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## Spatial variations in the sulfur chemistry of salt marsh sediments at North Inlet, South Carolina

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### ABSTRACT

Profiles of particulate and dissolved sulfur species have been measured in marsh sediments along three transects across the various growth zones (tall, medium and short) of *Spartina alterniflora*. In general, organic carbon, total sulfur, pyritic sulfur, pyritization index and dissolved sulfide increased with distance from tidal creek banks, whereas acid volatile sulfur (FeS), pH and Eh decreased with distance.

These patterns probably are controlled by spatial variations in belowground production, pore water movement and fiddler crab burrowing. The creekside marsh (tall *Spartina*) is characterized by lower rates of belowground production (and thus lower rates of sulfate reduction and sulfide production), more vigorous drainage of pore water and more intense fiddler crab burrowing as compared to the high marsh (short *Spartina*). Lower dissolved sulfide concentrations in the creekside marsh are promoted by lower rates of sulfate reduction and removal of dissolved sulfide by drainage at low tide. Higher pH in the creekside marsh is fostered by removal of reduced sulfur (dissolved sulfide by drainage and pyrite by fiddler crab burrowing) which then cannot be oxidized in the sediment to yield acid. The higher pH and lower dissolved sulfide of the creekside marsh, in turn, slow rate of conversion of iron oxide into pyrite in accordance with Rickard's (1974, 1975) rate laws and thus foster a lower pyritization index. The lower pyritization index of the creekside marsh also is promoted by fiddler crab burrowing which removes pyrite from the sediment and replaces it with fresh iron oxide from the surface or suspended source. Finally the greater availability of reactive iron oxide in the creekside marsh may shift the relative rates of FeS and FeS<sub>2</sub> formation such that a higher steady state concentration of FeS can be maintained there as compared to the high marsh.

### 1. Introduction

Recent attempts to measure the annual belowground growth of roots and rhizomes in salt marshes indicate that belowground production commonly exceeds aboveground production (Good *et al.*, 1982). As a large fraction of this production is decomposed via sulfate reduction, these results have stimulated interest in the dynamics of sulfur cycling in salt marshes (e.g. Howarth and Giblin, 1983; King, 1983). Rates of sulfate reduction have been estimated by diagenetic modelling (Lord and Church, 1983) or by

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direct measurements with  $^{35}\text{S}$ , (Skyring *et al.*, 1979; Christian *et al.*, 1983; Howarth and Teal, 1979; Howarth and Giblin, 1983; Howarth and Marino, 1984; King, 1983). The resultant formation of iron sulfide minerals, by the reaction of sulfide or polysulfides (byproducts of sulfate reduction) with dissolved or particulate iron species, has been studied by Lord and Church (1983), King (1983), King *et al.* (1985) and Howarth and Giblin (1983). However, most of the research undertaken on the sulfur cycle in marsh sediments has been conducted in short *Spartina alterniflora* zones, which cover a large areal percentage of the salt marshes along the northeastern coast of the United States (Lord and Church, 1983; Howarth and Teal, 1979; Howarth and Marino, 1984). In contrast, the marshes of the southeastern United States have extensive areas vegetated by tall and medium *S. alterniflora*. At present little is known about the spatial distribution and fractionation of particulate sulfur in these sediments.

As part of the Long Term Ecological Research Project (LTER) conducted at the Belle W. Baruch Institute for Marine Biology and Coastal Research (University of South Carolina), studies have been undertaken to examine variations in sediment chemistry along three transects in the North Inlet system. These transects include sites on mud flats, creek banks, and zones vegetated by all the phenotypes of *Spartina alterniflora*. As part of this research, cores and pore water samples were taken at each site along the transects to investigate the distribution of particulate and dissolved sulfur species in various marsh zones as a function of depth and distance from the tidal creek.

## 2. Methods

*a. Site description.* North Inlet is an intertidal saline marsh located in Georgetown County, South Carolina (see Fig. 1). This marsh is dominated by *Spartina alterniflora*, although along the upper fringes of the marsh adjacent to the forest, stands of *Juncus roemerianus* and *Salicornia* can be found. Cores and pore water samples were taken at four sites along three transects extending from tidal creeks to the back marsh or high marsh. The Goat Island (GI) transect is situated in a geologically young, predominantly sandy marsh adjacent to a maritime forest. This area has only recently been converted from forest into a saline marsh by the rise in sea level (Gardner and Bohn, 1980) and is vegetated by tall, medium and short *S. alterniflora*. The Bread and Butter (BB) and Town Creek (TC) transects are both situated in the older, muddy marsh and are vegetated by tall and medium *S. alterniflora*. BB has a well developed levee along the creek bank with tall *Spartina* and grades away from the levee into a back marsh vegetated by medium *S. alterniflora*. TC is similar to BB but lacks a distinct levee on the creek bank.

*b. Sediment sampling and analyses.* Cores, approximately 85 cm long, were taken during November, 1984. Cores from each transect were numbered in order of distance from creek bank (e.g. BB1 = creek bank, BB2 = levee, BB3 = back marsh, etc.).

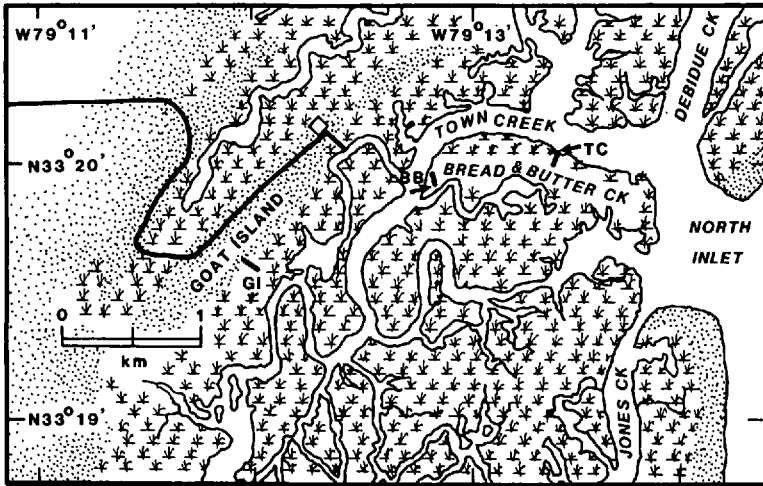


Figure 1. Site map.

Cores were taken with a modified piston corer and extruded on site. Samples from each core were taken at 2.5 cm intervals down to 10 cm, and then every 5 cm to the bottom of the core. The core segments were placed into separately labelled ziplock bags and returned to the laboratory on ice within one hour where the samples were immediately processed. Each sample was subdivided. One subsample was dried, ground with a mortar and pestle and analyzed for pyrite sulfur (PS) and total sulfur (TS). The second subsample was frozen and later used to determine concentrations of acid volatile sulfide (AVS). No detectable reddish color developed in the samples during the short interval between collection and drying or freezing indicating that oxidation of iron sulfides, if any, was negligible. This contention is in agreement with laboratory oxidation and leaching experiments on pulverized pyritic rocks which show sulfate production rates of about 1.0 mg per gram  $\text{FeS}_2$  per day (Taylor and Wheeler, 1984; Pugh *et al.*, 1984).

Analyses of total sulfur (TS), pyritic sulfur (PS) and total available iron (TAFE) were performed at the University of South Carolina Acid Mine Drainage Research Laboratory. Total sulfur was determined on dried subsamples using a Leco Sulfur Analyzer (Model 532). Sample runs on the Leco Analyzer began and ended with triplicate analyses of reagent grade ammonium sulfate. Recovery on standards fell in the range of 92-94% and established the recovery factor for the samples. Between standardizations samples were run in groups of six. The second and fourth samples were run in duplicate while the sixth was run in triplicate. Samples were rerun if the recovery factor at the beginning and end of the run differed by more than five percent and if the relative deviation of duplicate analyses differed by more than ten percent. This was necessary for only two of our samples.

Pyritic sulfur was estimated by using the nitric acid digest procedure developed by Burns (1970). In this technique nonpyritic iron-bearing minerals were removed by

placing one gram of sample (dried and ground) into a 250 ml flask with 50 ml of hydrochloric acid (5N). This mixture was boiled for 15 minutes and then filtered and washed several times in both hydrochloric acid and distilled water. The filter which contains the pyritic fraction was placed in another 250 ml flask with 50 ml of nitric acid (2N). This mixture was boiled for 30 minutes, filtered, and then analyzed for iron colorimetrically. The weight percent pyritic sulfur (PS) was calculated using the weight of the sample and the stoichiometric relation between pyritic iron and sulfur. Our use of 2N nitric acid was dictated by previous experience (F.T. Caruccio, personal communication) which showed that more concentrated  $\text{HNO}_3$  can extract organic sulfur, as well as pyrite. The recovery by our method has been checked repeatedly by examining pelletized residues under the reflecting microscope. Such examination fails to reveal the presence of pyrite in the residue except in cases where the original pyritic sulfur content exceeds 12.0%, which is about twice the maximum concentration found in our samples. In such cases, small amounts of pyrite are sometimes found to have survived extraction. Caruccio has found that the extent of grinding and the duration of extraction have a greater effect on recovery than the strength of the acid. Accordingly, our samples were ground to pass a 63 micron sieve before analysis. Pyritic sulfur values in short *Spartina* sediments obtained by using this technique are within the concentration range obtained by the chromium II reduction assay for other high marsh sites in North Inlet (G. King, personal communication).

Acid volatile sulfide (AVS) was measured on the frozen subsamples using the technique described by Jorgenson and Fenchel (1974). This involves digesting a sediment sample in a 4N HCl solution and trapping the resultant  $\text{H}_2\text{S}$  in a  $\text{CdCl}_2$  solution. The amount of CdS formed was used to calculate the weight percent of AVS. Residual sulfur (RS) was estimated by subtracting pyritic sulfur and acid volatile sulfide from total sulfur.

In order to evaluate the role of particulate iron in pyrite accumulation in the North Inlet marsh we estimated total available iron (TAFe) for some of our samples by making separate measurements of acid (5N HCl) soluble iron (ASFe), using a standard technique (Berner, 1970), and adding these results to our pyritic iron measurements (i.e.  $\text{TAFe} = \text{ASFe} + \text{PFe}$ ). ASFe estimates the sediment content of iron oxides/oxyhydroxides and the labile iron sulfide minerals including amorphous iron sulfide, gregite, and mackinawite. It may also include some iron embedded in silicate minerals which may be another iron source for pyrite formation, albeit small (Lord and Church, 1983).

Total carbon was measured on dried subsamples using a Hewlett-Packard CHN Analyzer. Inorganic carbon ( $\text{CaCO}_3$ ) was determined by measuring the volume of  $\text{CO}_2$  evolved upon acidification. Organic carbon was estimated by subtraction of inorganic carbon from total carbon. In all of our samples inorganic carbon was negligible compared to total carbon.

We did not undertake systematic measurement of elemental sulfur because in most of our samples total sulfur only slightly exceeds the sum of pyritic sulfur and acid

volatile sulfide. In some samples, however, the deviation between TS and PS plus AVS was large enough to warrant further investigation. Three samples with large deviations were selected at random and analyzed for elemental sulfur using CS<sub>2</sub> extraction as described by Troelsen and Jorgensen (1982). In these three cases residual sulfur (TS-PS-AVS) ranged from 0.86% to 4.04%, whereas, elemental sulfur was less than 0.2%. As elemental sulfur is not abundant in marine sediments (Burns, 1970; Lord and Church, 1983) we assume that residual sulfur is largely organic in nature.

*c. Pore water sampling and analyses.* The original objective of our pore water sampling was to obtain a time-averaged characterization of pore water chemistry for the purpose of seasonal, as well as spatial, comparisons. We chose to use *in situ* dialysis samplers (equilibrators) because Agosta (1985) has shown that creek bank pore water chemistry varies on a tidal time scale as a result of seepage toward the creek at low tide and infiltration during rising tide. Considerable repetitive sampling over a number of tidal cycles would be required to obtain time-averaged profiles of pore water chemistry using sippers or core squeezing. The type of equilibrator that we used has been described and extensively tested by Simon *et al.* (1985) in both sandy and muddy sediments of the Potomac River estuary. In their study replicate core and equilibrator profiles of alkalinity, SO<sub>4</sub><sup>-2</sup>, Cl<sup>-</sup>, PO<sub>4</sub><sup>-3</sup>, NH<sub>4</sub><sup>+</sup>, Fe and Mn from one square meter plots were compared. With the possible exception of Mn the average equilibrator concentration at a given depth agreed with the corresponding average for cores to within the combined sampling and analytical error. Although we have not directly compared our equilibrator results with adjacent cores our H<sub>2</sub>S results agree closely with preliminary data collected by Dr. Gary King (personal communication) using sippers from similar sites at North Inlet. Thus despite the potential problems with equilibrators, we feel that our results are sufficiently accurate to discern the spatial patterns described below and for the qualitative interpretations that we attach to these results.

Plexiglas equilibrators with a design similar to that described by Simon *et al.* (1985) were inserted at each site four times a year (November, February, May and August) during 1981–1982. These samplers were used to characterize the vertical profiles of Eh, pH, total dissolved sulfide, total dissolved iron, SO<sub>4</sub><sup>-2</sup> and Cl<sup>-</sup>. Most of the samplers were 50 cm long with 12 depth sampling ports 2.5 cm apart, for a vertical profile of 30 cm. The ports, three at each depth, were filled with deaerated, half salinity, filtered sea water and covered with a 0.2 micron polycarbonate membrane. The samplers were deployed in the marsh sediments for 17 days thus allowing ample time for equilibration with the interstitial water (Simon *et al.*, 1985; Carignan, 1984).

Eh and pH measurements were made immediately upon returning the samplers to the laboratory. The rest of the water from each port of the sampler was split into three fractions and frozen; (1) 2 ml + zinc acetate for total sulfide, (2) nontreated sample for SO<sub>4</sub><sup>-2</sup> and Cl<sup>-1</sup>, and (3) an acid treated sample (1% HCL) for total iron. These

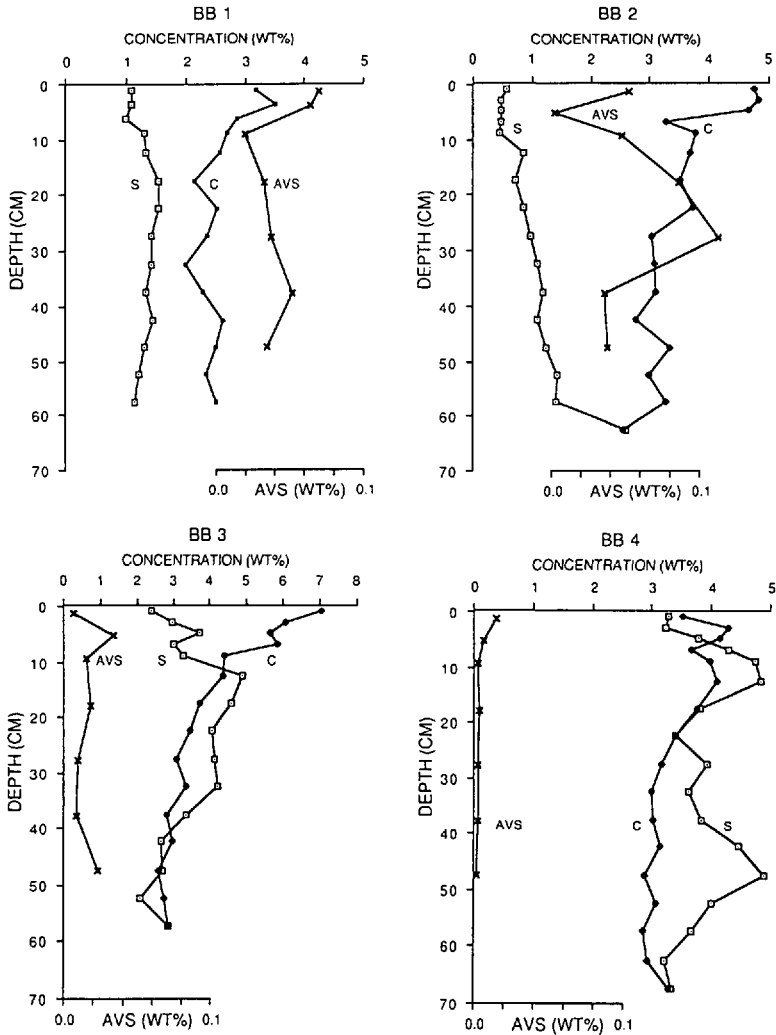


Figure 2a. Vertical profiles of organic carbon, total sulfur and acid volatile sulfur (AVS) along Bread and Butter Creek (BB) transect.

samples were then stored for later analysis.  $\text{SO}_4^{-2}$  and  $\text{Cl}^{-1}$  determinations were made using an Autoanalyzer II system ( $\text{Cl}^{-1}$ ; thiocyanate method [O'Brien, 1962],  $\text{SO}_4^{-2}$ ; methythymol blue + barium chloride method [Lazarus *et al.*, 1966]). Total sulfide measurements were made using the titration method (iodine + sodium thiosulfate; Golterman, 1971), while total iron values were obtained using the ferrozine technique (Gibbs, 1979). The total sulfide method measures thiols, polysulfides and thiosulfate, as well as sulfide. In marsh sediments their concentrations are usually low in comparison to  $\text{H}_2\text{S}$  (Boulegue *et al.*, 1982).

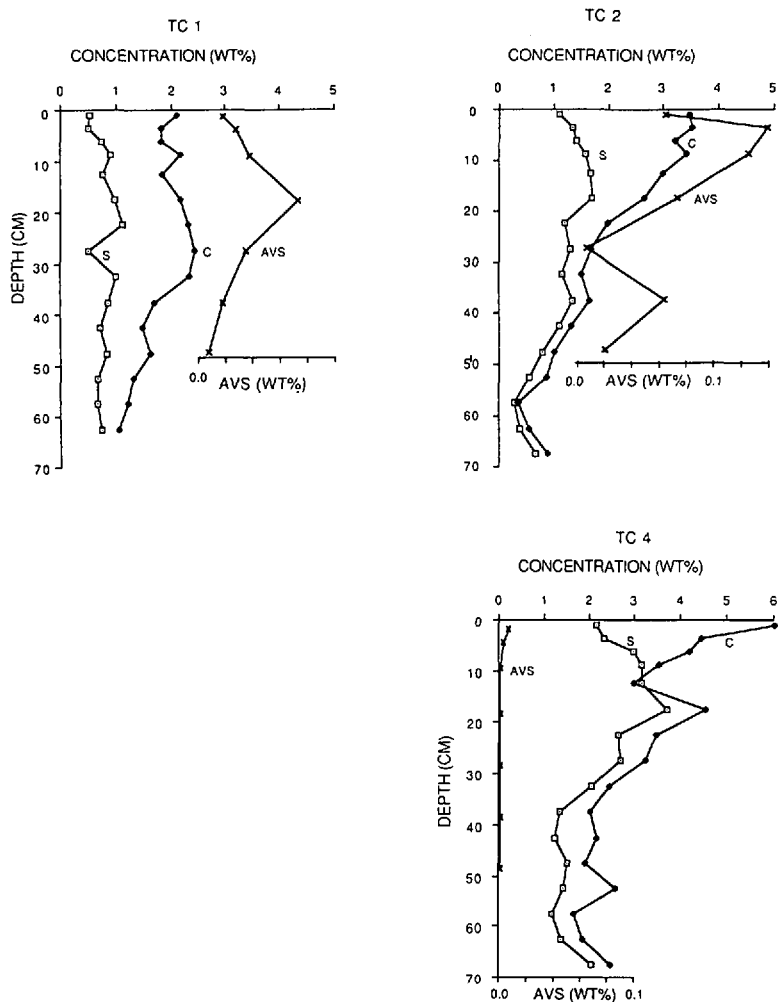


Figure 2b. Vertical profiles of organic carbon, total sulfur and acid volatile sulfide (AVS) along Town Creek (TC) transect.

### 3. Results

*a. Sediment chemistry.* Sediment profiles of organic carbon, total sulfur and acid volatile sulfide are shown in Figure 2. Each of the profiles shows a general decrease in organic carbon with depth. The rate of decrease, however, ranges from barely detectable in TC1 and BB1 to pronounced in BB3 and in all of the GI profiles. In the mature muddy marsh (TC and BB transects) total sulfur generally increases with depth to a maximum at 10–20 cm and thereafter, with the exception of BB2, tends to decrease. In the immature sandy marsh (GI transect) total sulfur profiles generally follow the profiles of organic carbon except in the upper part of GI4 where the total



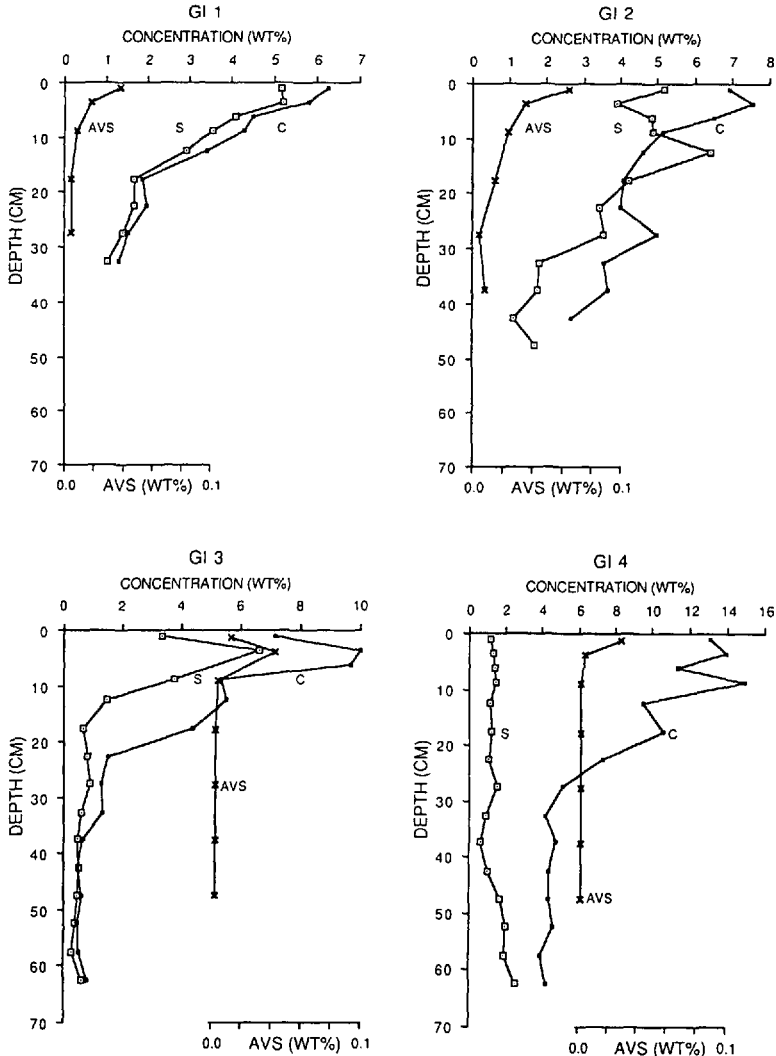


Figure 2c. Vertical profile of organic carbon, total sulfur and acid volatile sulfur (AVS) along Goat Island (GI) transect.

sulfur content is anomalously low in comparison to the high concentration of organic carbon. Grain size analyses of the GI profiles indicate that the dramatic decrease in carbon (and sulfur in GI 1-3) is correlated with an increase in the sand content of the sediment with depth (Fig. 3). The change in texture with depth at the GI sites is a reflection of the fact that these soils were formerly low-carbon, sandy forest soils and have only recently begun to accumulate mud via deposition from tidal waters. The profiles of sulfur in the deeper parts of TC2 and TC4 also show a similar correlation

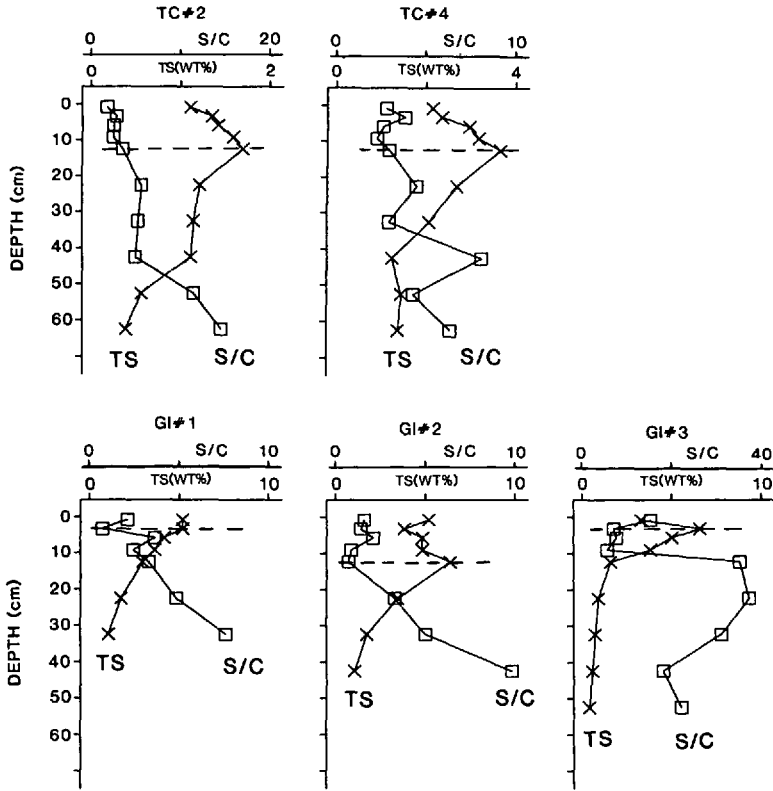


Figure 3. Vertical profiles of the total sulfur content and sand/clay ratio at sites TC2, TC4, GI1, GI2, and GI3.

with increasing sand content. Downward coarsening of texture, however, cannot be detected in the other mature marsh profiles.

In addition to vertical trends, the carbon and sulfur contents of the marsh sediment also show geographical trends along the transects. In the mature marsh both the carbon and sulfur content of the sediment generally increase with distance from the creek bank. With the exception of sulfur at GI4 similar geographic trends in carbon and sulfur are observed along with GI transect. There also appear to be geographical trends in acid volatile sulfide and pyritization index ( $PI = PFe/TAFe$ ). The content of AVS seems to be greatest at levee sites (TC2, BB2 and GI2) and to diminish both toward the creek bank and toward the back marsh or high marsh. In the back marsh and high marsh AVS is extremely low. The pyritization index (Fig. 4) of the creekside and levee sites is generally lower (about 40%) than in the back and high marsh where it is about 80%. There is also some suggestion that the ratio of pyritic sulfur to total sulfur is higher in the muddy marsh (70–90%) than in the high marsh transect (40–60%).

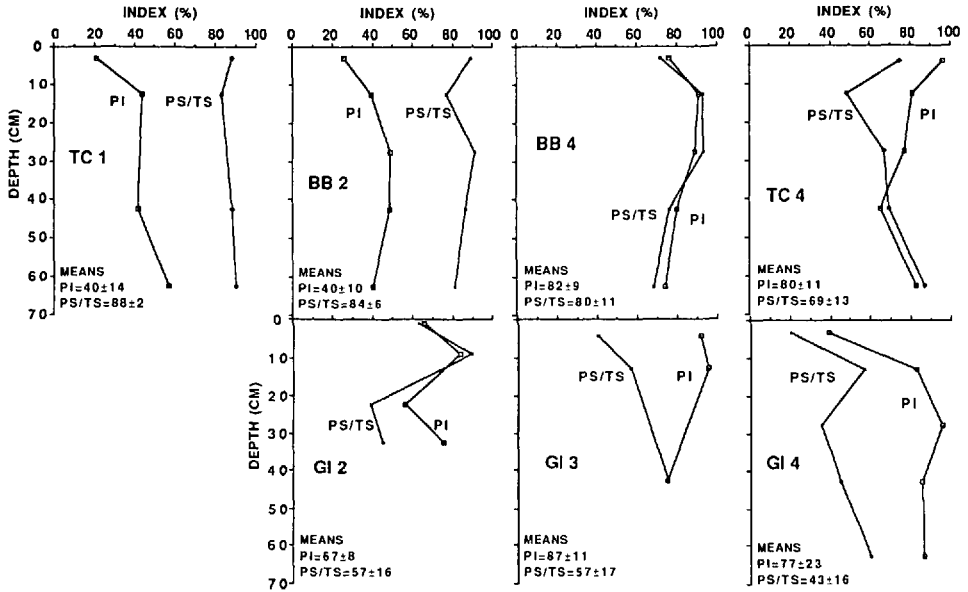


Figure 4. Vertical profiles of pyritization index and PS:TS ratio.

*b. Interstitial water chemistry.* Space does not permit a complete presentation of the results of our pore water chemistry measurements (12 sites  $\times$  12 depths  $\times$  4 seasons  $\times$  6 parameters). A summary of the data is given in Table 1 which shows the depth averaged values of the parameters for each site and sampling date. In order to ascertain the relative importance of geographical versus seasonal factors in controlling pore water chemistry we performed analysis of variance on our raw data using the SAS GLM procedure. The sources of variation in our ANOVA model were transect, site and date as well as interactions among them. The F values for Type I sum of squares are summarized in Table 2 for the three sources of variability. Even though the error term is large, partly because we ignored vertical variability, each of the sources is statistically significant for all six parameters. As can be seen the F values for transect and site are substantially larger than for date in the case of pH, Eh, H<sub>2</sub>S and Fe indicating that geographical variations in these parameters are greater than temporal variation. For sulfate depletion and chloride the date F values are somewhat larger than those for transect and site, but not substantially so. In general, it appears that geographical variation in pore water chemistry is greater than temporal variation. Accordingly, we have chosen for detailed presentation four sites which represent an idealized transect from creek bank (BB1, unvegetated) to levee (BB2, tall *Spartina*) to mid marsh (BB3, medium *Spartina*) to sandy high marsh (GI4, short *Spartina*). These results are shown in Figure 5 which portrays time-averaged depth profiles of pH, Eh, H<sub>2</sub>S and sulfate depletion of these sites. The horizontal bars shown on some of the data points represent the typical seasonal range of variation of the various parameters at

Table 1. Depth averaged pore water chemistry by transect, site and date.

TR	Site	Date	N	pH	Eh mv	SO <sub>4</sub> mmoles	H <sub>2</sub> S mmoles	Cl mmoles	Fe mmoles
BB	1	NOV	12	7.38	54	-6.9	0.44	486	0.11
BB	1	FEB	12	7.37	98	-8.9	0.62	472	0.03
BB	1	MAY	12	7.17	78	-4.9	0.73	486	0.04
BB	1	AUG	12	7.23	96	-9.7	0.41	493	0.07
BB	2	NOV	12	7.08	122	-6.0	0.60	476	0.19
BB	2	FEB	12	6.95	239	-7.9	0.41	455	0.01
BB	2	MAY	12	6.79	91	-9.9	0.24	496	0.84
BB	2	AUG	11	6.88	72	-8.3	0.32	503	0.47
BB	3	NOV	12	6.79	-59	-7.6	1.96	446	0.01
BB	3	FEB	12	6.35	17	-6.5	0.96	490	0.10
BB	3	MAY	12	6.16	-86	-13.8	1.25	465	0.33
BB	3	AUG	12	6.48	-169	-17.8	2.90	479	0.001
BB	4	NOV	12	6.69	-104	-6.8	2.26	429	0.003
BB	4	FEB	11	6.45	-86	-11.5	1.04	467	0.07
BB	4	MAY	12	6.51	-85	-15.7	1.32	464	0.09
BB	4	AUG	12	6.58	-151	-15.8	2.20	513	0.001
TC	1	NOV	12	7.58	64	-3.7	0.60	458	0.01
TC	1	FEB	12	7.66	148	-10.8	0.35	492	0.01
TC	1	MAY	12	7.73	129	-14.5	0.91	478	0.02
TC	1	AUG	0						
TC	2	NOV	12	7.18	-32	-5.6	0.66	454	0.07
TC	2	FEB	12	7.60	81	-8.3	0.46	484	0.04
TC	2	MAY	12	7.00	-40	-12.5	0.53	442	0.06
TC	2	AUG	12	7.08	-105	-14.8	1.82	534	0.02
TC	3	NOV	12	6.98	-141	-12.1	2.29	430	0.03
TC	3	FEB	12	7.14	-69	-10.7	0.98	515	0.03
TC	3	MAY	12	7.00	-80	-17.0	3.26	465	0.05
TC	3	AUG	12	6.99	-131	-12.4	2.11	518	0.008
TC	4	NOV	12	6.79	-120	-10.9	1.87	452	0.02
TC	4	FEB	12	6.65	-101	-12.6	1.80	508	0.03
TC	4	MAY	12	6.67	-152	-15.0	1.99	446	0.006
TC	4	AUG	12	6.54	-109	-18.2	2.31	450	0.01
GI	1	NOV	5	6.91	-35	-6.0	0.82	470	0.04
GI	1	FEB	8	6.66	165	-9.8	0.57	461	0.09
GI	1	MAY	6	6.88	-29	-8.4	0.69	492	0.03
GI	1	AUG	6	6.77	-105	-13.5	1.76	517	0.01
GI	2	NOV	11	6.86	-124	-7.9	2.69	439	0.005
GI	2	FEB	12	6.69	-80	-13.7	1.07	483	0.04
GI	2	MAY	10	6.64	-104	-10.2	1.59	464	0.02
GI	2	AUG	11	6.69	-133	-17.2	3.11	454	0.001
GI	3	NOV	12	7.02	-139	-6.6	1.86	334	0.005
GI	3	FEB	12	6.59	-107	-18.0	1.89	488	0.02
GI	3	MAY	12	6.82	-177	-20.0	3.26	462	0.01
GI	3	AUG	12	6.69	-149	-14.7	2.49	416	0.006
GI	4	NOV	12	6.40	-60	-9.5	2.19	403	0.08
GI	4	FEB	12	6.38	-129	-17.9	1.93	517	0.03
GI	4	MAY	12	6.25	-139	-20.4	2.59	433	0.01
GI	4	AUG	12	6.03	-134	-18.3	3.09	435	0.005

Table 2. *F* values (Type I SS) and Model *R*<sup>2</sup> for ANOV.

Source	pH	Eh	SO <sub>4</sub>	H <sub>2</sub> S	Fe	Cl
Transect	220	66	43	83	82	22
Site	280	102	50	107	47	7
Date	20	22	84	37	29	38
<i>R</i> <sup>2</sup>	0.78	0.58	0.59	0.63	0.70	0.44

each site. Chloride showed no discernible pattern of spatial or temporal variation and generally was between 16,000 and 19,000 mg l<sup>-1</sup>.

The most obvious and consistent geographical trend is for pH. As can be seen (Fig. 5) there is a progressive drop in pH from the creekside (pH = 7.3) to the sandy high marsh where the time averaged pH is generally less than 6.5. This trend of decreasing pH away from the creek bank is present in the individual transects as well. The decrease in pH is associated with a decrease in Eh from somewhat oxidizing in the creek bank and levee (+100mv) to strongly reducing in the marsh interior (-200mv). This in turn coincides with generally higher sulfide and greater sulfate depletion inward from the creek bank. Finally dissolved iron (not shown) ranges from nearly millimolar levels at creekside sites to micromolar levels in the back and high marsh sites.

#### 4. Discussion and interpretation

The geographical patterns in pH, dissolved sulfide, dissolved iron, acid volatile sulfide and pyritization index described above are similar to those observed by King *et al.* (1982) in a Georgia marsh and are thus probably representative of marshes in the southeastern United States. It is thus also likely that the patterns of individual sulfur species are governed by some common process or set of factors.

King *et al.* (1982) attributed the patterns they observed to spatial variation in the dynamic interaction of bacterial sulfate reduction, iron input, pore water movement and possible sulfide oxidation. In the following discussion we will attempt to elaborate and, where possible, quantify the various mechanisms proposed by King *et al.* (1982) for controlling geographic patterns of sulfur chemistry in marshes. We will then attempt to develop a detailed and comprehensive theory for the geographical patterns of pH, Eh, H<sub>2</sub>S, FeS, FeS<sub>2</sub> and pyritization index in southeastern salt marshes.

The rate of sulfate reduction determines the gross rate of sulfide production and is largely controlled by the rate of net belowground production. The net annual belowground production of *Spartina* at North Inlet has been measured in tall and short *Spartina* by Dame and Kenney (1986). They found rates of 2300 and 5400 g dry wt m<sup>-2</sup> yr<sup>-1</sup> for the tall and short zones respectively. Thus, sulfate reduction rates in the short *Spartina* marsh could be almost twice as large as in the tall *Spartina* marsh. King (personal communication) has measured rates of sulfate reduction in tall and short *Spartina* sites at North Inlet and has found consistently higher rates in the high marsh, in rough agreement with the measured higher rates of belowground production in the

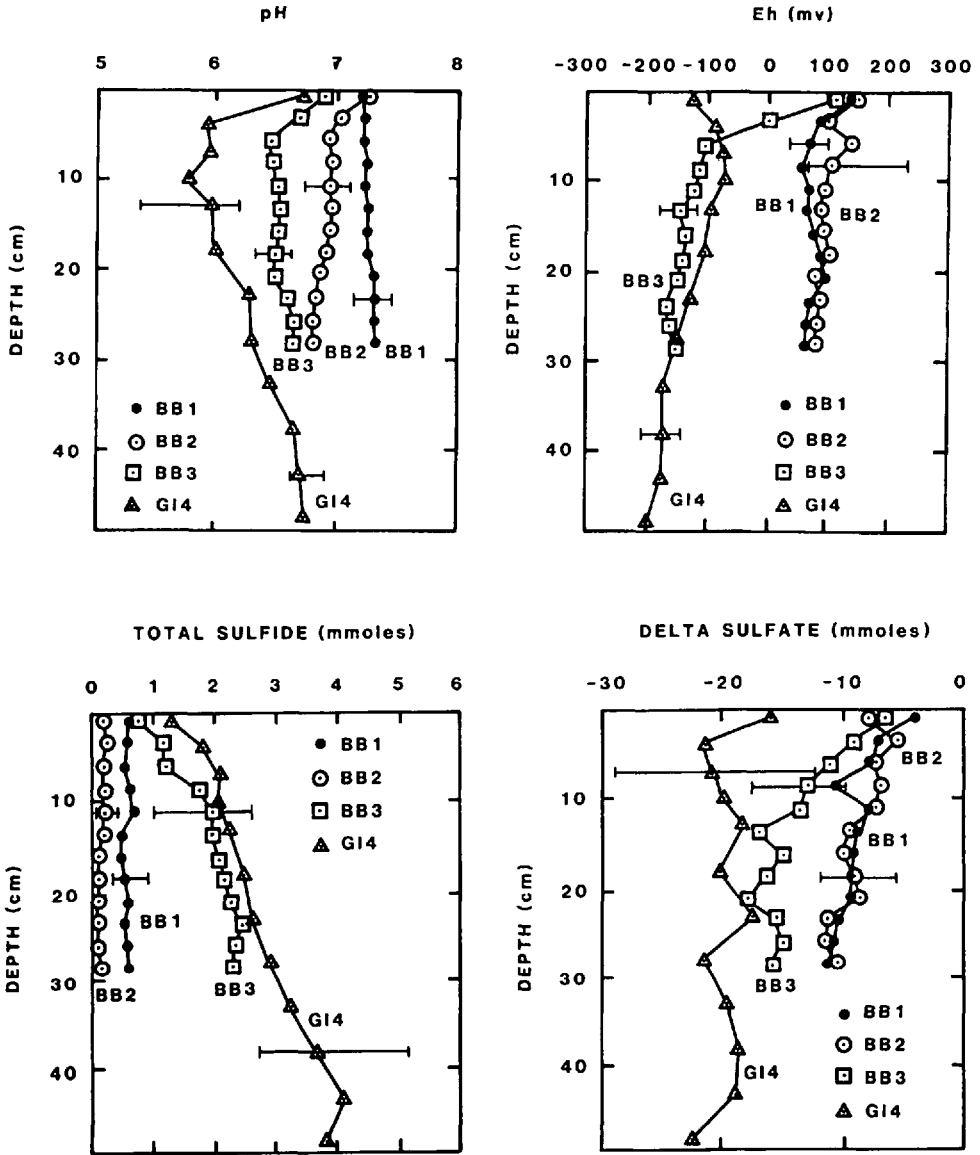


Figure 5. Plots of time averaged values of pH, Eh, H<sub>2</sub>S and sulfate depletion versus depth for selected sites. Bars at selected data points represent typical seasonal ranges for various parameters.

high marsh. Thus if belowground production and rates of sulfate reduction are greater in the high marsh than in the creekside marsh, this can partly explain the lower concentration of dissolved sulfide in the creekside marsh. However, differences in rates of sulfate reduction cannot adequately explain the lower pyritization index of the creekside marsh as compared with the back marsh and high marsh. Net creekside

belowground production rates of  $2300 \text{ g dry wt m}^{-2} \text{ yr}^{-1}$  (or  $77 \text{ moles C m}^{-2} \text{ yr}^{-1}$ ) imply sulfate reduction rates of about  $38 \text{ moles SO}_4^{-2} \text{ m}^{-2} \text{ yr}^{-1}$  or a potential gross rate of pyrite formation of  $19 \text{ moles FeS}_2 \text{ m}^{-2} \text{ yr}^{-1}$ . This can be compared with the rate of supply of reactive iron via simple sedimentation, approximately  $0.2 \text{ moles Fe m}^{-2} \text{ yr}^{-1}$  given typical sedimentation rates ( $2 \text{ mm yr}^{-1}$ , Sharma *et al.*, 1987) sediment bulk density ( $0.5 \text{ g cm}^{-3}$ ) and iron content (1.0–2.0 wt %). These rough calculations indicated that the potential gross rate of pyrite formation is about two orders of magnitude greater than the rate of supply of iron by simple sedimentation. Given the enormous excess of pyritization potential to iron supply, it would not be unreasonable to expect the pyritization index of marsh sediment, even on creek banks, to approach 100% as observed in the high marsh and back marsh. The observed lower pyritization index of the creekside marsh must therefore be due to creekbank processes that enhance the supply of reactive iron (e.g. bioturbation) and/or inhibit the accumulation or formation of pyrite (e.g. bioturbation, oxidation, removal of dissolved sulfide by seepage at low tide).

Creekside marsh sediments are commonly riddled with numerous fiddler crab burrows (Bertness and Miller, 1984) which may play an important role in regulating the sulfur chemistry of the creekside marsh. During burrowing, crabs remove sediment containing pyrite from depth and place it at the marsh surface where the pyrite may be oxidized and/or washed away. Abandoned burrows tend to be filled in with fresh iron oxide from the surface and/or the suspended source. This nonlocal, nonrandom process of mixing via fiddler crab bioturbation results in a net upward movement of pyrite toward the surface and a corresponding downward movement of fresh iron oxide to replace the pyrite lost by upward mixing. Thus, some of the iron oxide that is consumed by pyrite formation is replaced or regenerated by fiddler crab bioturbation. This regeneration process tends to prevent the pyritization index from rising to values that it might otherwise reach in the absence of bioturbation. The resulting presence of fresh reactive iron oxide throughout the sediment column of the creekside marsh also tends to suppress the buildup of dissolved sulfide by reacting with sulfide to form FeS and FeS<sub>2</sub>. Lower sulfide concentrations in turn may permit more positive Eh values.

Recently published <sup>210</sup>Pb profiles in some of our cores by Sharma *et al.* (1987) provide a basis for quantitative assessment of the importance of fiddler crab burrowing on sulfur chemistry. Two back marsh profiles (BB4 and TC4) and a creekside profile (BB2) are shown on Figure 6. The back marsh profiles give <sup>210</sup>Pb sedimentation rates of about  $0.2 \text{ cm yr}^{-1}$  which are in rough agreement with historic sea level rise based on tide gage records at Charleston, South Carolina (Kjerfve *et al.*, 1978). The creekside site on the other hand gives an apparent sedimentation rate of  $3.0 \text{ cm yr}^{-1}$ . Aerial photographs dating back to 1939, however, do not reveal any detectable changes in the configuration of the channel or creek bank at this site as might be expected if the sedimentation rate was indeed  $3.0 \text{ cm yr}^{-1}$ . Accordingly, we believe that the <sup>210</sup>Pb profile at BB2 is due to intense burrowing by the abundant population of fiddler crabs at this site.

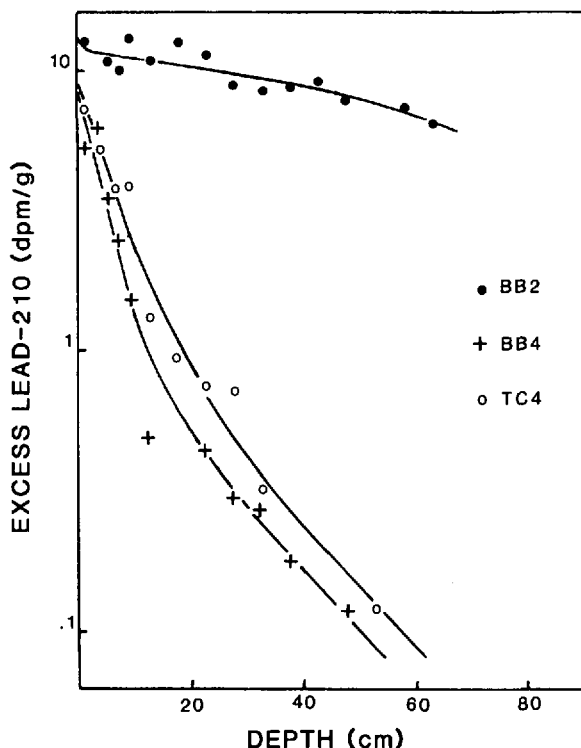


Figure 6. Plots of excess  $^{210}\text{Pb}$  activity versus depth for creek side (BB2) and back marsh (BB4 and TC4) sites. Solid lines through data points represents fit of regeneration model (Eq. 1) to the data.

Gardner *et al.* (1987) were able to closely simulate the effect of fiddler crab burrowing on their  $^{210}\text{Pb}$  profiles using a nonlocal, nonrandom mixing (or regeneration) model (Boudreau, 1986). The differential equation that describes the regeneration model is given as follows:

$$Sd^{210}\text{Pb}/dz = -K_{\text{Pb}}^{210}\text{Pb} + K_{\text{B}}(^{210}\text{Pb}_0 - ^{210}\text{Pb}_z) \exp(-z/U_{\text{B}}) \quad (1)$$

where  $z$  is depth (cm),  $K_{\text{Pb}}$  is the  $^{210}\text{Pb}$  decay constant ( $\text{yr}^{-1}$ ),  $S$  is the sedimentation rate ( $\text{cm yr}^{-1}$ ),  $^{210}\text{Pb}_0$  is the activity of  $^{210}\text{Pb}$  in the sediment source ( $\text{dpm g}^{-1}$ ),  $U_{\text{B}}$  is the mean burrow depth (cm) and  $K_{\text{B}}$  is the burrowing frequency ( $\text{cm}^2 \text{cm}^{-2} \text{yr}^{-1}$ ). The model assumes that during burrowing parcels of sediment are removed from depth and placed at the marsh surface where they are washed away. When abandoned, the burrows are assumed to be filled in with source sediment. The model assumes that the probability of a burrow reaching depth  $z$  is exponential. The term,  $^{210}\text{Pb}_0 - ^{210}\text{Pb}_z$ , gives the net increase in  $^{210}\text{Pb}$  resulting from the replacement of a sediment parcel at depth by source sediment.

As shown by Gardner *et al.* (1987) the product of  $K_{\text{B}}$  times  $U_{\text{B}}$  gives the volume of



sediment turned over per unit area per unit time. Calculated turnover volumes for sites BB2, BB4 and TC4 are 7.02, 0.070 and 0.085  $\text{cm}^3 \text{cm}^{-2} \text{yr}^{-1}$  respectively. Thus annual sediment turnover along creek banks is about 100 times greater than in back marsh sites. This is in rough agreement with direct measurements of burrow density and frequency of formation by Bertness and Miller (1984) in a New England marsh which reveal that burrowing by crabs is an order of magnitude more intense on creek banks than in back marsh areas. Thus it is likely that pyrite is replaced by fresh iron oxide much more rapidly along creek banks than in back marsh sites. If the rate of replacement is similar in magnitude to the rates of sulfate reduction and pyrite formation, then a low pyritization index will be maintained. The values of  $K_B$  and  $U_B$  that best fit the BB2 data shown on Figure 6 are 0.234  $\text{cm}^2 \text{cm}^{-2} \text{yr}^{-1}$  and 30 cm respectively (Gardner *et al.*, 1987). The value of  $U_B$  is approximately the depth at which measurable sulfate reduction ceases in a Georgia tall *Spartina* salt marsh (Skyring *et al.*, 1979). The annual volume of sediment turnover between the surface and a depth of 30 cm is equal to about 75% of the total annual sediment turnover or about 5.3  $\text{cm}^3 \text{cm}^{-2} \text{yr}^{-1}$  and is given by the product of  $K_B$  times the integral of  $e^{-z/U_B} dz$  evaluated between zero and  $U_B$ . Accordingly, about 17.5% ( $100\% \times 5.3 \text{ cm}/30.0 \text{ cm}$ ) of the sediment between 0 and 30 cm is turned over in a given year. Thus, crab burrowing could potentially remove 17.5% of the pyrite produced via sulfate reduction each year. As only 1% or so of the total pyritization potential actually accumulates in the sediment as pyrite, we therefore must invoke oxidation and/or pore water movement to dissipate the remaining 81.5% of the total pyritization potential. As the intensity of bioturbation is much lower in the high marsh and back marsh, pore water movement and/or oxidation are essentially the only means for the dissipation of the pyritization potential of such sites.

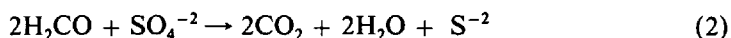
Movement of pore water in marsh sediments is driven by two processes, evapotranspiration and seepage into tidal creeks at low tide. Evapotranspiration occurs across all areas of the marsh but seepage is largely confined to the creekside environment. The amount of evapotranspiration probably varies across the marsh as a function of spatial variations in soil texture, frequency of tidal inundation and *Spartina* production. At present, measurements of water loss by evapotranspiration are only available for short *Spartina* sites at North Inlet, S.C. and in the Great Sippewissett Marsh, Massachusetts during summer (Morris and Whiting, 1985; Dacey and Howes, 1984). These measurements indicate water loss of about 4.0  $\text{l m}^{-2} \text{day}^{-1}$  and water table drawdowns of 6 to 34 cm during tidal exposure. In comparison, available estimates of water loss from creek banks by seepage at low tide lie roughly between 5.0 and 20.0  $\text{l m}^{-2} \text{day}^{-1}$  (Yelverton and Hackney, 1986; Harvey and Odum, 1987). Thus water loss by evapotranspiration and seepage appear to be similar in magnitude. However, this does not mean that their effect on dissolved sulfide concentrations will be similar. Neglecting, for the moment, indirect effects such as aeration and oxidation, the removal of water by evapotranspiration does not result in the removal of dissolved

sulfide from the sediment. Indeed, in the absence of secondary effects, evapotranspiration should tend to increase the concentration of dissolved sulfide during tidal exposure. Subsequent infiltration of replacement water at high tide should then dilute the dissolved sulfide back to its original concentration. Thus evapotranspiration should have little, if any, direct effect on sulfide concentration. Seepage, on the other hand, involves the movement of both pore water and its dissolved load from the creekside sediment into the adjacent tidal creek. This constitutes an actual advective movement of dissolved sulfide through the sediment. In the back marsh and high marsh, where drainage is negligible, downward advection of sulfide is due almost entirely to sedimentation ( $0.2 \text{ cm yr}^{-1}$ ). In the creek bank advection of dissolved substances is given by the sum of sedimentation plus the rate of infiltration required to replace seepage losses. Infiltration rates corresponding to seepage losses of  $5.0$  to  $20.0 \text{ l m}^{-2} \text{ day}^{-1}$  are  $180$  to  $730 \text{ cm yr}^{-1}$  respectively. As can be seen from these figures, advection of dissolved sulfide in the creekside environment is roughly two orders of magnitude greater than in the back or high marsh. All other factors being equal this should cause sulfide concentrations in the creek bank to be substantially lower than in the back or high marsh.

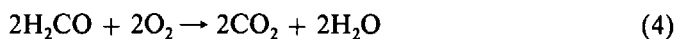
As noted above, loss of water by evapotranspiration and seepage causes temporary periods of sediment aeration and thus possible sulfide oxidation. Replacement infiltration at rates of  $5.0$  to  $20.0 \text{ l m}^{-2} \text{ day}^{-1}$  would cause a flux of dissolved oxygen into the sediment at a rate of  $0.36$  to  $1.4 \text{ moles O}_2 \text{ m}^{-2} \text{ yr}^{-1}$  assuming the infiltrating water is saturated with dissolved oxygen ( $0.2 \text{ millimoles l}^{-1}$ ). The amount of oxygen that would be required to oxidize the creekside belowground production ( $76 \text{ moles C m}^{-2} \text{ yr}^{-1}$ ) or the equivalent reduced sulfur ( $\text{H}_2\text{S} + \text{FeS} + \text{FeS}_2$ ) produced by sulfate reduction, ( $38 \text{ moles S m}^{-2} \text{ yr}^{-1}$ ) is about  $76 \text{ moles O}_2 \text{ m}^{-2} \text{ yr}^{-1}$ . For the high marsh the oxygen required would be about twice as great or about  $150 \text{ moles O}_2 \text{ m}^{-2} \text{ yr}^{-1}$ . Thus in either case the amount of oxygen brought in by infiltrating water is small compared to the amount required to dissipate the pyritization potential and probably would have little effect on the profiles of  $\text{H}_2\text{S}$ ,  $\text{FeS}$ ,  $\text{FeS}_2$  and iron oxide. On the other hand, the flux of air into and out of the sediment as a result of water loss and expulsion by infiltration is substantial ( $2.0 - 4.0 \text{ l m}^{-2} \text{ day}^{-1}$  or  $32-64 \text{ moles air m}^{-2} \text{ yr}^{-1}$ ). Measurements by Morris and Whiting (1985) indicate that on average about 30% of the oxygen in the air is taken up during its residence in the sediment. This amounts to about  $0.011 \text{ moles O}_2 \text{ m}^{-2}$  per tidal cycle or about  $7.8 \text{ moles O}_2 \text{ m}^{-2} \text{ yr}^{-1}$  which would be capable of oxidizing about 5% of the high marsh reduced sulfur production or about 10% of its creekside reduced sulfur production. These figures, however, are probably maximum estimates because the measurements were made during daylight hours in the summer when water loss, and thus air entry, are at a maximum. In any event, these calculations indicate that oxidation associated with pore water movement can only partially dissipate or circumvent (by aerobic oxidation of organic matter) the pyritization potential of salt marsh sediments. By default it thus appears that most of the

dissipation and/or circumvention must be assigned to the diffusive flux of oxygen from the surface into the sediment and/or to sediment oxidation by *Spartina* roots. We can make a generous estimate of the diffusive flux of oxygen into the sediment by assuming that the pore water dissolved oxygen concentration drops from saturation (0.2 millimole  $l^{-1}$ ) at the marsh surface to zero at a depth of 0.1 cm. Using this gradient and a diffusion coefficient of  $400 \text{ cm}^2 \text{ yr}^{-1}$  the diffusive flux of oxygen into the sediment is about  $8.0 \text{ moles O}_2 \text{ m}^{-2} \text{ yr}^{-1}$  which again is about 5.0 or 10.0% of the amount required to dissipate and/or circumvent the pyritization potential of creek side or high marsh respectively. Thus, we are left with the conclusion that the major mechanism of dissipation and/or circumvention must be oxidation by *Spartina* roots.

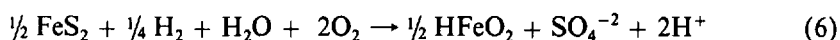
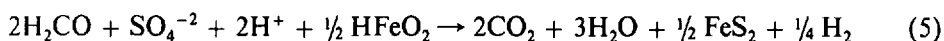
With this discussion of oxidation and water movement behind us we can now turn our attention to the effects of these processes on pore water pH. This is important not only because we wish to understand the mechanisms that control the geographical pattern of pH but also because, as we will see, pH affects the rates of formation of FeS and  $\text{FeS}_2$  and thus the pyritization index. Giblin and Howarth (1984) have proposed that the sulfide and pyrite produced by sulfate reduction are largely recycled to sulfate by the oxidation processes discussed above thereby circumventing the build up of sulfide and/or pyrite that would otherwise occur. In simple terms, the cycle can be described by the following reactions:



The sum of these two reactions is



If we wish to consider the effects of pyrite formation and oxidation we can rewrite reactions 2 and 3 as follows:



Again the sum of reactions 5 and 6 is reaction 4. Thus if reactions 2 and 3 proceed to exactly the same extent and/or reactions 5 and 6 do likewise, the decomposition of organic matter is effectively an aerobic process described by reaction 4 even though it takes a circuitous route through the sulfur cycle. Reaction 4 produces no alkalinity and will lower the pH of the pore water. Theoretical calculations indicate that reaction 2 by itself should lower the pore water pH to an asymptotic lower limit of 6.6 (Gardner, 1973) whereas reaction 5 should leave the pH near that of normal seawater (Ben-Yaakov, 1973). However, both reactions produce alkalinity by virtue of sulfate removal. Thus lowering of pH via reaction 4 will be retarded to the extent that reaction 5 exceeds reaction 2 and, more importantly, to the extent that reactions 2 and 5 exceed

reactions 3 and 6. Reaction 5 will tend to exceed reaction 2 to the extent that reactive iron oxide remains available in the sediment. As indicated earlier, intense fiddler crab burrowing acts in this direction and thus toward maintaining high pH. Reactions 2 and 5 will exceed reactions 3 and 6 if the dissolved sulfide and pyrite produced by reactions 2 and 5 can be removed from the sediment by processes other than oxidation. Thus high pH also should prevail in the creekside sediments because of removal of dissolved sulfide by drainage (and replacement by high pH surface seawater) and because of the removal of pyrite by fiddler crab bioturbation.

Experimental studies of the kinetics of iron sulfide precipitation by Rickard (1974, 1975) indicate that the rates of formation of FeS and FeS<sub>2</sub> are dependent on pH in accordance with the following rate equations:

$$d(\text{FeS})/dt = K_t[\text{H}^+]^2 (\text{H}_2\text{S})^{1.5} A_g \quad (7)$$

$$d(\text{FeS}_2)/dt = K_p [\text{H}^+] (\text{H}_2\text{S}) A_t^2 A_s \quad (8)$$

where  $K_t$  and  $K_p$  are rate constants,  $[\text{H}^+]$  is hydrogen ion activity,  $(\text{H}_2\text{S})$  is the concentration of total dissolved sulfide ( $\text{H}_2\text{S}$ ,  $\text{HS}^-$ ,  $\text{S}^{2-}$ ) and  $A_g$ ,  $A_t$  and  $A_s$  are the surface areas of goethite, troilite (FeS) and elemental sulfur respectively. As the activity of  $\text{H}^+$  in the creekside marsh is five to ten times lower than that of the back marsh and high marsh the rate of conversion of iron oxide into pyrite should be correspondingly lower, assuming the molar surface areas of goethite, troilite and elemental sulfur are uniform over the entire marsh. Thus the pyritization index of the creekside marsh is lower than that of the back marsh and high marsh because of the combined effects of a lower rate of sulfate reduction, removal of pyrite by fiddler crab bioturbation and its replacement with reactive iron oxide and a lower rate of pyritization imposed by higher pH and lower dissolved sulfide.

## 5. Summary and conclusion

Similar spatial patterns of sulfur chemistry are found in marsh sediments at North Inlet S.C. (this study) and Sapelo Island, GA (King *et al.*, 1982). Along transects from creeksides to high marsh we observe systematic decreases in pH and Eh, dissolved iron, acid volatile sulfide and increases in sulfate depletion, dissolved sulfide, total sediment sulfur and pyritization index. These patterns are probably controlled by spatial variations in belowground production, pore water movement and fiddler crab burrowing. The creekside marsh is characterized by lower rates of belowground production (and thus lower rates of sulfate reduction), more vigorous drainage of pore water and more intense fiddler crab burrowing as compared to the high marsh. Lower dissolved sulfide concentrations in the creekside marsh are promoted by lower rates of sulfate reduction and removal of dissolved sulfide by drainage at low tide. High pH in the creekside marsh is fostered by removal of reduced sulfur (dissolved sulfide by drainage and pyrite by fiddler crab burrowing) which then cannot be oxidized within the

sediment to yield acid. The higher pH and lower dissolved sulfide of the creekside sediment in turn slows the rate of conversion of iron oxide into pyrite in accordance with Rickards's (1974, 1975) rate laws, and thus fosters a lower pyritization index. The lower pyritization index of the creekside marsh also is promoted by fiddler crab burrowing which tends to remove pyrite from the sediment and replace it with fresh iron oxide from the surface or suspended source. The greater availability of reactive iron oxide in the creekside marsh also may shift the relative rates of FeS and FeS<sub>2</sub> formation such that a higher steady state concentration of FeS can be maintained in the creekside marsh as compared to the high marsh.

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