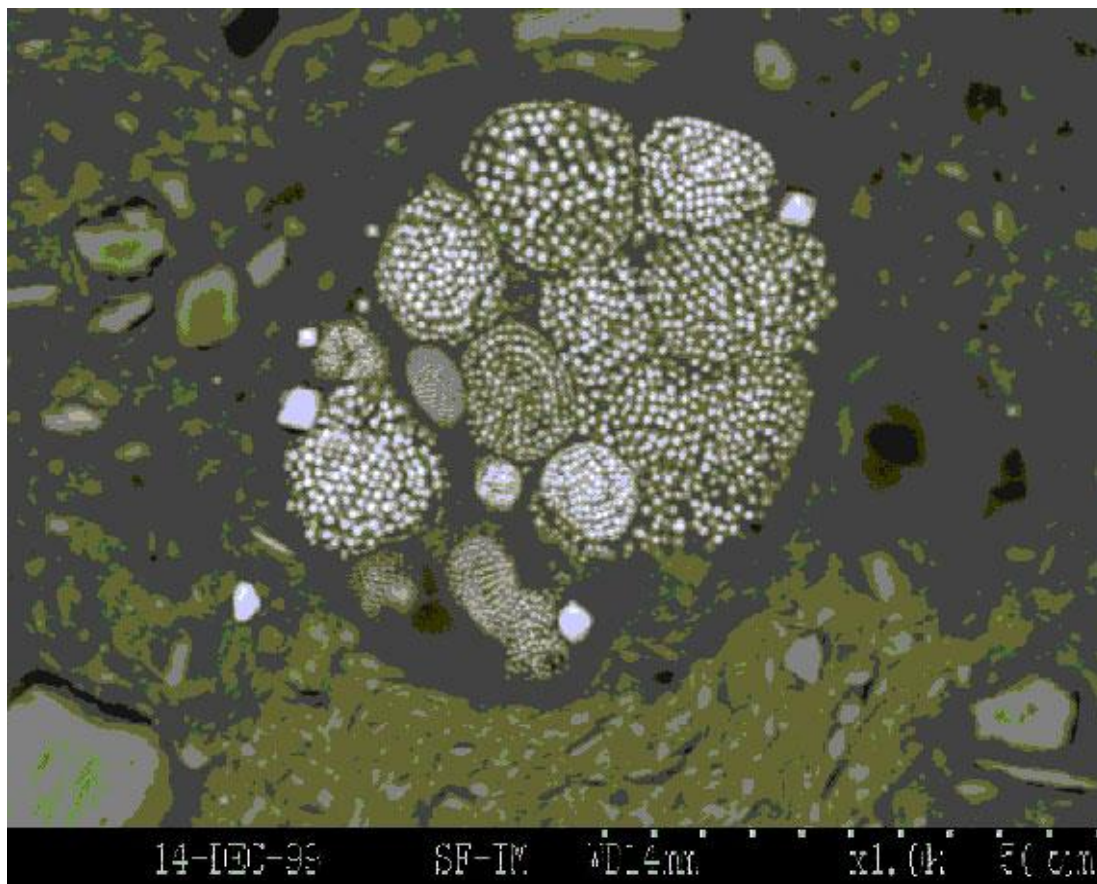
The combined ΣH_2S-and Fe-data at the MC-2 and MC-4 sites also suggest that once the available dissolved Fe has reacted, ΣH_2S may accumulate in the sediment porewaters. This is demonstrated by the increase in ΣH_2S below ~ 11 cm at MC-2 and below ~ 3 cm at MC-4. Recall that the sediments at MC-4 are more than 100 years old; while the sediment at the MC-2 and MC-5 sites are less than 20 years old. It is possible that much of the Fe in the older sediment at MC-4 may have already reacted to form Fe-sulfides. The lack of reactive Fe allows ΣH_2S to accumulate in the sediment porewaters.

The behavior of dissolved Fe and ΣH_2S at the MC-5 appears to be more complicated. The Fe concentration reaches a maximum in the 10-12 cm interval without concomitant change in any of the other species. This inconsistency may be due the oxidative dissolution of pyrite. When pyrite is dissolved, acid is generated (e.g., Luther, 1995).:

Reaction 9: $FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+$
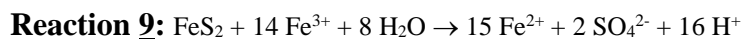
Note that there the decrease in pH occurs in the in this same depth interval as the maximum in dissolved Fe concentration, consistent with pyrite dissolution. The stoichiometry of Reaction 9 is such that the amount of SO_4^{2-} produced does not significantly alter the measured SO_4^{2-} concentrations within analytical precision. The reason for such pyrite dissolution is not yet apparent.

Evidence for the reduction of Mn-oxides during organic matter decay (Reaction 3) is found at the MC-5 Site. Dissolved Mn does not readily combine with ΣH_2S to form sulfides, and can accumulate in sediment porewaters (Berner, 1981). At the MC-5 site, the concentration of dissolved Mn reaches the maximum concentrations observed at all the sites and increases steadily with depth to concentrations greater than in surface waters. At the MC-2 and MC-4 sites, Mn concentrations in the porewater are generally less than in surface waters and may indicate either a lower extent of the Mn-reduction reaction than at MC-5 or that dissolved Mn may have diffused out of the sediments to overlying water.

The concentration PO_4^{3-} in surface water at all sites is lower than concentrations in associated porewaters. At all sites, the concentration in the uppermost sediment interval increases sharply relative to the overlying surface water. Concurrent with the rapid increase in PO_4^{3-}, the concentration of dissolved Fe also increases dramatically in the uppermost interval. As described previously, the source of PO_4^{3-} is from both the decay of organic matter and the release from Fe-oxyhydroxides during dissolution. Caraco et al. (1989) suggested that when the ratio between dissolved PO_4^{3-} and ΣCO_2 is greater than ~3-10 µmol P/mmol C, the average ratio in organic matter, additional phosphate must also be derived from the breakdown of Fe-oxyhydroxides. For MC-2 porewaters, the P:C ratio ranges from 13-125 µmol P/mmol C; for MC-5 porewaters, the range is 15-89 µmol P/mmol C, and for MC-4 porewaters, the range is 4-40 µmol P/mmol C. Therefore, it is highly probable that much of the dissolved PO_4^{3-} is being desorbed from complexes with Fe-oxyhydroxides and is being released into the pore waters during the breakdown of Fe-oxyhydroxides. The relatively low PO_4^{3-} concentrations in porewaters at the MC-2 site may be due to the relatively low extents of microbial mediated organic matter reaction and Fe-oxyhydroxide dissolution during the relatively quiescent early springtime. In contrast, the presence of much higher concentrations of PO_4^{3-} in porewater at the MC-5 site suggest greater microbial activity and a greater degree of organic matter decomposition and breakdown of Fe-oxyhydroxides in the late summer. The relatively low concentrations of PO_4^{3-} in porewaters at the MC-4 sites may due to more limited availability of reactive phosphate in these older sediments. However, the spike in PO_4^{3-} in the uppermost (0-2 cm) interval at MC-4 along with the corresponding maximum in dissolved Fe concentrations suggest desorption of phosphate during the breakdown of Fe-oxyhydroxides is taking place in the near-surface interval.

Conclusions

In these marsh sediments, the large amounts of organic detritus undergoing decay facilitates the build up of excess carbon. When the carbon concentration exceeds the concentration of dissolved oxygen, anoxic conditions are created and anaerobic decay of organic matter is prevalent. Sulfate reduction is the dominant anaerobic degradation process in these sediments. The reduction of SO_4^{2-} generates S^{2-} (measured as ΣH_2S). As depth increases, SO_4^{2-} concentrations in the porewaters decline while ΣH_2S and ΣCO_2 concentrations increase concomitantly. The extent of sulfate reduction isre greater during the late summer to fall than in the spring due to higher levels of microbial activity.

Fe and Mn-oxyhyrdoxides are also breaking down under these conditions. This results in the release of dissolved Fe and Mn into the porewater. The dissolved Fe then reacts with ΣH_2S to form Fe-sulfides. The Fe concentrations are most depleted when ΣH_2S is in excess. These trends are concurrent with the precipitation of Fe-sulfides, e.g., pyrite. Mn does not react readily with ΣH_2S; instead, Mn accumulates in porewaters and diffuses into the overlying surface waters.

The high P:C ratios in porewaters indicate that PO_4^{3-} is being desorbed from complexes with Fe-oxyhydroxides, in addition to being released from organic matter degradation. The PO_4^{3-} concentrations are higher in the late summer to fall than in the spring due to the increase in microbial activity and organic matter decay.

Acknowledgments

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