

Temporal and spatial variability of reduced sulfur species (FeS_2 , $\text{S}_2\text{O}_3^{2-}$) and porewater parameters in salt marsh sediments

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Abstract. Porewater species and solid inorganic sulfur speciation were measured before and after the spring tide (which occurs over a 6–7 day period) during a portion of the summer seasons of 1987, 1988 and 1989 in Great Marsh, Delaware. Samples were taken from two locations in the marsh (near creek and mid-marsh) inhabited by the short form of *Spartina alterniflora*. In 1987, pyrite and thiosulfate decreased over the spring tide. Other porewater species also underwent large changes in concentration — in some cases order of magnitude. However, in 1988 and 1989, there was no evidence for short term changes of pyrite. In 1988, drought conditions were prevalent throughout the sampling whereas in 1989 wet conditions were prevalent. Porewater parameters demonstrated that oxidation was extensive during the sampling period in 1988 and related to dessication. Both climatic and spring tidal flooding conditions have a pronounced affect on the chemistry of the system.

Data from atmospherically derived radionuclides (^{210}Pb , ^{137}Cs , ^7Be) indicate that bioturbation is not as important at the mid-marsh site as at the near creek site. Porewater chloride and ^7Be data support infiltration of overlying waters at both sites.

The decrease in pyrite over the spring tide in the 1987 samples is related to oxidation. The possible oxidants are discussed and Fe(III) is the favored direct oxidant based upon a review of field and laboratory data. Iron(III) was measured in several filtered porewater samples. However, we cannot indicate with certainty that the Fe(III) is always soluble. The Fe(III) measured may be colloidal or complexed. Pyrite oxidation is noted when the Fe(III) to Fe(II) ratio, pH and alkalinity are all low.

Introduction

In an earlier report (Luther & Church 1988) at a near-creek salt marsh site, we noted that pyrite decreased over the course of six days (or less) and corresponded to the monthly spring tidal inundation of Great Marsh, Delaware. Pyrite decreases were correlated with soluble iron increases and

the reprecipitation of iron oxyhydroxide phases. That work showed the possibility of dynamic sulfur cycling coupled to iron cycling in salt marsh sediments dominated by *Spartina alterniflora* over a short time scale.

Previous work has documented the biogeochemistry of sulfur on predominantly seasonal time scales (Giblin & Howarth 1984; Hines et al. 1989; Howarth & Teal 1979; King 1988; Lord & Church 1983; Luther et al. 1986, 1988). Recently, Hines et al. (1989) have also noted that rapid changes, based primarily on porewater measurements and sulfate reduction rates, occur on the time scale of a week. They indicated that these changes were related to changes in *Spartina alterniflora* physiology.

In addition to temporal variability of sulfur biogeochemistry in marsh sediments, several groups have noted that there is considerable spatial variability. In most studies, the spatial variability has centered on understanding sulfur chemistry and below ground production in sediments with the short-form versus the tall-form of *Spartina alterniflora* (Gardner et al. 1988; Giblin & Howarth 1984; Hines et al. 1989; King 1988).

There is general agreement among most workers that the observed sulfur biogeochemistry in marsh sediments is related to redox processes. However, there is no general agreement on what is the direct oxidant(s) for the oxidation of reduced sulfur compounds. Most suggestions indicate that molecular oxygen could be the direct oxidant via (1) infiltration of oxygenated waters to sediments which lost water by evapotranspiration and/or groundwater drainage (King et al. 1982; Dacey & Howes 1984), (2) infiltration of oxygenated waters by bioturbation (Aller 1978) and (3) advection of air into sediment during periods of desiccation (Morris & Whiting 1985). Gardner et al. (1988), demonstrated that only 10% of the reduced sulfur oxidized in a South Carolina marsh can be accounted for by infiltration of oxygenated waters into sediments. Recently, Gardner (1990) has performed a detailed model calculation on carbon, sulfur and oxygen diagenesis and has suggested that enzymes from roots rather than oxygen is necessary to support the intense oxidation observed in sediments. Luther and Church (1988) suggested that Fe(III) is the primary oxidant of pyrite and other reduced sulfur compounds. Based on earlier laboratory studies (Moses et al. 1987; Singer & Stumm 1970) and using a molecular orbital theory approach, Luther (1987, 1990) demonstrated that molecular oxygen is a poor oxidant for pyrite and thiosulfate, and suggested that Fe(III) is the direct oxidant for many reduced sulfur compounds. In a companion work (Luther et al. in press), seasonal changes and related laboratory experiments with Fe(III) organic complexes and pyrite are presented.

In this study, our main objectives were to (1) compare the porewater and solid phase iron and sulfur chemistry of near-creek and mid-marsh

sites to examine spatial variability, and (2) repeat the short term changes of sedimentary pyrite across a spring tide as observed in Luther & Church (1988). Research to date generally focuses on changes in pore-water parameters (Howarth & Teal 1979; Giblin & Howarth 1984; Lord & Church 1983; Luther & Church 1988), and on sulfate enriched with S-35 added to sediments or slurries (Howarth & Merkel 1984; Hines et al. 1989; King 1988) to understand sulfur biogeochemistry and sulfate reduction rates over time, respectively. In this study, we report on the differences in concentration of solid inorganic sulfur and porewater species in sediments near a creek (about 2 m from the creek) and mid marsh (about 15 m from the creek bank) over the spring tide for one period in 1987 (normal climatic conditions). Also, we report on two other sampling periods (1988, drought period; 1989, rainy period) at the near-creek site. These sediments are dominated by the short-form of *Spartina alterniflora*. Our results show that short term changes can be significant at both locations.

Atmospherically derived radionuclides (^{210}Pb , ^{137}Cs , ^7Be) were measured in sediments at both sites. These data in conjunction with porewater data support infiltration of overlying waters into the sediment at both sites. Bioturbation is not as important at the mid-marsh site as at the near creek site.

Experimental

In 1987, eight cores were obtained from the Great Marsh, Delaware at site 1, third location as per our previous study (Luther & Church 1988). This site is similar in location to other studies (Boulegue et al. 1982; Lord & Church 1983; Luther et al. 1986; Luther & Church 1988). Replicate cores were taken approximately 2 m from and along the creek bank on August 3, 1987 on the ebb tide three hours after high tide and on August 11, 1987 on the flood tide three hours before high tide. The crest of the spring tide occurred Aug. 7, 1987 and the sampling periods were chosen within four days of the crest. During this time the entire marsh is flooded twice daily. At other times, the mid-marsh site is not flooded on a daily basis unless storm surges occur. Likewise, replicate cores were taken mid-marsh about 15 m from the creek bank on August 4, 1987 and August 12, 1987. The cores taken closest to the creek bank will be referred to as near-creek whereas the other cores will be referred to as mid-marsh. Near-creek cores were also taken on August 22, 1988 (on the flood tide three hours before high tide) and August 29, 1988 (on the ebb tide three hours after high tide); and on June 27, 1989 (on the flood tide three hours before high tide) and July 6, 1989 (on the ebb tide three hours after high

tide). Observations made on previous core holes show that the water table is within 1 cm of the sediment air interface during the entire spring tide period. In 1990 wells placed across these locations (normal climatic conditions as in 1987), showed similar results.

Sediment cores in 1987 were taken hermetically by driving 1 m lengths of 5.6 cm i.d. cellulose-acetate-butyrate core liner into the marsh. The liner was sealed at the sediment interface with a piston, capped and returned immediately to the laboratory. The cores were extruded at once and sectioned into 2.5 cm intervals under a nitrogen atmosphere in a glove box. Porewaters were expressed through 0.40 μm Nuclepore membrane filters using pneumatic squeezers (Reeburgh 1967). Approximately 15 ml of porewater were collected from each depth for subsequent analysis.

Sediment cores in 1988 and 1989 were collected with a 15 cm i.d. core liner and treated in the same manner as those obtained in 1987. However, these sediments were sectioned at 2 cm intervals and loaded into 50 ml trace metal cleaned polypropylene centrifuge tubes and centrifuged at 6000 rpm for 30 min. The supernatant was filtered as above. In the August 22, 1988 core, no porewater was obtained from two depths (4–6 and 8–10 cm) because of intense desiccation. The sediments from all cores were sealed in plastic bags under nitrogen or argon and frozen for storage.

Polarographic analysis of porewater samples for sulfur speciation was performed as described previously (Luther et al. 1985). To measure low levels of sulfur species ($<0.5 \mu\text{M}$), square wave voltammetry was performed on samples as per Luther et al. (1988). The method of standard additions was typically used to perform quantitative analysis on undiluted porewater samples. Samples diluted in base buffers were determined by a standard calibration curve in the base buffer. Precision was typically 5% and frequently less than 1%. Oxygen was not measurable in any porewater analyzed by polarography (minimum detectable limit is estimated at 0.5 μM).

Iron (II) was measured by the method of Stookey (1970) which uses ferrozine as a selective Fe(II) chelator. Total iron was measured by adding hydroxylamine to the sample to reduce Fe(III) to Fe(II) and then analyzing for Fe(II). Iron(III) may consist of soluble Fe(III) complexes or amorphous solid phases smaller than 0.40 μm in size. Chloride and sulfate were analyzed by argentometric titration and gravimetry in 1987 and by ion chromatography using a Dionex 4000i system in 1988 and 1989. Alkalinity was measured by Gran titration with NaOH after adding an aliquot of the sample to 1 mM HCl solution ($\text{pH} = 3$) to remove CO_2 and H_2S (adaptation of Gieskes and Rogers (1973) by Lord (1980)). The back titration was performed at the low pH region where organic buffering capacity

would be significant. Thus, alkalinity includes carbonate species and other weak acids such as organic ligands which can complex metal ions. Organic ligands are likely present since porewaters typically have some yellow coloration. The pH was measured potentiometrically. Total dissolved reduced species (sulfide, thiosulfate, thiols, etc.) were determined with Ellman's reagent (1959), 5,5'-Dithiobis(2-nitrobenzoic acid) in pH 7.5 phosphate buffer. Fe(II) was complexed with ferrozine to prevent its reaction with Ellman's reagent; we performed separate experiments and found that Fe(II) complexed with ferrozine did not react with Ellman's reagent. Mn(II) uncomplexed does not interfere with Ellman's reagent at a pH of 7.5. Tables 2 and 4 list data for total thiols which is operationally defined as the Ellman's reagent concentration minus the sum of the concentrations of sulfide [S(-2)] and thiosulfate. Precision for all these analyses is typically better than 2%.

Acid volatile sulfide (AVS) and pyrite were measured according to the method of Cutter and Oatts (1987) with modifications to the H₂S trapping and analysis procedures. Sulfide from AVS was released with 3 M HCl and the resulting sulfide was trapped in 1 M NaOH solution which had been deaerated previously. Aliquots of this solution were added to a sodium chloride solution at pH 12 and analyzed for sulfide by square wave voltammetry (Luther et al. 1988). Recovery of standard sulfide solutions is 99.6% ± 3.9% (N = 8). Sulfide from pyrite was released with acidic Cr(II) solution and the resulting H₂S was trapped and analyzed as above. Using freshly cleaned pyrite as per Moses et al. (1987) which was sieved to <64 μm in size, recovery is 97% ± 5% (N = 7). Zerovalent sulfur, S(0), in the sediments was extracted three times in a nitrogen purged organic solvent (3 parts toluene or freon to 1 part methanol). The solvent extracts were pooled and dried under nitrogen. To the residue was added 10 ml of 0.01 M sodium sulfite to convert S(0) to thiosulfate which is analyzed as per Luther et al. (1985). Zerovalent sulfur forms include all forms of elemental sulfur and some organic polysulfides — precision for S(0) is typically better than 5%. AVS, FeS₂, and S(0) are reported in units of μmoles S (g⁻¹ dry weight)⁻¹. Triplicate measurements were made on all samples unless otherwise indicated.

Radionuclide methods

Duplicate cores from the mid-marsh and near-creek sites were collected on November 11, 1988 for gamma analysis of ²¹⁰Pb, ¹³⁷Cs and ⁷Be. The cores were taken back to the laboratory where they were sectioned into 1.5 or 3.0 cm sections. Identical sections of wet sediment from the duplicate cores were placed in aluminum cans of known weight and volume

and the cans sealed. After gamma counting the cans were reopened and dried at 60 °C.

Sealed cans were counted after 15 days (to allow the short-lived isotopes of ^{222}Rn to come into secular equilibrium) on a Princeton Gamma-Tech Intrinsic Ge gamma detector. Self-absorption of the 47 keV gamma isotope of ^{210}Pb by the sample was corrected using the method of Cutshall and Larsen (1983). $^{210}\text{Pb}_{\text{excess}}$ was calculated by subtracting the activity of ^{226}Ra from the total calculated ^{210}Pb activity. ^{226}Ra was estimated by averaging the calculated activities from ^{214}Bi (609 keV) and ^{214}Pb (295 and 353 keV) peaks.

Radionuclide results for near-creek and mid-marsh locations

Differences between the mid-marsh and near-creek sites, with respect to accretion, bioturbation, dessication and porewater advection can be examined using the distributions of the atmospherically deposited radionuclides ^{210}Pb ($t_{1/2} = 22$ yrs.), ^{137}Cs ($t_{1/2} = 30$ yrs.) and ^7Be ($t_{1/2} = 53$ days). For example, Sharma et al. (1987) have successfully fit observed ^{210}Pb distributions using a regeneration model in South Carolina marsh sediments that are extensively bioturbated by fiddler crab (*Uca pugilix*) burrowing. This type of bioturbation has the effect of significantly reducing the surface activity of ^{210}Pb and ^7Be while increasing their activities at depth. For a pulse input tracer, such as ^{137}Cs , the peak in activity is also displaced downwards.

We can calculate a sedimentation rate in the mid-marsh site, where bioturbation, especially by fiddler crab burrowing, is thought to be minimal relative to near-creek and creek-bank sediments. Using the $^{210}\text{Pb}_{\text{excess}}$ data from the mid-marsh site (Fig. 1A), we calculate a sedimentation rate of $0.15 \pm 0.02 \text{ g cm}^{-2} \text{ yr}^{-1}$. From the sedimentation rate we can estimate accretion rates for the upper (rooty) and lower portions of the mid-marsh sediments using the relationship described by Berner (1980):

$$\omega = S/(\rho_s(1 - \phi))$$

where: ω = accretion rate (cm yr^{-1})
 ρ_s = average particle density (g mL^{-1})
 ϕ = porosity

Using an average dry weight density $\rho_s(1 - \phi)$ in the upper 10.0 cm of $0.31 \pm 0.07 \text{ g cm}^{-3}$, we calculate an accretion rate for the upper 10 cm of $0.47 \pm 0.10 \text{ cm yr}^{-1}$. This result agrees with that of Church et al. (1981)

who reported 0.46 cm yr^{-1} for the same mid-marsh site. Below 10 cm the accretion rate is determined to be $0.25 \pm 0.03 \text{ cm yr}^{-1}$.

The predicted ^{137}Cs peak should fall between 9.25 and 14.00 cm depth, based upon the accretion rate determined for the upper 10 cm and assuming that the peak in ^{137}Cs should correspond to 1963 (the year of peak ^{137}Cs fallout from aboveground nuclear testing). The observed peak in ^{137}Cs activity does fall within this range. Therefore, within the error of the model calculation, we can detect no net advection of ^{137}Cs either by bioturbation or porewater advection in the mid-marsh sediments. Thus, ^{137}Cs appears to be governed by particle bound interactions at this site.

Our ^7Be data, however, do suggest that there may be some downward porewater advection to at least three cm at this site. ^7Be should be retained within the upper one cm of marsh sediment if accretion and particle dominated processes are the principal control over ^7Be distribution. Casey et al. (1986) have observed downward penetration after artificially applying ^7Be to an undersaturated, vegetated marsh surface, whereas ^7Be was retained at the surface when the marsh sediments were saturated. Downward diffusion of ^7Be is also possible due to low pH values as observed in the surface marsh sediments in this study. Be, which has an hydrolysis constant of $\text{pK} = 6.5$, shows enhanced mobility at pH's below 6 (Casey et al. 1986; Measures & Edmond 1980). Thus, while some infiltration of waters into the upper few centimeters may occur, large scale advective processes — either bioturbation or porewater movement — are not apparent in the radionuclide data for our mid-marsh site.

The near creek site stands in contrast with respect to the ^{210}Pb , ^{137}Cs and ^7Be profiles (Fig. 1). The nearly constant $^{210}\text{Pb}_{\text{excess}}$ activity down to 16 cm is indicative of bioturbation, as is the presence of ^7Be at depths of 11 cm. The peak in ^{137}Cs activity is observed at 15.6 cm, which is significantly below the peak at the mid-marsh site of 11 cm and just beyond the upper range of 14 cm predicted for the ^{137}Cs peak. The ^{137}Cs profile appears more diffused and exhibits high activities both at depth and at the surface relative to the mid-marsh site. The radionuclide data generally point to bioturbation of marsh sediments and associated porewaters at the near-creek site. Displacement of the ^{137}Cs peak and downcore penetration by ^7Be can be also attributed to desorption and porewater advection due to hypersalinity and reduced pH, respectively (Casey et al. 1986).

While the profiles at the mid-marsh and near-creek sites are dissimilar, the inventories of the individual radionuclides are the same at both sites. As can be seen in Table 1, the inventory of $^{210}\text{Pb}_{\text{excess}}$ at the near-creek site is approximately 1.2 times that of the mid-marsh and may reflect a slightly greater particle trapping efficiency nearer to the creekbank. The deposi-

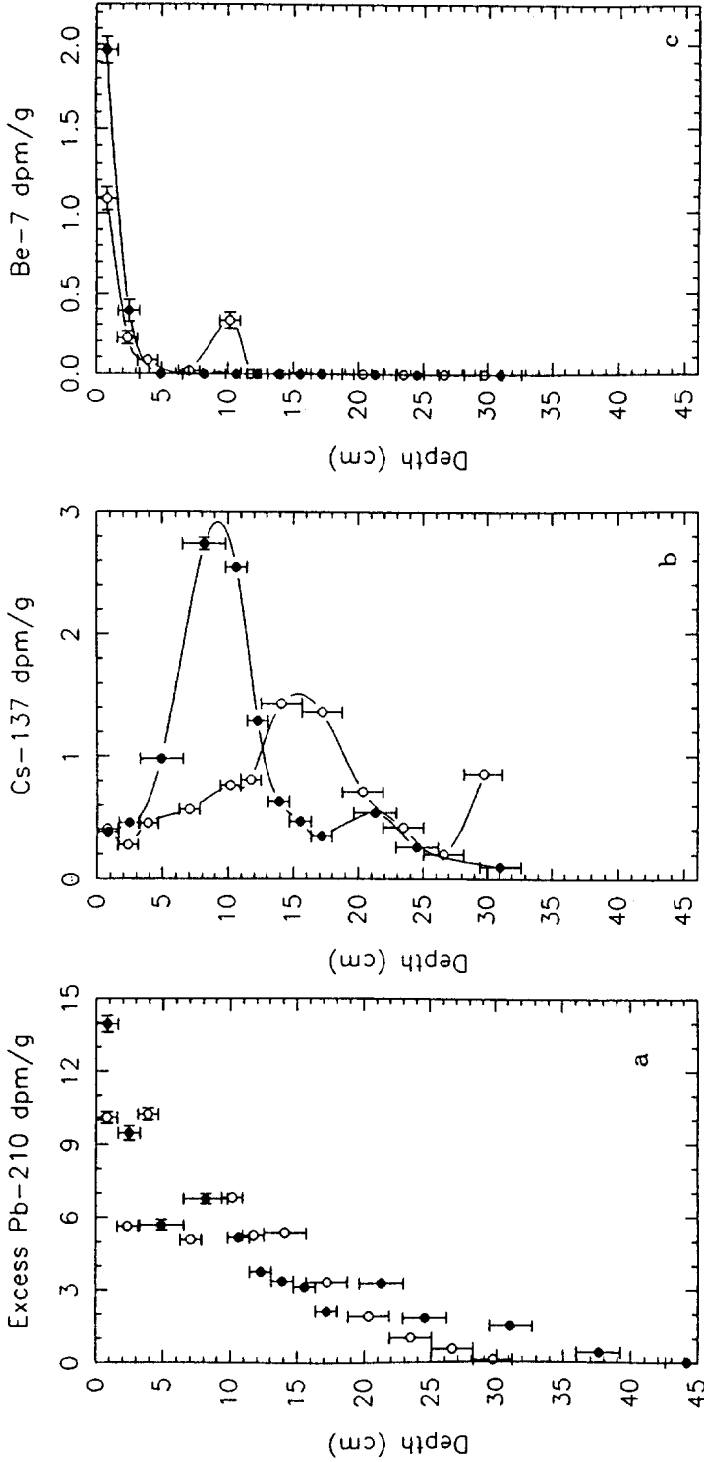


Fig. 1. A) $^{210}\text{Pb}_{\text{excess}}$ profile versus depth, and B) ^{137}Cs and C) ^7Be profiles over depth at the mid-marsh (●) and near-creek locations (○).

Table 1. Total radionuclide inventories for near-creek and mid-marsh locations integrated over the upper 30 cm.

Nuclide	Site	dpm cm ⁻²	dpm cm ⁻² yr ⁻¹
²¹⁰ Pb _{excess}	Near-creek	57.8	1.80
	Mid-marsh	48.3	1.50
¹³⁷ Cs	Near-creek	> 11.5	
	Mid-marsh	11.9	
⁷ Be	Near-creek	1.09	5.2
	Mid-marsh	1.16	5.5

tion of ²¹⁰Pb_{excess} is calculated (by multiplying the inventory by the mean-life of ²¹⁰Pb, 0.03114 yr⁻¹) to be 1.50 and 1.80 dpm cm⁻² yr⁻¹ for the mid-marsh and near-creek sites respectively. This is approximately twice the measured atmospheric rate of 0.7 dpm cm⁻² yr⁻¹ for Lewes, DE (Hartman 1987). The ⁷Be and ¹³⁷Cs inventories are nearly identical for both sites. This data indicates that loss of the atmospherically deposited radionuclides by lateral advection or drainage at the near-creek site is negligible. Whether or not porewater flow occurs independent of fiddler crab bioirrigation (e.g. burrowing, feeding, etc.), cannot be inferred from the radionuclide data alone. As discussed below our chloride data (Fig. 2) does support porewater flow on short time scales.

Differences in the radionuclide profiles between sites can principally be ascribed to fiddler crab bioturbation, which may facilitate porewater flow. Thus, bioturbation and porewater flow will likely affect the hydrology of the near-creek site and consequently its iron and sulfur chemistry (Gardner et al. 1989). However, the near-creek site bioturbation reported here is not nearly as extensive as that observed in creekbank (tall form *Spartina*) sediments from South Carolina (Sharma et al. 1987). The pH values of our near-creek sediments are variable and typically below 6.5. Sharma et al. (1987) observe pH values of 7.4 which are constant over depth indicating that sediment pH was close to that of adjacent creek water because of massive fiddler crab bioturbation at their creekbank location.

Results (1987)

Tables 2 and 3 contain the porewater results and solid inorganic sulfur speciation, respectively for the cores taken near-creek in August 1987.

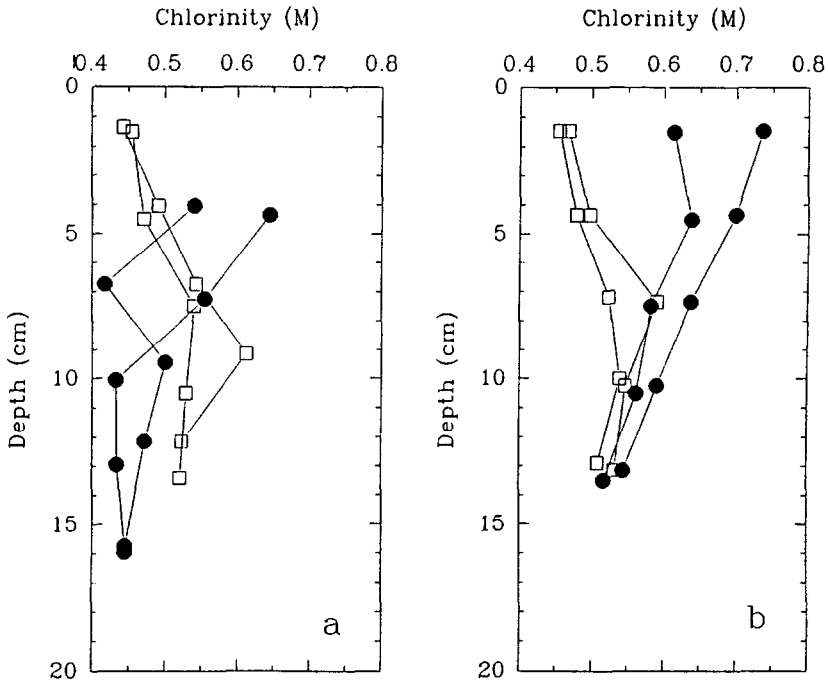


Fig. 2. Chloride profiles for A) Near creek and B) Mid marsh locations in August 1987. Squares indicate duplicate cores taken after the flood; filled circles indicate duplicate cores taken before the flood.

Tables 4 and 5 contain the porewater results and solid inorganic sulfur speciation, respectively for the cores taken mid-marsh in August 1987. In the following presentation of results, certain comparisons between locations will be made under the mid-marsh results.

Major porewater species near-creek

Cores 1 and 2 were taken 1 m apart before the spring tide and show interesting physical characteristics based on chloride levels. The samples over the first 8 cm show variable chloride and sulfate values at each depth — as much as 15% from the mean value for the same depths. Below 8 cm the chloride and sulfate values show little or no variability. Variability in the upper 8 cm is related to desiccation which is indicated in Fig. 2A by the decreasing chloride ion concentrations with depth (Casey & Lasaga 1987; Lord & Church 1983). Flooding seawater has a concentration of 0.44 M (see also Lord & Church 1983).

Cores 5 and 6 were taken along the same creek bank transect after the

Table 2. Porewater constituents for the near creek location during August 1987.

August 3, 1987 near creek before the flood										
Depth (cm)	Cl ⁻ M	SO ₄ ²⁻ mM	∅ SO ₄ ²⁻ mM	ALK meq/L	pH	S(-2) μM	THIOL μM	S ₂ O ₅ ²⁻ μM	Fe ²⁺ μM	Fe ³⁺ μM
Core 1										
0 - 2.7								NA		
2.7 - 5.4	0.541	38.34	10.38	12.11	4.55	39.2	21	22.44	22.4	127.4
5.4 - 8.1	0.418	30.35	8.75	18.52	6.03	271	NA	61.04	6.0	30.7
8.1 - 10.0	0.500	25.39	-0.45	33.27	6.65	1,400	NA	NA	ND	1.5
10.8 - 13.5	0.472	15.18	-9.21	43.38	7.02	1,140	NA	287.4	ND	0.5
13.5 - 16.2	0.445	10.83	-12.17	45.18	7.15	1,530	NA	228.8	ND	6.1
Core 2										
0 - 2.9										
2.9 - 5.8	0.645	52.46	19.12	11.74		16.3	ND	52.26	44.6	130.2
5.8 - 8.6	0.555	46.89	18.21	11.49	5.35	139	NA	77.67	128.2	47.9
8.6 - 11.5	0.433	41.20	18.82	16.93	6.02	132	NA	82.62	24.2	3.7
11.5 - 14.4	0.434	33.43	11.00	24.86		32.9	NA	NA	ND	ND
14.4 - 17.3	0.445	21.95	-1.05	38.31	6.56	1,220	NA	191.3	ND	ND

Table 2. (Continued)

August 11, 1987 near creek before the flood											
Depth (cm)	Cl ⁻ M	SO ₄ ⁻ mM	δ SO ₄ ⁻ mM	ALK meq/L	pH	S(-2) μM	S(0) μM	THIOL μM	S ₂ O ₃ ⁻ μM	Fe ²⁺ μM	Fe ³⁺ μM
Core 5											
0 - 2.7	0.443	30.82	7.92	2.3	6.45	NA	ND	177	ND	148.2	108.4
2.7 - 5.4	0.491	31.86	6.48	13.12	6.89	1.97	ND	275	ND	192.1	306.0
5.4 - 8.1	0.543	33.82	5.76	14.32	6.17	65.7	24.6	298	ND	118.8	17.8
8.1 - 10.8	0.612	32.38	0.75	5.21	6.52	767	ND	ND	16.95	65.1	28.2
10.8 - 13.5	0.523	40.20	13.17	5.18	5.50	1,080	ND	ND	87.47	162.8	20.4
Core 6											
0 - 3.0	0.455	36.38	12.86	7.37	6.17	1.63	ND	308	ND	636.6	48.6
3.0 - 5.9	0.471	36.03	11.69	6.67	5.98	9.80	ND	510	ND	906.6	61.6
5.9 - 8.9	0.540	40.07	12.16	4.09	5.41	427	ND	1153	ND	353.3	-0-
8.9 - 11.8	0.529	40.86	13.52	5.13	5.47	638	42.7	NA	37.93	301.3	97.4
11.8 - 14.8	0.521	37.73	10.80	10.64	6.12	1,640	ND	NA	28.99	7.3	28.9

NA = Not Analyzed

ND = Not Detected

Table 3. Inorganic solid phase sulfur speciation for near-creek location cores taken in 1987.

Near creek before the monthly flood		Core #1 (August 3, 1987)				Core #2 (August 3, 1987)			
Depth (cm)		FeS ₂	AVS	S(0)	Depth (cm)	FeS ₂	AVS	S(0)	
0 - 2.7		22.6 ± 3.7	1.03 ± 0.55	7.62	0 - 2.9	31.6 ± 3.9	NM	8.14	
2.7- 5.4		60.9 ± 0.87	7.03 ± 0.73	34.3	2.9- 5.8	117.4 ± 11.6	4.74 ± 2.3	54.1	
5.4- 8.1		113.0 ± 10.5	6.41 ± 1.43	60.7	5.8- 8.6	113.7 ± 1.6	9.21 ± 0.7	40.0	
8.1-10.8		171.7 ± 8.8	2.38 ± 1.0	25.87	8.6-11.5	66.1 ± 8.7	7.16 ± 0.5	82.1	
10.8-13.5		168.1 ± 23.0	2.09 ± 0.31	19.0	11.5-14.4	95.9 ± 5.3	NM	45.7	
13.5-16.2		327.6 ± 11.8	1.36 ± 0.1	NM	14.4-17.3	452.5 ± 66.5	NM	24.1	
After the monthly flood									
		Core #5 (August 11, 1987)				Core #6 (August 11, 1987)			
Depth (cm)		FeS ₂	AVS	S(0)	Depth (cm)	FeS ₂	AVS	S(0)	
0 - 2.7		42.3 ± 3.6	7.02 ± 2.2	15.6	0 - 3.0	30.2 ± 8.5	3.13 ± 1.39	11.0	
2.7- 5.4		34.7 ± 9.3	2.62 ± 0.86	33.9	3.0- 5.9	41.6 ± 5.6	8.03 ± 1.9	26.6	
5.4- 8.1		42.3 ± 7.2	4.33 ± 0.29	76.3	5.9- 8.9	50.9 ± 3.0	10.3 ± 0.88	32.4	
8.1-10.8		52.1 ± 1.6	4.68 ± 1.5	33.3	8.9-11.8	95.9 ± 4.9	5.25 ± 2.22	14.6	
10.8-13.5		68.0 ± 12.4	5.22 ± 1.7	NA	11.8-14.8	155.6 ± 10.2	3.44 ± 1.33	40.4	

All values are given in $\mu\text{mole S (g dry weight)}^{-1}$.

NA = Not Analyzed

NM = Not Measured

Table 4. Porewater constituents for the mid marsh location during August 1987.

August 4, 1987 mid marsh before the flood										
Depth (cm)	Cl ⁻ M	SO ₄ ⁻² mM	δ SO ₄ ⁻² mM	ALK meq/L	pH	S(-2) μM	THIOL μM	S ₂ O ₃ ⁻² μM	Fe ²⁺ μM	Fe ³⁺ μM
Core 3										
0 - 3.0	0.614	67.75	36.02	13.12	5.75	1.55	155	ND	126.1	17.2
3.0 - 6.0	0.639	53.54	20.52	13.88	5.93	4.35	148	5.93	136.1	33.2
6.0 - 9.0	0.584	48.72	18.53	11.74	5.81	9.26	139	7.20	79.7	10.6
9.0 - 12.0	0.563	44.46	15.36	16.91	6.34	91.1	19	57.91	27.1	3.0
12.0 - 15.0	0.519	39.08	12.26	20.16	6.43	1,060.0	189	46.27	8.5	11.3
Core 4										
0 - 2.9	0.736	68.71	30.67	8.86	5.49	2.82	202	ND	106.7	14.4
2.9 - 5.9	0.700	58.10	21.92	9.96	5.76	16.4	158	14.26	80.4	20.9
5.9 - 8.8	0.639	48.76	15.74	13.55	6.32	17.5	198	33.89	27.8	3.8
8.8 - 11.7	0.592	42.55	11.96	12.37	6.65	256	32	95.32	5.4	6.5
11.7 - 14.7	0.546	36.68	8.46	26.02	6.76	883	ND	55.08	2.3	3.2

Table 4. (Continued)

August 12, 1987 mid marsh after the flood											
Depth (cm)	Cl ⁻ M	SO ₄ ²⁻ mM	δ SO ₄ ²⁻ mM	ALK meq/L	pH	S(-2) μM	S(0) μM	THIOL μM	S ₂ O ₃ ²⁻ μM	Fe ²⁺ μM	Fe ³⁺ μM
Core 7											
0 - 2.9	0.468	33.16	8.97	12.86	6.09	<1	ND	230	ND	117.2	67.7
2.9 - 5.9	0.498	37.67	11.93	13.12	5.66	2.70	ND	264	ND	99.3	68.9
5.9 - 8.8	0.592	38.64	8.04	15.02	5.97	35.70	ND	249	23.07	68.4	44.9
8.8 - 11.7	0.548	37.47	9.15	17.58	6.52	307	ND	NA	24.09	8.1	8.5
11.7 - 14.7	0.533	37.90	10.35	24.68	6.44	1,340	ND	NA	52.04	4.9	8.4
Core 8											
0 - 2.9	0.455	30.77	7.26	15.97	6.30	2.94	ND	284	ND	24.4	105.5
2.9 - 5.8	0.479	60.36	35.60	17.35	6.66	29.3	ND	217	34.10	22.8	22.2
5.8 - 8.6	0.525	35.16	8.03	35.51	6.42	491	ND	980	29.36	6.5	15.2
8.6 - 11.5	0.540	31.82	3.91	19.55	6.58	1,363	ND	NA	24.81	6.5	11.8
11.5 - 14.4	0.510	51.93	25.57	7.08	6.80	1,890	ND	NA	23.24	6.5	5.2

NA = Not Analyzed

ND = Not Detected

Table 5. Inorganic solid phase sulfur speciation for mid-marsh location cores taken in 1987.

Mid marsh before the monthly flood							
Core # 3 (August 4, 1987)			Core # 4 (August 4, 1987)				
Depth (cm)	FeS ₂	AVS	S(0)	Depth (cm)	FeS ₂	AVS	S(0)
0 - 3.0	43.5 ± 2.9	4.73 ± 1.8	13.5	0 - 2.9	52.2 ± 8.6	3.20 ± 0.32	15.5
3.0- 6.0	84.2 ± 9.9	7.6 ± 2.2	38.6	2.9- 5.9	228.6 ± 15.5	3.45 ± 0.83	49.0
6.0- 9.0	78.2 ± 10.3	7.4 ± 0.97	53.3	5.9- 8.8	110.2 ± 5.8	8.08 ± 1.3	45.3
9.0-12.0	387.4 ± 38.2	11.7 ± 1.8	65.7	8.8-11.7	338.6 ± 36.1	4.36 ± 2.3	34.5
12.0-15.0	267.2 ± 26.1	10.5 ± 1.0	7.7	11.7-14.7	349.1 ± 48.0	4.52 ± 2.2	5.0
After the monthly flood							
Core # 7 (August 12, 1987)			Core # 8 (August 12, 1987)				
Depth (cm)	FeS ₂	AVS	S(0)	Depth (cm)	FeS ₂	AVS	S(0)
0 - 2.9	44.9 ± 3.5	3.56 ± 2.0	10.5	0 - 2.9	50.9 ± 2.1	6.54 ± 1.53	33.6
2.9- 5.9	31.8 ± 1.8	3.86 ± 0.95	31.4	2.9- 5.8	74.3 ± 1.8	4.05 ± 1.3	54.3
5.9- 8.8	39.9 ± 1.7	9.26 ± 1.83	67.9	5.8- 8.6	141.6 ± 15.2	6.1 ± 1.5	45.8
8.8-11.7	302.2 ± 14.0	7.35 ± 2.1	24.0	8.6-11.5	313.0 ± 22.1	4.84 ± 0.97	25.9
11.7-14.7	273.8 ± 14.5	2.02 ± 0.89	15.6	11.5-14.4	271.2 ± 4.9	2.16 ± 0.28	8.1

All values are given in $\mu\text{mole S (g dry weight)}^{-1}$.

spring tide. They are 1 m from each other (core 5 was taken 1 m from core 2). In these cores the chloride and sulfate values show less variability (< 6% of the mean) at each depth. The spring tide has reversed the effects of desiccation as expected. Closer inspection indicates that below 8 cm, chloride and sulfate values increased significantly (about 10%) after the flooding, presumably from advection within the sediment (Casey & Lasaga 1987; Casey 1986). The ^7Be and ^{137}Cs data show that downward displacement of material is a common feature. As will be shown, the spring tide has a significant impact on the other porewater and solid sulfur species in 1987.

The δ sulfate is the increase (+) or decrease (-) in sulfate normalized to the molar $\text{SO}_4^{2-}/\text{Cl}^-$ ratio of seawater. Before and after the flooding event, δSO_4^{2-} varies for the replicate cores. In general δSO_4^{2-} is more positive after the spring tide which suggests that there was oxidation of reduced sulfur compounds in addition to the effect of mixing processes. The alkalinity also decreases at all depths. The pH shows general decreases after the flood at many of the depths, but is buffered by the relatively high alkalinity (particularly before the flood). The high alkalinity values at low pH (e.g. < 5) demonstrate that alkalinity is due to other weak acids (which are metal complexers) as well as carbonate species. Oxidation processes are competing with sulfate reduction as has been noted in other studies (Gardner et al. 1988; Howarth & Teal 1979; Hines et al. 1989; Luther & Church 1988).

Dissolved sulfur and iron species near-creek

Hydrogen sulfide [S(-2)] decreases substantially after the spring tide over the upper 8 cm. Thiosulfate decreases sharply over all depths after the spring tide and is not detected (minimum detectable limit is 200 nM) in the upper 8 cm. Polysulfides expressed as total soluble zerovalent sulfur [S(0)] and sulfite are generally not detected when measurements were made. Sulfite was not detected at any depth. All these sulfur species are susceptible to oxidation and generate acidity during oxidation.

Iron(II) and Fe(III) increase sharply after the spring tide. Iron(II) increases are typically an order of magnitude at most depths and Fe(II) is measurable to a depth of 15 cm after the flood. This is similar to our earlier report (Luther & Church 1988) and is related to pyrite oxidation (see below). Iron(III) also increases after the flood but is not as high in concentration as Fe(II). We cannot indicate precisely whether the Fe(III) is from soluble Fe(III) complexes or solid phase Fe(III) particles (amorphous or crystalline) less than 0.40 μm in size. Boyle et al. (1977) demonstrated that during estuarine mixing much of the total iron passing through 0.40

μm filters is colloidal. Giblin et al. (1986) have shown that up to 53% of the total iron in salt marsh porewaters is organically complexed. We suspect that before the flood, the Fe(III) is mainly solid phase material since dissolved Fe(III) is reduced quickly in the presence of thiosulfate (Luther 1987). After the flood, we believe that Fe(III) values reported in the upper 8 cm may consist of some soluble Fe(III) complexes because no thiosulfate is detected.

Inorganic solid sulfur speciation near-creek

Pyrite is the dominant pool of inorganic sulfur in the upper 15 cm of sediment although total solid phase zerovalent sulfur [S(0)] is significant in concentration (Table 3). AVS is of minor importance in these sediments in comparison to FeS₂ and S(0). The data indicate that FeS₂ oxidation is occurring at both sites and that there is more FeS₂ in the mid-marsh sediments. We will discuss these data at length below. However, the change in the FeS₂ data is consistent with the porewater parameters discussed above [S(-2), thiosulfate and alkalinity decreases; Fe(II) increases after the flood].

Major porewater species mid-marsh

Cores 3 and 4 were taken 1 m apart before the monthly flood. As in cores 1 and 2, the chloride values (Fig. 2B) over the upper 8 cm vary at each depth (> 10% from the mean of the same depths). However, the sulfate values show little or no variability. The mid-marsh chloride values before the spring tide are significantly higher (> 10%) than the chloride values for the near-creek cores at all depths; the sulfate values show a similar trend. The mid-marsh sediments undergo greater net desiccation than the near-creek sediments because vertical and lateral flushing is less important at the mid-marsh location on a daily basis. As in the near-creek cores (1 and 2), chloride concentration decreases with depth.

For cores 7 and 8 chloride ion concentration (Fig. 2B) increases to about the 8 cm depth at the mid-marsh site after the spring tide. Below 5 cm, the chloride concentrations for mid-marsh samples do not change substantially. This is in contrast to the near-creek samples which showed an increase in chloride levels after the flooding below 5 cm. The chloride values at each depth for mid-marsh cores 7 and 8 are remarkably similar to those of the near-creek cores 5 and 6 — all these cores were taken after the spring tide and within one day. These data show that the upper 5–8 cm of marsh sediment undergo infiltration of water during the spring tide at both locations. The spring tide event should have similar impact on

biogeochemical processes at both locations of the marsh (see also Casey & Lasaga 1987).

The δSO_4^{2-} values are consistently positive both before and after the flood at the mid-marsh site indicating that sulfide oxidation processes are important. However, the alkalinity values for the mid-marsh site show less change or a slight increase on flooding in contrast to the near-creek location which showed a significant decrease on flooding (Fig. 3), and the pH also shows less change at the mid-marsh location. These data show that both sulfate reduction and sulfide oxidation processes are occurring and their rates may be nearly equal. The 30 mM decrease in sulfate after the flood at the surface sediments of the near-creek site is due to dilution and to possibly sulfate reduction. Based on this decrease and the solid phase density and porosity, $85.0 \mu\text{mole S g}^{-1}$ could be buried in the form of organic sulfur which is about 50% of the total sulfur in these sediments (Ferdelman et al. 1991).

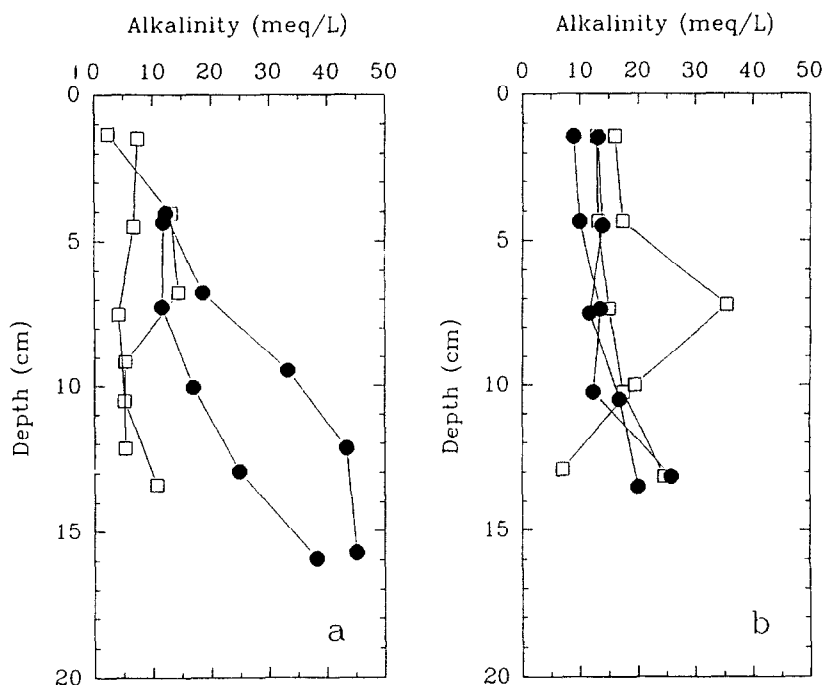


Fig. 3. Alkalinity profiles for A) Near Creek and B) Mid marsh locations in August 1987. Squares indicate duplicate cores taken after the flood; filled circles indicate duplicate cores taken before the flood.

Dissolved sulfur and iron species (mid-marsh)

Hydrogen sulfide increases regularly with depth both before and after the spring tide with a slight increase in concentration after the spring tide. Thiosulfate decreases also but not to the extent as at the near-creek location. Polysulfides and sulfite were not detected.

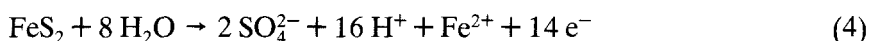
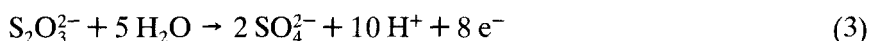
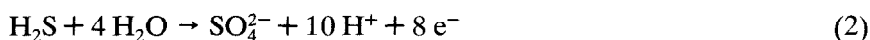
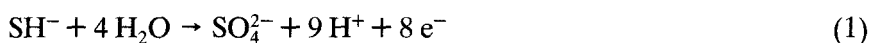
Iron(II) concentrations are typically lower after the spring tide whereas Fe(III) concentrations are higher. These changes are minor compared to the changes at the near-creek site. The total dissolved iron concentrations for the mid-marsh location both before and after the flood are comparable to those for the near-creek location before the flooding event. The ratio of Fe(III) to Fe(II) is typically less than or equal to one and is indicative of pyrite oxidation (see below). The Fe(III) is a solid phase species because thiosulfate and sulfide are present at almost each depth at the mid-marsh location.

Inorganic solid sulfur speciation (mid-marsh)

As in the near-creek location, FeS_2 is the dominant pool of inorganic reduced sulfur in the mid-marsh sediments followed by $\text{S}(0)$ and AVS (Table 5). Pyrite increases begin to occur at 5 to 8 cm. Over the upper 8 cm, the pyrite concentrations are generally comparable at both locations. Below 8 cm, pyrite concentrations are typically higher (about two times) at the mid-marsh location. The radionuclide (Fig. 1) and chloride (Fig. 2) data demonstrate that infiltration of porewater are similar at both sites for the upper 8 cm. However, at the near creek site bioturbation is evident which would allow for more mixing of porewater and sedimentary material below 8 cm and more oxidation of FeS_2 . The $\text{S}(0)$ levels show maxima near the 5 to 8 cm depth interval at both locations indicating that $\text{S}(0)$ is forming from H_2S oxidation and is converted into pyrite and perhaps other organic sulfur forms which account for 50% of the total solid sulfur inventory in this marsh (Ferdelman et al. 1991).

Discussion of results – 1987 data

In an earlier study (Luther & Church 1988), we suggested that the oxidation of reduced sulfur compounds occurs over the spring tide period at Great Marsh, Delaware. The following discussion demonstrates that the short term oxidation is ongoing at both near-creek and mid-marsh locations, but is more pronounced at the near-creek site. The operative half reactions for reduced sulfur oxidation are given in equations 1–4.



All reactions generate considerably acidity which can consume alkalinity. From these equations, direct measurements of the reactant reduced sulfur species, pH, alkalinity and iron species should give information regarding oxidation processes.

Fig. 3 presents the alkalinity results for near-creek (A) and mid-marsh sites (B). Alkalinity is significantly lower after the flood for the near-creek site but not for the mid-marsh location. This demonstrates that short term flooding significantly enhances oxidation processes near-creek. Because the alkalinity values are high before the spring tide and never reach zero, pH alone is not as good a parameter in this suite of cores to indicate oxidation processes. Fig. 4A (near-creek) and 4B (mid-marsh) show thiosulfate levels before and after the spring tide. Thiosulfate decreases more sharply after the flooding event at the near-creek location. Likewise, Fig. 5A (near-creek) shows that Fe(II) increases after the flood in accordance with Eq. (4).

Although porewater parameters are more sensitive to solid phase changes, pyrite changes can be used to understand the redox properties of these sediments as well. The data in Tables 3 and 5 indicate that pyrite was undergoing short term oxidation at both sites over similar depths. To assess variations in pyrite concentrations in a more quantitative manner, we calculated pyrite concentrations integrated over the upper 11 cm of depth by Simpson's rule for each duplicate set of cores and performed a model I two-way ANOVA to compare near-creek with mid-marsh cores. Core location and tide were considered to be fixed factors. Table 6 presents the data and the ANOVA analysis. Pyrite was assumed to vary according to the spring tide and location within the marsh. These results show that pyrite concentration variations are significantly different between marsh locations (higher at the mid-marsh site) as well as significantly lower after the spring flood at each site. There was no significant variation due to the interaction of location and spring tide effects.

In an earlier report (Luther & Church 1988), we calculated pE values for the porewaters of the upper surface sediments according to Eq. (5)

$$\log \{ \text{FeS}_2 \} / \{ [\text{Fe}^{2+}] \} = 2 \log \{ \text{SO}_4^{2-} \} - 16 \text{pH} - 14 \text{pE} + 86.8 \quad (5)$$

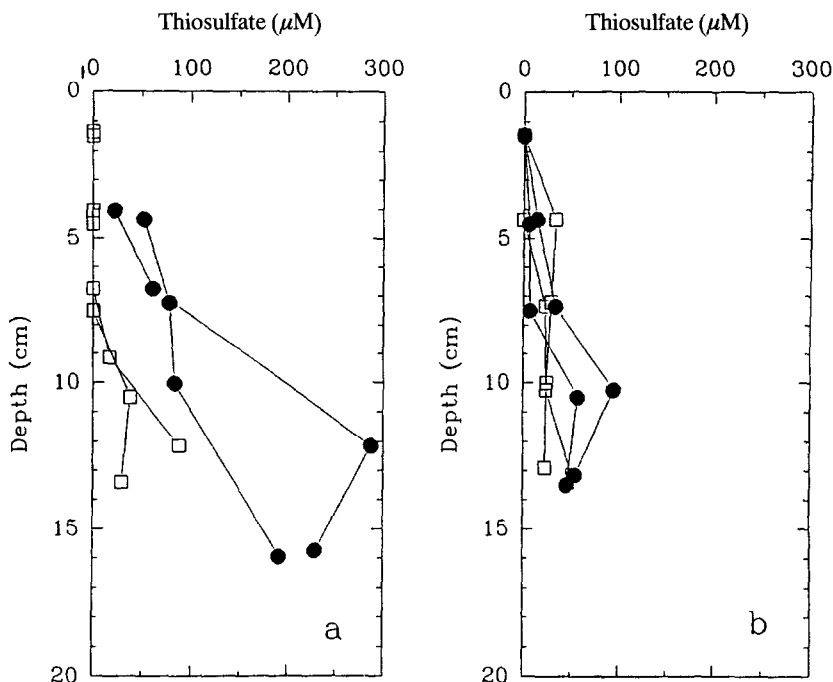


Fig. 4. Thiosulfate profiles for A) Near Creek and B) Mid marsh locations in August 1987. Squares indicate duplicate cores taken after the flood; filled circles indicate duplicate cores taken before the flood.

which is based on Eq. (4) where $\{ \}$ are ion activities of the soluble components. The pE for the 5–7.5 cm depth interval was +0.316 before the flood and -1.60 after the flood for the near-creek site. The “mild” oxidizing (before the flood) and reducing (after the flood) conditions were attributed to an order of magnitude increase in the Fe(II) concentration and a slight decrease in sulfate concentration after the flooding event. In the present study at the near-creek location, Fe(II) concentrations again increased an order of magnitude or more with slight sulfate concentrations. Thus, the system is poised again between “mild” oxidizing and reducing processes. However, at the mid-marsh location there is no dramatic change in both Fe(II) and sulfate concentrations with flooding. This porewater data at the mid-marsh site parallels the smaller pyrite changes in the sediment (Table 6). These data show that the mid-marsh system was not affected to the same degree as the near-creek system.

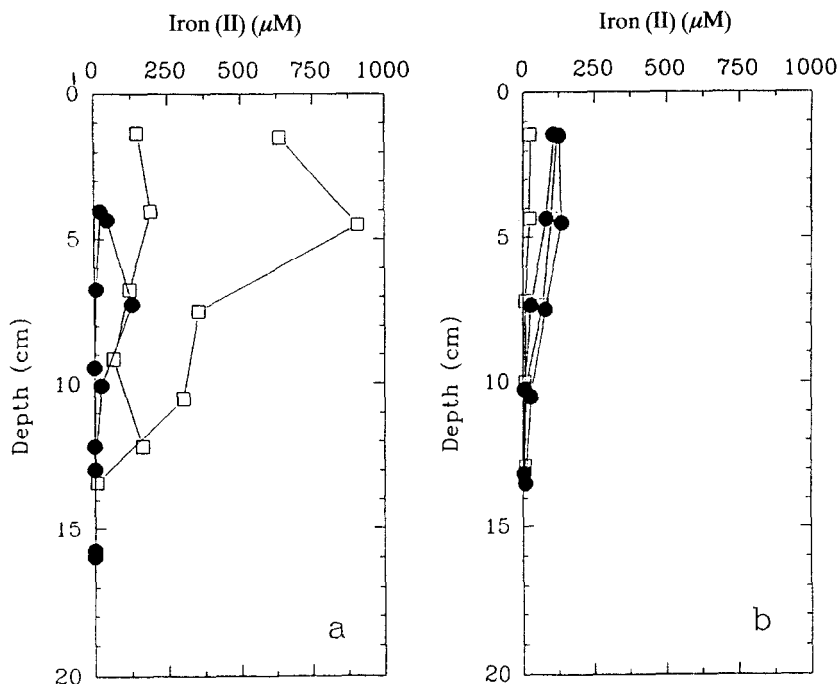


Fig. 5. Fe(II) concentrations for A) Near Creek and B) Mid marsh locations in August 1987. Squares indicate duplicate cores taken after the flood; filled circles indicate duplicate cores taken before the flood.

Table 6. Pyrite concentrations [$\mu\text{mole (g dry weight)}^{-1}$] integrated over all depths (Simpson's rule) for the average of the two cores at each site and tide.

	Before flood	After flood
Near creek	406.0	229.9
Mid marsh	874.0	648.2

ANOVA results of these data.

		F-ratio	F_c	p
Pyrite	Site	45.7	7.71	0.002
	Tide	9.40	7.71	0.037
	Site \times tide	0.144	7.71	0.724

F_c is given for the 0.05 confidence interval.

What is the oxidant(s) of reduced sulfur?

Based on field and laboratory data, molecular oxygen is not the direct oxidant of all reduced sulfur compounds. Many researchers have noted that oxygen concentrations in porewaters are not significant below a depth of 5 mm (see King 1988; Gardner et al. 1988; Gardner 1990). Our polarographic data on these and other samples supports this. Oxygen is measurable at the Hg electrode (reduction wave at -0.09 V vs. SCE). Our analyses of porewaters without purging show no detectable oxygen (minimum detectable limit is estimated to be below $0.5 \mu\text{M}$).

Several researchers have argued that oxygen must be the oxidant for reduced sulfur compounds in sediments [Dacey & Howes (1984), King et al. (1982) and Morris & Whiting (1985)]. However, Gardner et al. (1988) calculated that only 10% of the reduced sulfur in sediments from a near-creek So. Carolina salt marsh site could be oxidized by oxygen from infiltration of water into the sediments. Based on that work and detailed modeling (Gardner 1990), Gardner suggested that enzymes from roots may be primarily responsible for the oxidation of reduced sulfur compounds. Our porewater results and those of Giblin et al. (1986) show the presence of soluble Fe(II) and Fe(III). Iron(III) is a more powerful oxidant than O_2 for FeS_2 (Luther 1987, 1990; Moses et al. 1987; Singer & Stumm 1970) and for thiosulfate (Luther 1987, 1990). We propose that the plants and/or bacteria produce and release siderophores or other organic ligands which solubilize and complex the Fe(III) minerals at higher pH (near 6).

In support of this hypothesis, Table 7 shows available kinetic data for the oxidation of Fe(II), H_2S and FeS_2 with oxygen, and FeS_2 with Fe(III). The order of ease of oxidation by oxygen is $\text{Fe(II)} > \text{H}_2\text{S} > \text{FeS}_2$ and depends on pH for Fe(II) and H_2S . The reaction of FeS_2 with oxygen is invariant with pH and is the slowest reaction overall. For Fe(II) oxidation, the oxidation is slower at lower pH. However, in the presence of organic ligands containing carboxylate groups (Blesa et al. 1987; Sulzberger et al. 1989) or on adsorption of Fe(II) to clays (White & Yee 1985), Fe(II) oxidation is significantly enhanced at low pH values of 3–5. The reaction of FeS_2 with Fe(III) is fast at low pH and depends on the solubility of Fe(III); however, Fe(III) oxidation of FeS_2 is still faster than oxygen oxidation at near neutral pH (Moses et al. 1987). In a companion study, Luther et al. (in press) have reacted soluble Fe(III) salicylate complexes at pH 6.5 with FeS_2 demonstrating that FeS_2 reacts faster by a factor of at least 2 with complexed Fe(III) than Fe(III) in the absence of organic ligands as reported by Moses et al. (1987). The available kinetic data indicate that oxygen if it enters porewaters will be more quickly consumed by Fe(II) or H_2S

Table 7. Laboratory rates of oxidation for Fe(II), H₂S and FeS₂.

(1) Fe²⁺ + O₂ (from Millero et al. 1987)
rate law:

$$-\frac{d[\text{Fe(II)}]}{dt} = k_1[\text{Fe(II)}]$$
for [Fe²⁺] = 27.8 μM and saturated O₂
a) pH = 5.0; 25 °C; k₁ = 3.16 × 10⁻⁵ rate = 0.000878 μM/min
b) pH = 6.1; 25 °C; k₁ = 1.21 × 10⁻⁴ rate = 0.00336 μM/min
c) pH = 7.0; 25 °C; k₁ = 4.07 × 10⁻³ rate = 0.113 μM/min

(2) H₂S + O₂ (from Millero et al. 1987)
rate law:

$$-\frac{d[\text{H}_2\text{S}]_T}{dt} = k[\text{O}_2][\text{H}_2\text{S}]_T$$
for [H₂S]_T = 27.8 μM and saturated O₂
a) pH = 5; k = 75.8 (extrapolated from temperature dependence data)
rate = 0.0078 μM/min
b) pH = 8; k = 184.1
rate = 0.0192 μM/min

(3) FeS₂ + O₂ (from Moses et al. 1987)
no rate law
Rates are provided for 27.8 mmole FeS₂ placed in 1 liter H₂O and are reproduced here for 27.8 μmoles in 1 liter H₂O.
rate = 0.000051 μM/min; pH = 5.17
rate = 0.000048 μM/min; pH = 2.22

(4) FeS₂ + Fe³⁺ (from Moses et al. 1987)
no rate law
rate = 0.000069 μM/min; pH = 5.17
rate = 0.00528 μM/min; pH = 2.2

than FeS₂. Thus, oxygen should not exist in the porewaters. The Fe(II) which is oxidized will precipitate as authigenic Fe(III) oxide phases and/or will be complexed by dissolved organic ligands for oxidation of FeS₂.

Iron(III) is present in these surface sediments as discrete oxyhydroxides or oxides up to ten times the pyrite level and is also incorporated in clay minerals up to 50 times the pyrite level (Ferdelman et al. 1991; Lord & Church 1983; Tsamakis 1991). Once solubilized by increased acidity or

organic ligands, the Fe(III) can oxidize the reduced sulfur compounds and form large excesses of Fe(II) as we observe. The Fe(II) formed is then available for reoxidation by oxygen to Fe(III) solid phases (Blesa et al. 1987; Sulzberger et al. 1989) or for sulfide precipitation when sulfate reduction becomes a prominent process. This mechanism is consistent with the proposition of Gardner (1990) — that enzymes from roots cause reduced sulfur oxidation. The difference is that chelates which dissolve and complex Fe(III) are released from the plants and/or bacteria, and that the Fe(III) becomes the active or direct oxidant of reduced sulfur. The reduced sulfur will be partially or fully oxidized depending on the sedimentary conditions. The sulfur products of FeS₂ oxidation may produce soluble thiols as observed in this work and in Luther & Church (1988) or sedimentary humic sulfur (Ferdelman et al. 1991; Francois 1987).

Manganese was measured in the porewaters and the sediments obtained in 1988 and 1989 as described in Tsamakis (1991). The Mn(II) in porewaters was always lower than the iron concentration and was never higher than 26 μ M. Total manganese in the solid phase is two or more orders of magnitude lower than the total iron concentration in the solid phase. Thus, a mechanism as proposed by Aller & Rude (1988) for the Mn(III, IV) oxide oxidation of acid volatile sulfide in creek bank muds will not result in the release of soluble iron as we observed. In their experiments, Fe(II) generally decreases in concentration. Thus, Mn(III, IV) compounds are not responsible for the oxidation of FeS₂ and S₂O₃²⁻.

Results and discussion from 1988 and 1989 samplings

The data from 1987 (this study) and 1986 (Luther & Church 1988) raise the question whether the spring tidal flooding always results in biogeochemical change and whether the change is always an oxidation. In October 1987, we performed a similar study (data not shown) at both near-creek and mid-marsh locations and found similar porewater evidence for oxidation events. However, in August 1988 and June/July 1989, we performed a similar study at the near-creek location only. The porewater data are given in Table 8 and the FeS₂ data in Table 9. In these two studies, there is no evidence for oxidation of FeS₂ after the spring tide (sulfide was not detected at any depth in these cores). In fact, there is evidence for FeS₂ formation with flooding in a given year. However, below 4 cm there is a marked decrease in FeS₂ from 1988 to 1989.

The August 1988 cores (9 and 10) were taken during a record drought year, and the June/July 1989 cores (11 and 12) were taken during a wet period. The yearly rainfall at Lewes, Delaware for these years can be used as an indicator of the contrasting climatic conditions. The rainfall was 90

Table 8. Major porewater constituents for 1988–1989 cores I, II, III and IV.

Depth (cm)	pH	Alka- linity (meq/l)	Cl ⁻ (mM)	SO ₄ ⁻² (mM)	δ SO ₄ ⁻² (mM)	Fe(II) (μM)	Fe(Tot) (μM)
Core I (August 22, 1988)							
0–2	5.22	1.33	576.4	45.2	15.4	NA	263.2
2–4	4.11	-5.27	675.6	51.2	16.3	NA	290.2
4–6	NA	NA	NA	NA	NA	NA	NA
6–8	3.38	-4.80	658.7	65.1	31.1	NA	1608.3
8–10	NA	NA	NA	NA	NA	NA	NA
Core II (August 29, 1988)							
0–2	6.37	2.17	454.4	32.1	8.6	141.6	725.6
2–4	5.23	-1.77	487.7	36.4	11.2	224.1	833.4
4–6	3.72	7.39	542.6	46.7	18.6	216.7	826.2
6–8	3.89	-2.25	600.6	56.5	25.4	240.3	850.5
8–10	4.23	-0.24	543.7	51.5	23.4	235.7	809.6
Core III (June 27, 1989)							
0–2	6.57	8.54	439.1	23.47	0.8	178.7	604.3
2–4	6.62	10.53	444.8	22.49	-0.5	75.0	391.3
4–6	6.54	8.72	485.1	24.61	-0.5	34.1	198.1
6–8	6.43	8.74	462.6	27.60	3.7	47.4	226.4
8–10	6.33	6.19	474.9	28.14	3.6	48.3	103.7
Core IV (July 6, 1989)							
0–2	6.41	12.33	422.4	23.76	1.9	197.4	486.3
2–4	6.59	11.43	435.9	22.78	0.3	107.5	444.5
4–6	6.55	9.52	434.9	22.28	-0.2	117.3	461.2
6–8	6.36	7.46	462.0	24.05	0.2	203.9	488.0
8–10	6.87	3.99	460.1	28.67	4.9	161.4	334.1

NA = Not Analyzed

cm (1987), 50 cm (1988) and 160 cm (1989) whereas the 30 year average is 118 cm. The lower FeS₂ values in 1989 relative to 1988 (dry period) below 4 cm are associated with flooding — in this case atmospheric precipitation which prevented dessication of the sediments. This observation is similar to that for spring tidal flooding in 1987.

We attribute the tidal flooding differences in 1988 and 1989 from 1987 (present study) and 1986 (Luther & Church 1988) primarily to climatic conditions. In 1989, the chloride and sulfate ion concentrations are similar at each depth both before and after the spring tide which indicates that there is no affect from the spring tide because of the rains which occurred during this time. In 1988, the chloride ion concentration

Table 9. Pyrite sulfur, as obtained from the Cr(II) reduction method.

Depth (cm)	Pyrite sulfur			
	Core I 8/22/88	Core II 8/29/88	Core III 6/27/89	Core IV 7/06/89
0—2	22.7 (3.4)	44.7 (6.9)	20.3 (6.7)	35.9 (7.3)
2—4	40.5 (6.4)	43.0 (0.4)	33.0 (3.3)	54.9 (8.6)
4—6	186.3 (1.3)	161.4 (8.7)	89.7 (7.5)	144.3 (3.4)
6—8	102.7 (4.5)	198.4 (14.5)	28.6 (7.1)	109.9 (10.0)
8—10	47.4 (7.7)	367.1 (21.5)	77.6 (6.7)	60.5 (20.0)

Values are in $\mu\text{mol S (g dry weight)}^{-1}$. The numbers in parentheses represent one standard deviation of triplicate analyses.

varied with flooding as in the 1987 data; that is, there was a decrease in chloride at each depth with tidal flooding. However, the alkalinity and pH values are lower before the flood than after the flood. In fact, the alkalinity and pH are so low that there is no buffer capacity remaining in the near-creek system. Thus, the extent of oxidation as measured by porewater parameters was greater in the 1988 sampling before the tidal flooding than in 1986, 1987 and 1989. On flooding in 1988, the alkalinity and pH values began to increase. These increases indicate that sulfate reduction may have been stimulated with tidal flooding for this year relative to oxidation of reduced sulfur. The short term changes in salinity observed herein due to weather and tidal effects can also have an effect on estuarine productivity (e.g. Morris et al. 1990). In fact, atmospheric precipitation may be more important in controlling salinity than tidal flooding for this high marsh site.

The Fe(III) to Fe(II) ratio may be useful as an indicator of pyrite oxidation and other iron mineral processes. Low ratios indicate Fe(II) enrichment which is consistent with Eq. (4). The soluble iron data for 1988 and 1989 indicate that the Fe(III) to Fe(II) ratio is one or greater for all samples which is in contrast to the 1987 data. Total iron is also generally higher in 1988 and 1989 than in 1987. In both 1988 and 1989, the increase in Fe(III) could be related to more solid Fe(III) phases of less than $0.40 \mu\text{m}$ size in the porewater or to precipitation of Fe(II) into sulfide phases. [We did not measure thiosulfate and sulfide was not detected in these samples which could give an indication of the type of Fe(III) species present.] Alternately, in 1988 increases of Fe(III) could be due to lower pH values which enhance Fe(III) mineral dissolution (Giblin & Howarth 1984).

Conclusion

The data from 1987 indicate that the monthly tidal flooding enhances reduced sulfur oxidation at the near-creek site, in particular pyrite. The effect is not as pronounced at the mid-marsh site. Pyrite levels are also higher at the mid-marsh location. Bioturbation is less important at the mid-marsh site as shown by the radionuclide data. Thiosulfate may undergo oxidation or conversion into organic sulfur as discussed by Francois (1987) and Luther et al. (1986). The oxidation occurs at both near-creek and mid-marsh locations, but is more pronounced at the near-creek location. Soluble Fe(III) complexes are considered to be the primary and direct oxidants of the reduced sulfur species based on a combination of field data, laboratory experiments with Fe(III) (see Moses et al. 1987; Luther et al. in press), modeling considerations of Gardner (1990) and molecular considerations (Luther 1987, 1990). We propose that the soluble Fe(III) is supplied by siderophores or organic ligands produced by plants or bacteria which link the organic and inorganic cycles of iron and sulfur. More analytical experiments would be helpful to better characterize soluble Fe(III).

The data from 1988 (dry year) and 1989 (wet year) show that the spring tidal flooding did not enhance pyrite oxidation in these years. These two samplings showed extreme climatic conditions compared to 1986 and 1987. The data suggest that atmospheric precipitation may play an important role in short term iron and sulfur cycling as well as salinity changes.

The short term changes of reduced sulfur compounds and dissolved iron are greatly influenced by climatic conditions, hydrology, microbiology and plant physiology. All of these physical and biological processes apparently work in concert to affect the chemical reactivity of Fe and S compounds. For example, when oxidizing conditions are extreme as evidenced by low porewater pH (< 5) and negligible alkalinity as in 1988, the spring tide enhances sulfate reduction rates over sulfide oxidation rates. When the rate of oxidation of reduced sulfur compounds is competitive with or less than the rate of sulfate reduction as evidenced by pH values nearer to 6 and by reasonable alkalinity concentrations in 1987, tidal flooding promotes reduced sulfur oxidation. The salt marsh ecosystem is a dynamic biogeochemical system which is poised between reducing and oxidizing conditions. The iron cycle in conjunction with organic ligands helps to maintain the ecosystem near steady state during the productive seasons through the formation of pyrite with Fe(II) and the oxidation of pyrite with Fe(III). Laboratory results supporting this proposal are reported by Luther et al. (in press).

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