Rates and controls of anaerobic microbial respiration across spatial and temporal gradients in saltmarsh sediments

JOEL E. KOSTKA[1,3,*], ALAKENDRA ROYCHOUDHURY[2,4] and PHILIPPE VAN CAPPELLEN[2,5]

[1]*Skidaway Institute of Oceanography, 10 Ocean Science Circle, Savannah, GA 31411, USA;* [2]*Georgia Institute of Technology, Atlanta, GA 30332, USA;* [3]*Current address: Department of Oceanography, Florida State University, Tallahassee, FL 32306-4320, USA;* [4]*Northwestern University, Evanston, IL 60208, USA;* [5]*Universiteit Utrecht, 3508 TA Utrecht, Netherlands; *Author for correspondence (e-mail: jkostka@ocean.fsu.edu; phone: 850-645-3334; fax: 850-644-2581)*

Abstract. This study was undertaken to determine the rates and controls of anaerobic respiration reactions coupled to organic matter mineralization as a function of space and time along a transect from a bioturbated creekbank to the midmarsh in Georgia saltmarsh sediments. Sulfate reduction rates (SRR) were measured at 3 sites during 5 sampling periods throughout the growth season. The sites differed according to hydrologic regime and the abundance of dominant plants and macrofauna. SRR and pore water / solid phase geochemistry showed evidence of enhanced sediment oxidation at sites exposed to intense bioturbation. Iron(III) reduction rates (FeRR) were directly determined in saltmarsh sediments for the first time, and in agreement with measured SRR, higher rates were observed at the bioturbated, unvegetated creekbank (BUC) and bioturbated, vegetated levee (BVL) sites in comparison to a vegetated mid-marsh (MM) site. An unexpected result was the fact that SRR varied nearly as much between sites (2–3 x) as it did with temperature or season (3–4 x). The BVL site, vegetated by the tall form of *Spartina alterniflora*, always exhibited the highest SRR and carbon oxidation rates (> 4000 nmol cm^{-3} d^{-1}) with high activity levels extending deep ($\geq$ 50 cm) into the sediment, while the MM site, dominated by the short form of *Spartina*, always exhibited the lowest SRR which were localized to the top 15 cm of sediment. SRR and FeRR at BUC were intermediate between those measured at the BVL and MM. Acetate was the most abundant microbial fermentation product (concentrations up to > 1 mM) in marsh porewaters, and its distribution reflected respiration activity. Chemical exchange, caused by bioturbation, appeared to be the primary control explaining trends in rates of sulfate and Fe(III) reduction with macrophytes and carbon source acting as secondary controls.

Introduction

Saltmarshes are among the most productive ecosystems on earth (Dame and Kenny 1986; Alongi 1998). These wetlands are vital components of coastal marine ecosystems, as they provide nursery grounds for commercially important fish and
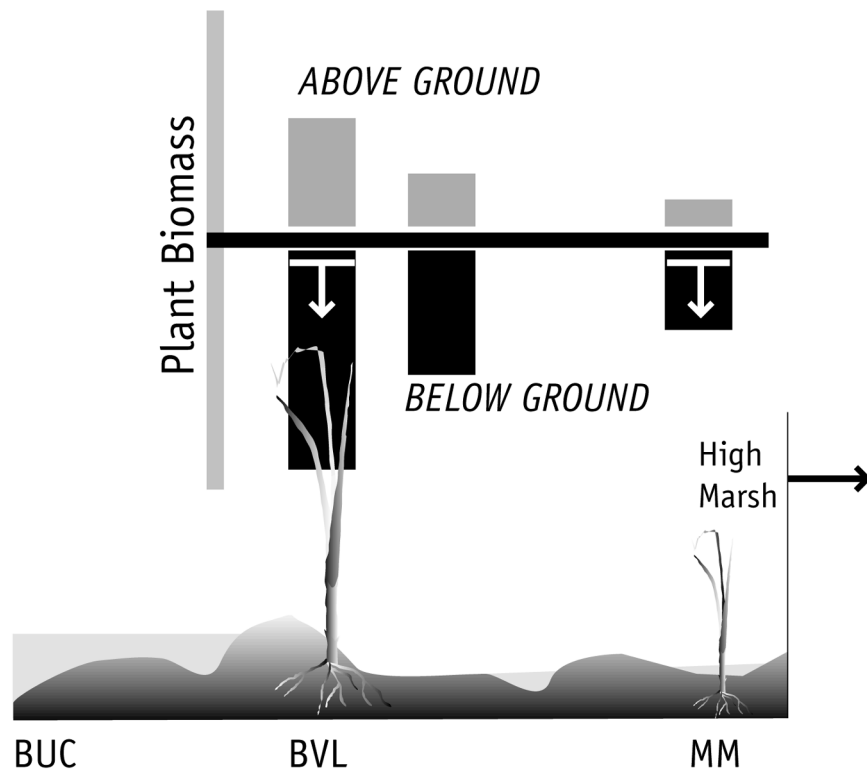
50

Figure 1. Schematic of a cross section of saltmarsh on Sapelo Island, Georgia, illustrating sampling sites and the relative biomass of smooth cordgrass, *Spartina alterniflora*, present at each site. Aboveground biomass (measured as the height of *Spartina*) at the Institute Marsh was used to scale the schematic. BUC = bioturbated, unvegetated creekbank; BVL = bioturbated, vegetated, levee; MM = midmarsh (see ″sampling area″ section of methods for complete description)

shellfish species, limit nutrient exchange at the land-sea boundary, and protect coastal municipalities from catastrophic storms (Pomeroy and Wiegert 1981).

Along the east coast of the U.S., primary production in saltmarshes is dominated by the macrophyte, smooth cordgrass or *Spartina alterniflora* (Pomeroy and Wiegert 1981). Belowground production of this grass (as roots and rhizomes) usually exceeds aboveground production (as shoots and leaves; Gallagher and Plumley (1979); Schubauer and Hopkinson (1984); Figure 1) by a factor of 2 to 4. The roots and shoots of *Spartina* are an important conduit for chemical exchange between the sediments and tidal waters or the atmosphere (Teal and Kanwisher 1961; Dacey and Howes 1984; Morris and Whiting 1985; Howes and Teal 1994). For example, studies have shown that the roots of *Spartina* may be a primary source of organic matter (Dame and Kenny 1986; Schubauer and Hopkinson 1984) and a source or sink of oxygen to the surrounding sediments (Dacey and Howes 1984; Howes and Teal 1994).

Saltmarsh sediments are rich in organic matter and relatively impermeable clay minerals. Therefore, oxygen is utilized rapidly in surface sediments (in the top few mm; King (1988); Luther et al. (1996)) and most organic matter remineralization occurs under anoxic conditions (Howarth 1993; Alongi 1998). Because of the abundance of sulfate in seawater, microbial respiration coupled to the terminal decomposition of organic matter in saltmarsh sediments is thought to be dominated by sulfate reduction (Howarth and Hobbie 1982; Howarth 1993; Alongi 1998). Microbial respiration reactions represent a transfer of carbon and nutrients between the organic and inorganic reservoirs (Jahnke and Craven 1995), and an understanding of this transfer is vital to the modeling of biogeochemical dynamics in estuaries.

Sulfate reduction rates have been measured in saltmarshes on the east coast of the U.S. since the late seventies (Howarth and Teal (1979); Howarth and Giblin (1983); Howes et al. (1984); King (1988); Hines et al. (1989); see review by Howarth (1993)). Few studies, however, have explored spatial variability within the marsh (King 1988) and, to our knowledge, no studies have incorporated an extensive comparison of vegetated vs. unvegetated sites within the marsh. Saltmarshes are exposed to a large number of physical, biological, and chemical forcings, resulting in complex biogeochemical cycles. This complexity has clouded interpretation of the mechanisms by which microorganisms interact with surrounding higher organisms (plants, macrofauna) to control predominating diagenetic reactions. Interpretations regarding the response of microbial respiration to different growth forms of *Spartina*, which exhibit large variability in aboveground production, remain equivocal, and few studies have experimentally determined the influence of bioturbating macrofauna.

Previous biogeochemical studies have suggested that microbial Fe(III) reduction may contribute to carbon cycling in saltmarsh sediments (Kostka 1993; Kostka and Luther 1995) and Fe(III)-reducing bacteria have been detected in abundance in these environments (King and Garey 1999; Lowe et al. 2000). However, rates of Fe(III) reduction have not been measured in saltmarsh sediments and the consensus of research has been that most Fe(III) reduction occurs via abiotic chemical reaction with dissolved sulfide (Howarth 1993; Jacobson 1994; Kostka and Luther 1995; Alongi 1998).

This study was undertaken to elucidate the rates and controls of anaerobic microbial respiration coupled to organic matter mineralization as a function of space and time in Georgia saltmarsh sediments. Since sulfate and Fe(III) minerals are the most abundant electron acceptors available for microbial respiration in saltmarsh sediments, we focused on sulfate reduction and Fe(III) reduction processes. A sampling scheme was designed to include 3 sites in the marsh which vary according to hydrological regime, macrofaunal abundance, and the growth form of *Spartina*. We also sampled deep into the sediment column (0.5 m) and combined microbial rate measurements with a characterization of sediment geochemistry.

Methods

Sampling area

This study was conducted at the Institute Marsh adjacent to the University of Georgia Marine Institute on Sapelo Island, Georgia, over 5 sampling periods from May, 1997 to November, 1998. The Institute Marsh is dominated by a nearly monospecific stand of smooth cordgrass or *Spartina alterniflora*, and the mud fiddler crab, *Uca pugnax*, has been observed in abundance throughout the marsh (Teal 1958; Basan and Frey 1977). *Uca* irrigates the sediment by building burrows which may extend to 25 cm depth, and these macroinvertebrates also continually rework the surface 2 to 3 cm of sediment through deposit feeding activities (Bertness 1985). Sediments were sampled at three sites, which differed according to their hydrology and ecology, from nearby a large tidal creek to the mid-marsh (Figure 1). These sites will henceforth be referred to as the bioturbated, unvegetated creekbank (BUC); the bioturbated, vegetated levee (BVL), and the mid-marsh (MM) sites. The BUC site was bioturbated by *Uca* but contained no visible higher plants. The BVL was located within a few meters of the BUC, but was sampled at approximately 1 meter higher elevation relative to mean low water. The MM site was located a few hundred meters inland from the large tidal creek (Figure 1). A gradient in above-ground *Spartina* biomass is observed with increasing distance from the tidal creek with the tall form of *Spartina* present at the BVL and the short form of *Spartina* at MM (Figure 1; Gallagher et al. (1980)). In parallel, bioirrigating and bioturbating macrofauna were very abundant at BUC and BVL, while their abundance decreased with increasing distance from the creek toward the MM (Teal 1958, 1962; Basan and Frey 1977).

Sediments sampled in the present study were clay-rich silts with occasional sandy layers. Sediment porosity and wet density ranged from 0.78 to 0.99, and from 1.2 to 1.4 g cm^{-3}, respectively. Organic carbon concentrations varied from 3 to 4 weight % (Roychoudhury 1999) gradually decreasing with depth. The range of organic carbon concentrations overlapped with those of previous studies in similar marshes (Giblin and Howarth 1984; Morris and Whiting 1985).

Sediment sectioning and porewater extraction

Sediments were sampled using a stainless steel wedge corer which minimizes compaction (Inglett et al., in prep). Within 15 to 20 min. of sampling, cores were transferred to a nitrogen-filled glove bag, where the sediment was sectioned into 1 to 4 cm depth intervals. Sediments for solid phase analysis were frozen under nitrogen for later use. Pore waters were sampled using diffusion equilibrators or peepers fitted with a nylon membrane. Peepers were left to equilibrate in the marsh for at least 1 month. Upon retrieval, each peeper was immediately placed into a glove bag in the field and transported to the field laboratory. Pore waters were drawn directly from the peeper using N$_2$-flushed syringes and filtered through 0.2 μm pore size cellulose acetate syringe filters into gas-tight vials for manipulation.

For determination of carbon mineralization rates, sediment from parallel cores (0 to 5 cm and 10 to 15 cm depth intervals) was incubated as described by Aller et al. (1996). Briefly, cores were sectioned, the sediment was homogenized, and parallel sections pooled under strict anoxia in a glove bag. After sectioning, sediment from each of the depth intervals was loaded into 50 ml centrifuge tubes (with no headspace) within a few hours of core retrieval. Tubes were then placed inside a N_2-filled glove bag as per Canfield et al. (1993b), and incubated in the dark at sediment temperature. The centrifuge tubes were then removed from the glove bag and sampled at regular intervals, and the pore waters were extracted by centrifugation (5000 × g for 15 min) plus filtration (through 0.2 μm syringe filters).

For determination of sulfate reduction rates (SRR), sediment was subsampled and transferred into 10 ml syringe microcores in a glove bag (according to Hines et al. (1989)). SRR were determined in duplicate with $^{35}SO_4^{2-}$ (Jørgensen 1978) in incubations at ambient sediment temperature. At termination, the sediment was fixed in 20% Zn acetate and frozen. The reduced ^{35}S was recovered by distillation with boiling acidic Cr^{2+} solution using the two-step method of Fossing and Jørgensen (1989). SRR measurements were carried out in short-term incubations (2 hrs) to minimize the effects of sulfide oxidation (Fossing 1995). In time course experiments, the accumulation of radioactive sulfides revealed that sulfate reduction rates were highly linear from 20 min. to 12 hours (data not shown).

Pore water analyses

Dissolved Fe^{2+} was determined on pore water immediately after filtration by colorimetry with a ferrozine solution (det. limit 1 μM; SD 2%; Stookey (1970); Viollier et al. (2000)). Sulfate concentrations were measured in acidified porewater using the turbodometric method of Tabatabi (1974). Dissolved sulfide was determined on filtered pore water after precipitation with zinc using the methylene blue method (det. limit 1 μM; SD 5%; Cline (1969)).

Pore water for the analysis of organic acids was mostly separated from the solid phase of parallel cores by centrifugation. In order to check for potential artifacts of sample retrieval on the organic acid determinations, we compared pore water extracted by centrifugation to pore water sampled nondestructively using a sipper device as described by Hines et al. (1994) during the November sampling trip. Organic acid analyses were carried out on filtered pore water using ion exclusion HPLC with conductivity detection on a Dionex DX-500 ion chromatography system. Standard calibration curves were obtained for the following organic acids: oxalate, pyruvate, citrate, malonate, malate, glycolate, formate, lactate, acetate, succinate, isobutyrate, and propionate (detection limits ranged from 1 to 10 μM). Filter blanks using seawater taken from the site showed that less than a few micromolar of any organic acid was produced and therefore no contamination occurred during the filtration procedure.

In sediment incubations, porewater for the determination of ΣCO_2 was filtered into 1.8 ml glass vials that were capped with Teflon-coated butyl rubber septa, leaving no gas phase and maintaining anoxia. The samples were stored at 4°C and

analyzed within a few days of sampling by flow injection with conductivity detection (Hall and Aller (1992); S.D. 2% for ΣCO_2) as modified by Lustwerk and Burdige (1995) to eliminate hydrogen sulfide interference.

Solid phase analyses

Wet chemical extractions were used to determine the poorly crystalline Fe oxide pool (Canfield 1989; Thamdrup et al. 1994; Kostka and Luther 1994). Iron was extracted in ascorbate (pH 8) or 0.5 M HCl for one hour (Kostka and Luther 1994). The concentration of Fe in the extract was determined by the ferrozine colorimetric method. Ascorbate-extractable Fe was operationally defined as the amorphous Fe(III) oxyhydroxide fraction and was highly correlated with that extracted by 0.5 M HCl in previous studies of saltmarsh sediment (Kostka and Luther 1994). Calibration experiments with pure Fe mineral phases have confirmed the selectivity of these extractions towards poorly crystalline Fe phases (Kostka and Luther 1994).

Acid-volatile sulfide (AVS = FeS + H_2S) and chromium-reducible sulfur (CRS = S^0 + FeS_2) were determined after a two-step distillation with cold 2 M HCl and boiling 0.5 M Cr^{2+} solution (Fossing and Jørgensen 1989). Sediment fixed with Zn acetate from the SO_4^{2-} reduction measurements was used for solid sulfide determinations.

Results

Pore water chemistry

During the summer (August, 1997, 30 °C sediment temp.), sulfate concentrations decreased markedly with depth at all sites. However, depletion was most pronounced at the mid-marsh (MM) site. Porewater sulfate concentrations at 20 cm depth were approximately 20 mM, 8 mM, and 4 mM at the BUC, BVL, and MM sites, respectively (Figure 2). Subsurface maxima in dissolved Fe were observed at 20 to 30 cm depth at the BUC and BVL sites, whereas little or no pore water Fe was observed at the MM site. Dissolved sulfide only accumulated in the mid-marsh where it increased to a maximum concentration of 10 mM at 10 cm depth after which it showed little down-core variation (Figure 2).

During the winter (January, 1998, 11°C sediment temp.), the general trends described were again observed but on a reduced scale. Little or no sulfate depletion was observed at the BUC or BVL, while substantial depletion was observed in the mid-marsh (Figure 3). Pore water Fe concentrations were approximately half those found in the summer. Dissolved sulfide levels were generally lower at MM during the winter but millimolar concentrations were still observed (Figure 3).

Depth distributions of organic acids were determined in July and November of 1998 (Figure 4). Only two compounds (of the 12 for which calibration curves were obtained- see methods), acetate and malonate, were regularly detected. The distri-
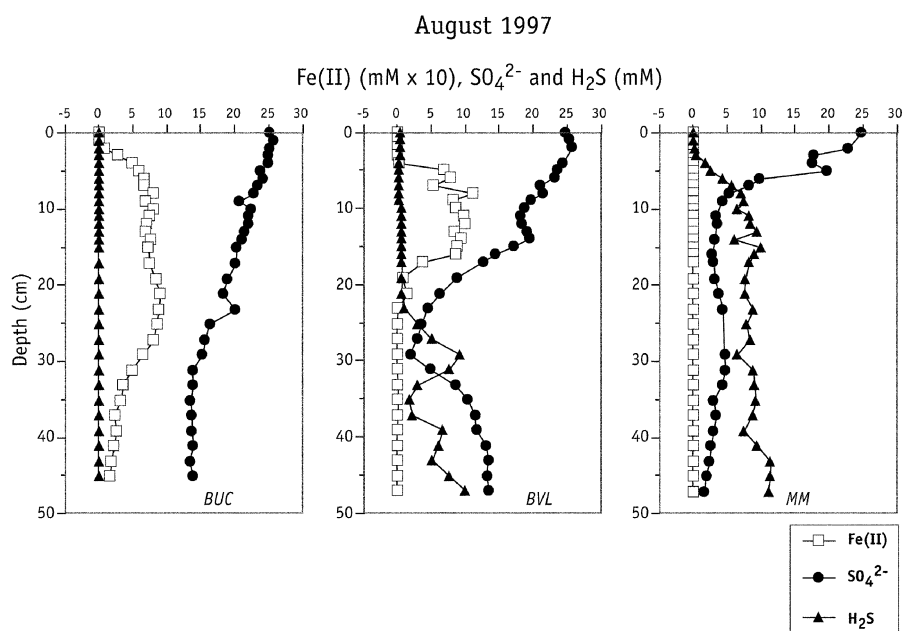
August 1997

Fe(II) (mM x 10), SO$_4^{2-}$ and H$_2$S (mM)

Figure 2. Reactants and products of microbial respiration are indicated by vertical profiles of pore water constituents at the BUC, BVL, and MM sites during the summer (August, 1997)

bution of pore water acetate concentrations with depth in July differed according to sample site. Higher acetate concentrations were observed, especially close to the sediment surface, in sediments vegetated by *Spartina* (BVL and MM sites) as compared to the unvegetated site (BUC; Figure 4a). The subsurface maximum in acetate observed at MM was 15 cm closer to the sediment surface as compared to the BVL site. Malonate concentrations in July were also higher at vegetated sites as compared to the unvegetated site, where malonate was only detected in the top 5 cm (Figure 4b). In November, only the MM site was sampled. In comparison to July, the malonate distribution appeared unchanged in November (Figure 4b and 4d). Acetate concentrations, however, were 2 to 9 times lower in the top 10 cm in November relative to July (Figure 4a and 4c).

In order to check for potential artifacts of sample retrieval on the organic acid determinations, we compared pore water extracted by centrifugation to pore water sampled nondestructively using a sipper device during the November sampling trip (see methods section). In the MM which had the highest root biomass close to the sediment surface, organic acid concentrations were measured on duplicate pore water samples extracted by the two methods at 2 sediment depths. Acetate and malonate concentrations were nearly identical using the two independent sampling methods (Figure 4c and 4d).
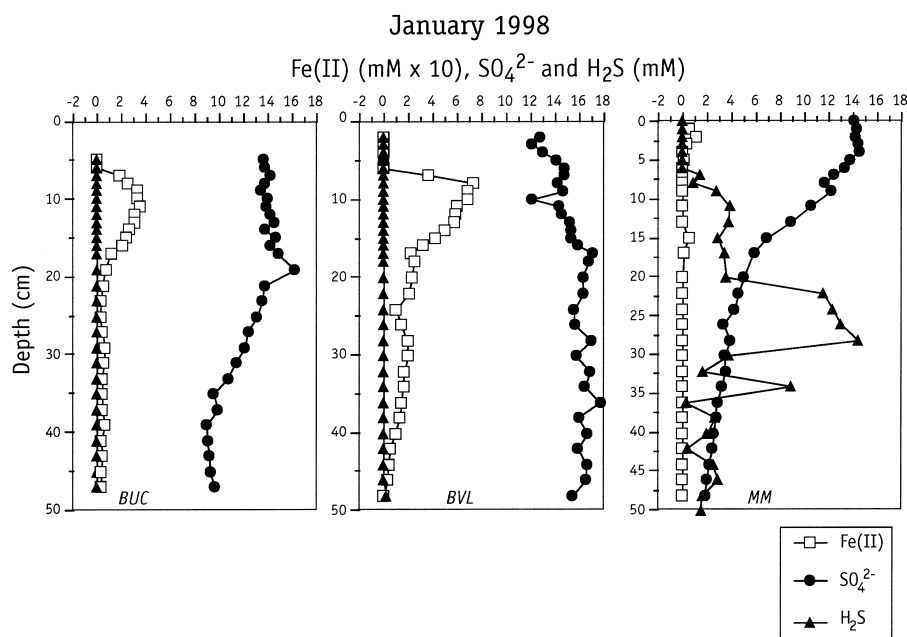
January 1998

Fe(II) (mM x 10), SO$_4^{2-}$ and H$_2$S (mM)

Figure 3. Reactants and products of microbial respiration are indicated by the pore water geochemistry of the 3 sites compared for samples collected during the winter (January, 1998)

Solid phase distributions

Reactive Fe concentrations were generally high in the upper 10 to 15 cm and decreased with sediment depth at all sites and seasons (Figure 5a). A subsurface maximum in reactive Fe, indicative of active precipitation of Fe(III) oxyhydroxides, was observed at BVL during all seasons. The MM showed the steepest gradient in reactive Fe with depth, and the gradient was more pronounced in summer. BUC and BVL sites contained higher reactive Fe concentrations relative to the MM. At BUC and BVL, there was little change in reactive Fe between seasons and a smaller depth gradient was observed.

Reactive Fe was speciated in the solid phase using HCl during the July, 1998, sampling trip in order to contrast the amount of oxidized Fe(III) present between sites, and to measure the turnover of Fe(III) in sediment incubations (see Rate Measurements section below). The total inventory of reactive Fe(III) measured in HCl extractions was similar at the BUC (1615 mmol m^{-2}; Figure 6a) and BVL sites (1480 mmol m^{-2}; Figure 6b), while the MM displayed much lower solid Fe(III) concentrations (146.6 mmol m^{-2}; Figure 6c). The concentration of solid Fe(II) and total Fe (FeII + FeIII) present in depth profiles (Figure 6) showed a similar pattern: BUC $\sim$ BVL $\gg$ MM.

Seasonal and spatial trends in acid-volatile sulfide (AVS) and chromium reducible S (CRS) fractions were in general inversely correlated to those of reactive Fe.
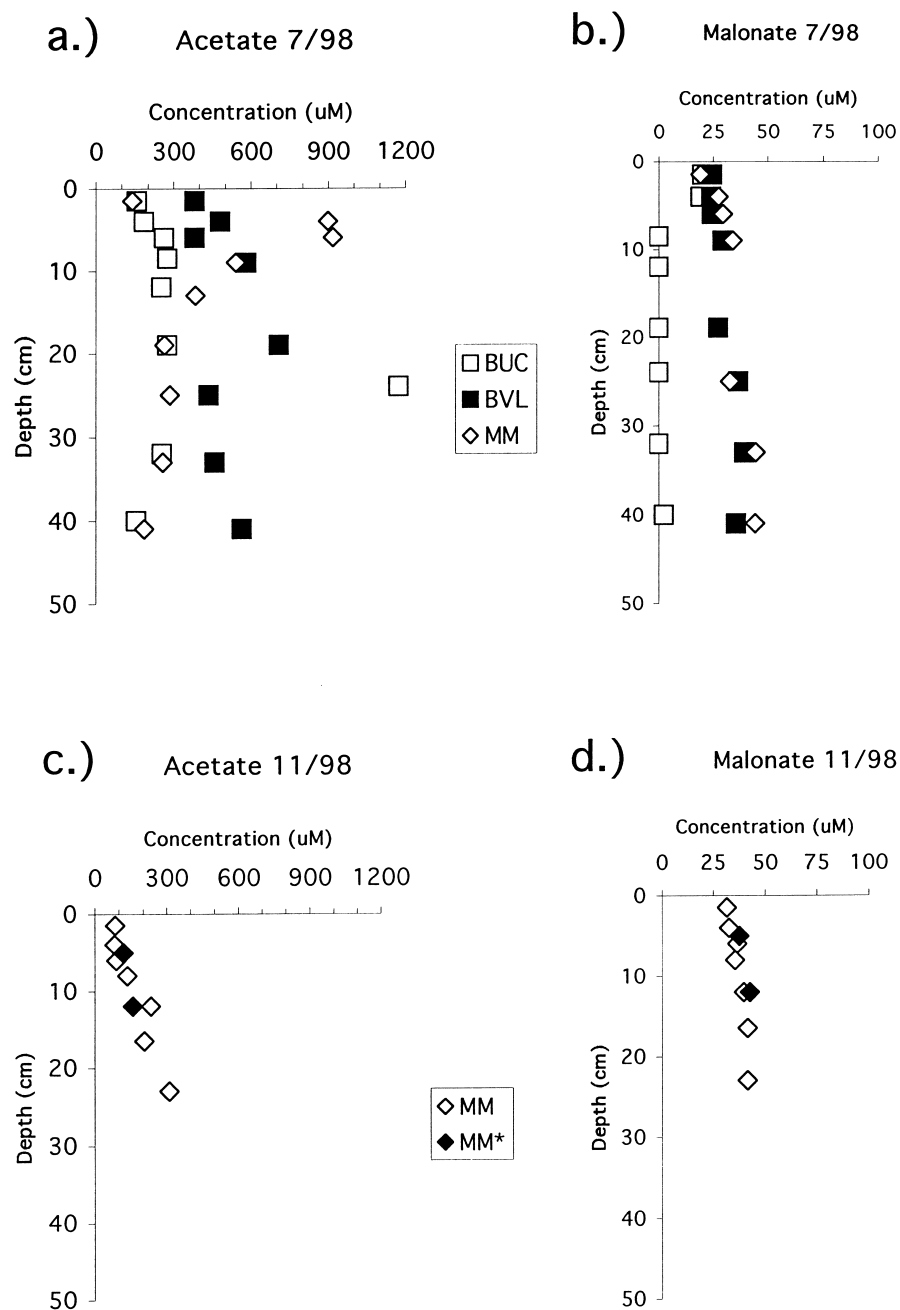
Figure 4. Small molecular weight organic acids measured in pore water during July and November sampling periods. Symbols are the averages of duplicate samples. The asterisk denotes samples collected by a nondestructive sipper device
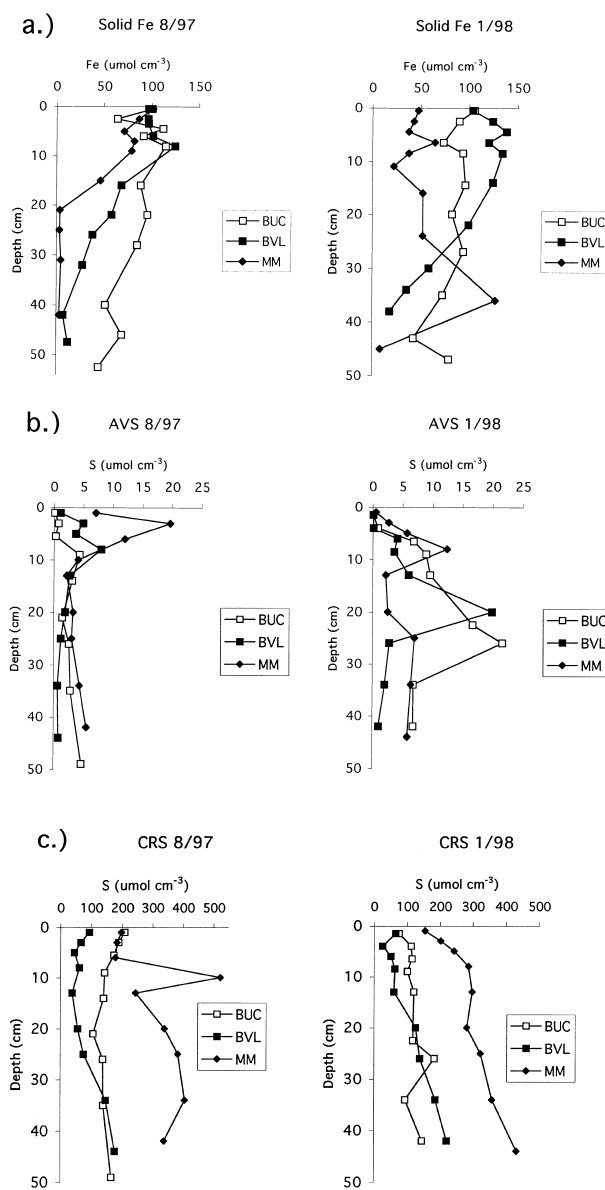
Figure 5. Distribution of solid phase reactive Fe and sulfides sampled from the same sediments represented in Figures 2 and 3

Solid S concentrations (AVS, CRS) increased from the BUC to the MM (Figure 5b and 5c). Similar to pore water sulfide, the depth of this subsurface maximum in AVS was shallower in summer and became shallower from the BUC to the MM
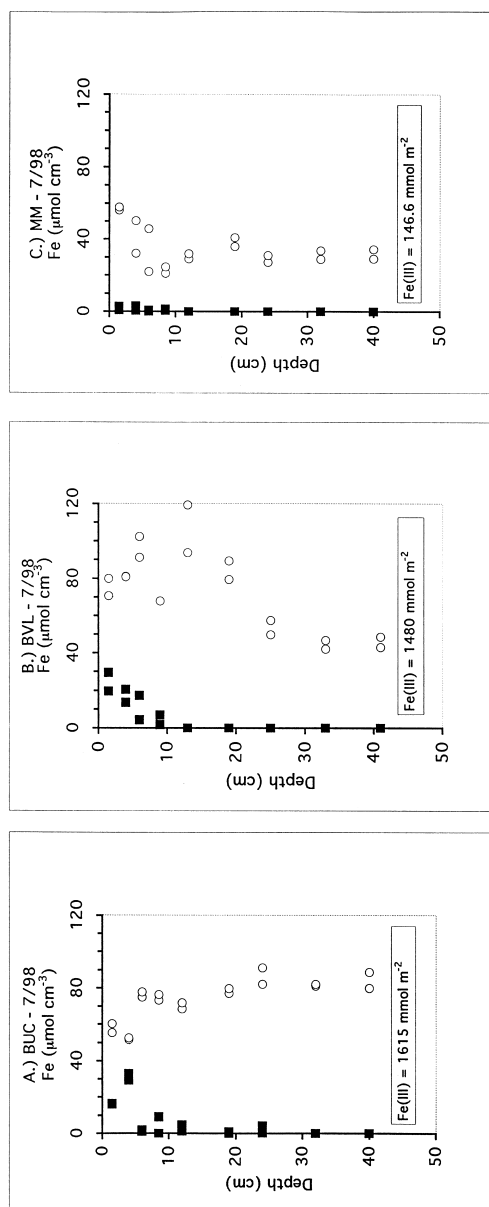
Figure 6. Speciation of solid phase Fe from sediments collected during the July, 1998, sampling period. Oxidized Fe(III) is represented by the squares and reduced Fe(II) is represented by the circles. The total inventory of oxidized Fe(III) integrated to 50 cm depth for each site is given in the inset box

(Figure 5b). CRS concentrations increased with sediment depth, and below the surface 10 cm, were 2 to 3 times higher at MM relative to the other sites.

Rate measurements

In order to constrain the spatial and temporal variability of microbial respiration coupled to C oxidation in saltmarsh sediment, we have measured rates of sulfate reduction, Fe(III) reduction, and C oxidation.

Sulfate reduction rates (SRR) measured by the radiotracer technique showed large variations according to sediment depth, the site sampled, and sediment temperature or season sampled (Figure 7). During most seasons, the highest SRR were observed at the sediment surface of all sites. In contrast, during the winter, a pronounced subsurface maximum in SRR was observed at around 5 cm depth at all sites. Sulfate reduction rates decreased rapidly with depth in the MM, often decreasing to less than 100 nmol cm^{-3} d^{-1} below 10 cm depth. The sharp gradients in SRR coincide with the large depletions of pore water sulfate and the accumulation of pore water (and solid) sulfides observed at the MM site. In contrast, substantial SRR (100 to 500 nmol cm^{-3} d^{-1}) persisted to between 20 and 50 cm depth at the BVL and throughout the entire sediment column of the BUC site (Figure 7).

Variability of SRR was assessed at the levee site during November, 1998. Duplicate rate measurements were made on duplicate cores taken approximately 1 m apart (Figure 7e). The mean of 1 standard deviation for all rate measurements was 23%. Thus at each site, we estimate intramarsh variability at around 20%.

Spatial and temporal trends are also evident when SRR is integrated over the entire sediment column to 50 cm depth (Figure 8). At every time period sampled, depth-integrated SRR was highest at BVL and lowest at MM. Integrated SRR showed a direct and strong correlation with sediment temperature with, of course, the highest rates observed in the summer followed by the spring/fall and then winter. A more surprising result was the fact that SRR varied nearly as much between sites as it did with temperature or season. At any one site, integrated SRR varied by a factor of up to 3 or 4 over the season sampled, while during each sampling period, integrated SRR was generally 2 to 3 times higher at BVL as compared to MM (Figure 8). When integrated SRR is plotted as a function of sediment temperature (Figure 8; inset), it is apparent that site-specific factors control sulfate reduction as each site shows a separate linear relationship with temperature.

A comparison of C oxidation rates (measured by the accumulation of ΣCO_2) at the various sample sites was made in sediment incubations during the July, 1998, sampling period. Accumulation rates were rapid and highly linear over the first 48 hrs at the depths sampled (Figure 9). From 48 to 72 hours, the rates decreased. Rates reported here were calculated from the initial 48 hr incubation period. Similar to SRR, C oxidation rates were highest at the BVL and lowest at the MM (Table 1). C oxidation rates were also 2 to 3 times more rapid in the surface 0 to 5 cm depth interval as compared to the 10 to 15 cm depth interval.

In the same incubations where total C oxidation was determined, Fe(III) reduction was directly measured as the accumulation of HCl-extractable Fe(II) (Figure 10). In the 0 to 5 cm depth interval, the turnover or reduction of solid Fe(III) (Figure 10) followed the same pattern observed between sites for the amount of reactive Fe present in the bulk phase (Figures 5 and 6). Similar to the trend ob-
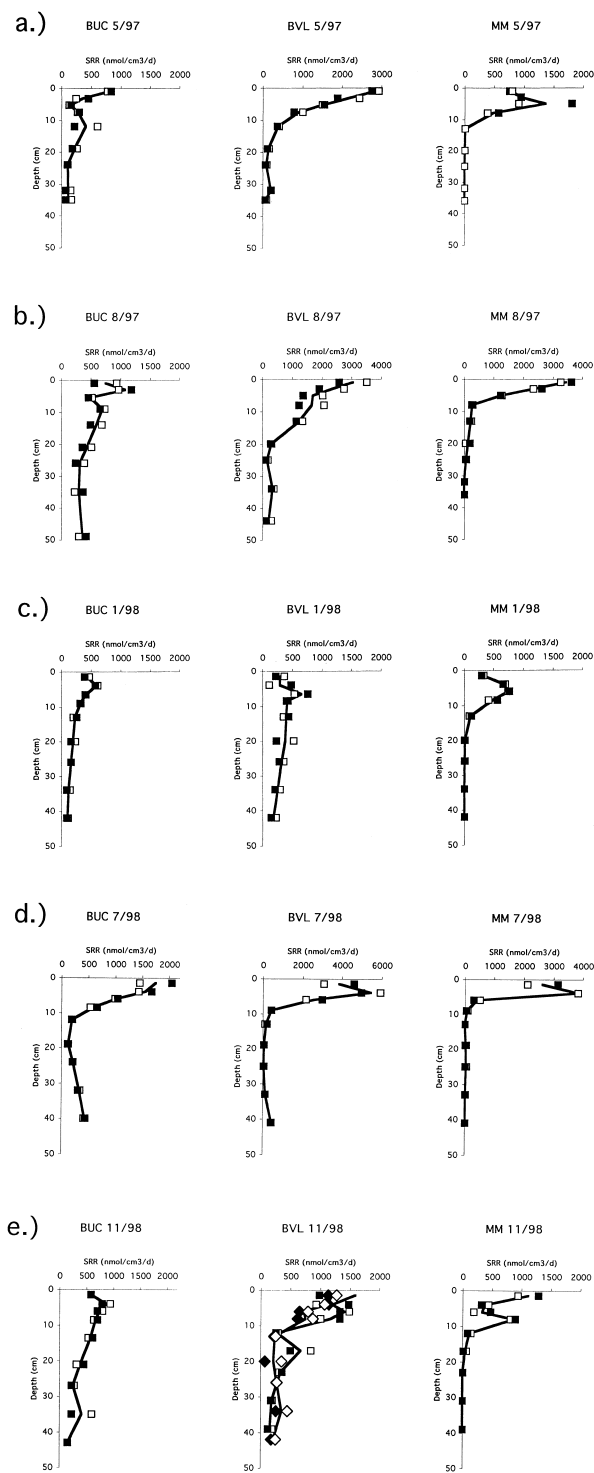
Figure 7. Depth profiles of sulfate reduction rates (SRRs) measured for the 3 sites over 5 sampling periods from May, 1997 (a.), to November, 1998 (e.). Symbols represent duplicate samples at each depth; solid lines represent the average rate measured
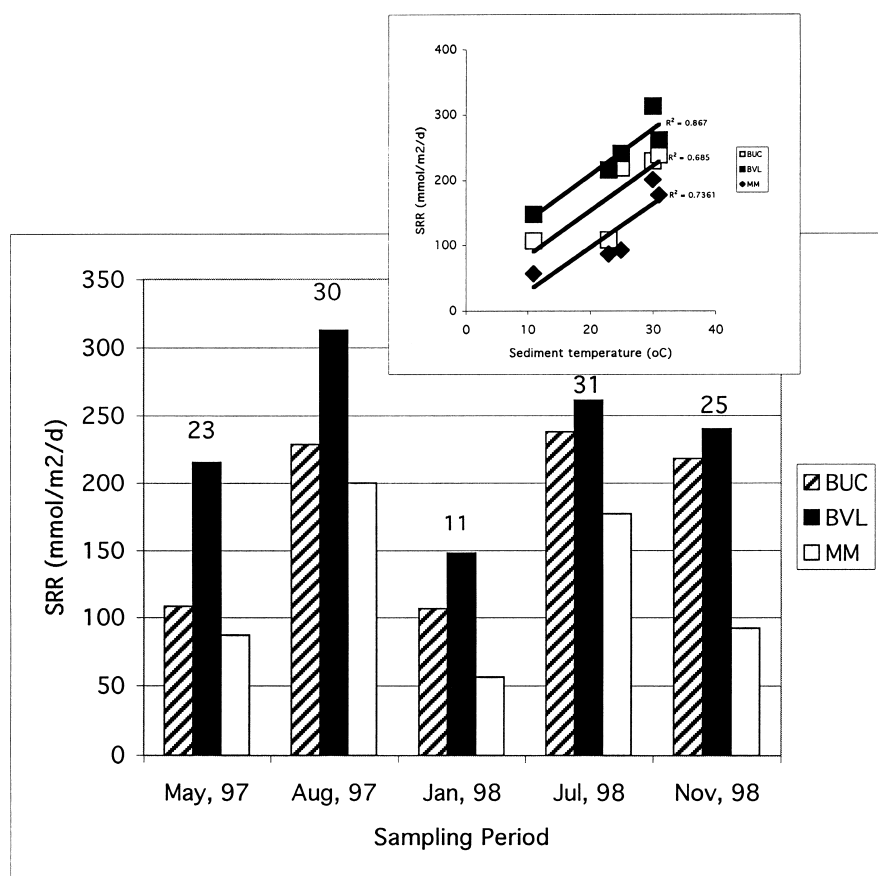
Figure 8. For comparison over space and time, SRRs are integrated to 50 cm depth in the sediment column. Numerical values on the histogram indicate sediment temperature. Inset graph indicates that integrated rates correlated with sediment temperature for each site sampled

served for SRR, Fe(III) reduction rates (FeRR) were most rapid at the BVL, followed by the BUC, and little or no Fe(III) reduction was detected at the MM site (Figure 10; Table 1). In the 10 to 15 cm depth interval, no Fe(III) reduction was detectable at any of the 3 sites (Table 1).

Discussion

Sulfate reduction and sediment geochemistry over spatial gradients in the saltmarsh

Most previous studies of anaerobic respiration in saltmarshes have focused on sulfate reduction in the zones inhabited by short *Spartina* which are drained at low
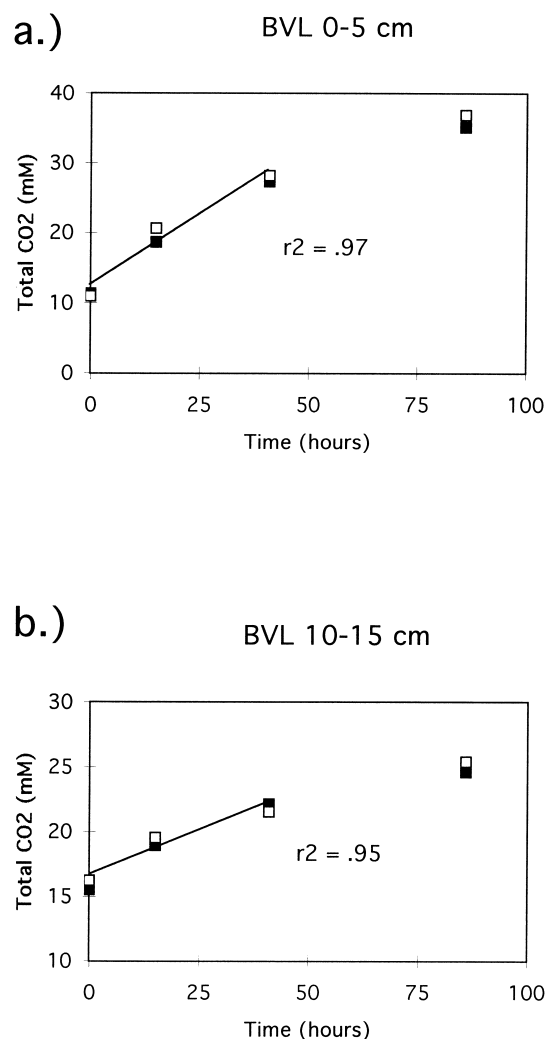
a.)

BVL 0-5 cm

b.)

BVL 10-15 cm

Figure 9. Examples of the accumulation of ΣCO_2 over time in sediment incubations carried out in July, 1998, at the BVL site inhabited by tall stands of *Spartina*. Symbols represent duplicate incubations. Regression coefficients are given for the first 48 hours of incubation (see results section for explanation)

tide (similar to our MM site), and no studies other than ours have incorporated rate measurements at an unvegetated creek bank environment adjacent to vegetated sites within the marsh. Based on previous studies, we hypothesized that the highest sulfate reduction rates (SRR) should occur in the MM. Conversely, we hypothesized that SRR should be lower and microbial FeRR higher at the BUC and BVL sites where a combination of factors (root activity, pore water flushing, bioturbation) lead to more oxidizing conditions. Though microbial respiration processes had not been studied in detail on the unvegetated creekbank of the marsh, we assumed that res-

Table 1. Partitioning of carbon oxidation pathways in sediments collected during July, 1998. Rates are integrated over the appropriate depth interval and expressed in units of mmol m^{-2} d^{-1}. Carbon oxidation and Fe reduction rates were measured in the same incubations by regression of concentration vs. time (see Figures 9 and 10). Sulfate reduction rates were measured using the radiotracer technique in parallel cores processed at the same time as for sediment incubations.

| | Sulfate reduction rate | | |
	BUC	BVL	MM
0–5 cm	136.2 (0.93*)	224.1 (1.06)	155.7 (1.02)
10–15 cm	9.9 (0.15)	8.5 (0.12)	0.0 (0.00)
	C oxidation rate		
0–5 cm	294.3	423.6	305.7
10–15 cm	131.4	145.4	45.4
	Fe(III) reduction rate		
0–5 cm	568.1	783.2	ND**
10–15 cm	ND	ND	ND

* Ratio determined as the integrated C equivalents oxidized via sulfate reduction divided by the integrated C oxidation rate. Integrated C equivalents oxidized via sulfate reduction was calculated using a 2:1 stoichiometry of C oxidized to sulfate reduced (Thamdrup and Canfield 1996; Kostka et al. 1999); ** ND = none detected.

piration and C oxidation rates would be low relative to vegetated marsh sediments due to the lack of belowground C input from *Spartina* roots. As has been shown for the majority of marine sediments, it was also hypothesized that most microbial activity occurred within the surface sediment layers (0–10 cm depth) of saltmarshes.

A comparison of our depth integrated sulfate reduction rates (SRR) to other studies which have measured SRR in saltmarshes of the U.S. inhabited by *Spartina alterniflora* is shown in Table 2. When rates (Figure 7) were integrated over the entire growth season, annual SRR rates were 64, 84, and 42 mol SO$_4$ $^{2-}$ m^{-2} yr^{-1}, for the BUC, BVL, and MM sites, respectively. At the BVL, in the presence of the tall form of *Spartina*, we observed the highest integrated annual rate yet reported for any natural ecosystem studied, about 10 times higher than the range reported by King (1988) for a South Carolina marsh, and slightly higher than that reported for a New England marsh (Howarth and Teal 1979).

Site characteristics exhibited at least as much effect on the range of SRR as did temperature or season (Figures 7 and 8). Rate measurements contrasted with the abovementioned hypotheses to show that both sulfate reduction and C oxidation rates were higher at the BVL as compared to the MM, while rates at the unvegetated creekbank were intermediate in comparison to those at the vegetated sites. One previous study observed higher SRR in a levee environment as compared to the mid-marsh in the Georgia saltmarsh (Skyring et al. 1979). However, this study was called into question due to methodological problems associated with quantification of sulfate reduction (Howarth and Giblin 1983). Another study measured
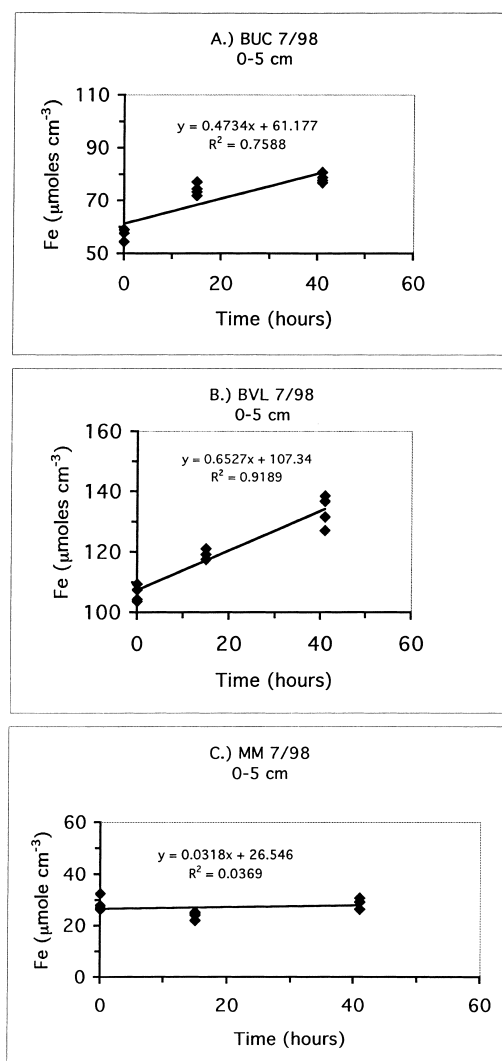
Figure 10. Iron(III) reduction rates measured as the accumulation of extractable Fe(II) in sediment incubations carried out in July, 1998 (same incubations as those represented in Table 1 and Figure 9)

SRR in stands of tall vs. short *Spartina alterniflora* and concluded, in contrast to the results of this study, that SRR were higher in short *Spartina* stands of a South Carolina marsh (King 1988) (Table 2). The discrepancy between our study and that of King (1988) may be due to incomplete sampling of the sediment column or to variability in sediment characteristics between marshes. Because the maximum in sulfate reduction activity is located closer to the sediment surface (top 10 cm depth) in the MM (Figure 7), and King (1988) only integrated over the surface 10 to 15 cm of sediment, much sulfate reduction activity, such as that observed in this study

Table 2. Sulfate reduction rates measured in saltmarsh sediments inhabited by saltmarsh cordgrass, *Spartina alterniflora*

	Study site	Integrated sulfate reduction rate mmol m^{-2} d^{-1}		
		BUC	BVL	MM
Howarth and Teal (1979)*	Cape Cod, MA	ND	ND	20–400
Howarth and Giblin (1983)*	Sapelo Isl., GA	ND	ND	80–120
Howes et al. (1984)**	Cape Cod, MA	ND	ND	69
King (1988)**	Georgetown, SC	ND	5–45	5–100
Hines et al. (1989)***	Great Bay, NH	ND	2–200	ND
This study****	Sapelo Isl., GA	106–238	148–312	56–200

ND = not determined; * integrated to between 30 and 40 cm sediment depth; ** integrated to 10 cm sediment depth; *** estimated from rates averaged over the 0 to 20 cm depth interval; **** integrated to 50 cm sediment depth.

in the BVL (Figure 7), may have been missed. The only other studies which incorporated SRR measurements deeper than 10–15 cm into saltmarsh sediment were those of Howarth and Teal (1979) and Hines et al. (1989) which incorporated measurements down to 30 or 40 cm depth in the sediment column (Table 2). As we would predict, the range of integrated SRR reported here overlaps with the range reported by Hines et al. or Howarth.

Vertical spatial gradients in sulfate reduction activity were observed to be large and reproducible between sites. At the two sites closer to the large tidal creek (within 20 m), this study showed SRR of 200 to 500 nmol cm^{-3} d^{-1} at greater than 40 cm depth in the sediment column (Figure 7). Farthest from the tidal creek (> 100 m) in the MM, SRR decreased to below 100 nmol cm^{-3} d^{-1} at less than 20 cm depth at all seasons (Figure 7). Subsurface rates measured near the tidal creek correspond to the high end of the range observed in the top 10 cm of shallow, subtidal marine sediments (Jørgensen 1977; Canfield et al. 1993a, 1993b; Thamdrup et al. 1994). While higher rates are to be expected in organic carbon-rich marsh sediments, our results indicate significant organic matter is being oxidized deeper down in the sediment column than was thought previously.

In parallel with the spatial gradients of SRR, pore water and solid phase geochemistry indicated enhanced sediment oxidation at sites located within a few meters of a large tidal creek (Figures 2, 3, 5 and 6). Results are supported by previous studies which observed a higher redox potential (E$_h$) in stands of tall *Spartina* (Mendelssohn et al. 1981; Howes et al. 1981, 1986). Several hypotheses for more oxidized sediment near tidal creeks have been proposed, including aeration due to drainage of interstitial water from creekbanks at low tide (Gardner 1980; King and Wiebe 1980; Nuttle and Hemond 1988), transport of O$_2$ into sediment by plant roots (Teal and Kanwisher 1961; Morris and Whiting 1985), an enhanced supply of Fe oxides which reacts with (and removes) dissolved sulfide via precipitation (King et al. 1982), and an increased abundance of bioturbating macrofauna (Montague 1982; Basan and Frey 1977; Sharma et al. 1987; Gardner 1980).

In this study, the porosity and density of the sediment did not change from the creek inland to the mid-marsh, and the permeability of the clay-rich Sapelo marsh sediment was previously shown to be low relative to other marsh sediments (Giblin and Howarth 1984), indicating that pore water advection through sandy sediments was probably not important. In contrast to a study carried out in a Delaware marsh (Kostka and Luther 1995), we observed that vegetated and unvegetated sediments near a large tidal creek (at BUC and BVL sites) displayed similar geochemistries, indicating that plant roots were not the primary factor affecting their redox state. Thus, it appears that bioturbation is overriding other factors in controlling sediment biogeochemistry at the Institute Marsh on Sapelo (see below discussion). Our interpretations are supported by ecological data which were collected from the same Sapelo marsh that was the subject of this study. As has been shown for other saltmarshes (Montague 1982; Bertness 1985), sites located close to a large tidal creek (BUC, BVL) were more heavily bioturbated as compared to those sites located in the midmarsh (MM). *Uca* was shown to be 2 to 3 times more abundant at the BUC or BVL sites (61 to 65 m^{-2}) as compared to the MM (27 m^{-2}; Teal (1962, 1958)). In addition, *Uca* burrows extended to greater depths at the BUC and BVL (Basan and Frey 1977). Thus, intense and deep macrofaunal activity at these sites would mix oxidants (O_2, FeIII, SO_4^{2-}) and reactive organic matter over appreciable depths. Further, in a nearby *Spartina* marsh in South Carolina, bioturbation by *Uca* was indeed shown to be more intense at creekbank sites (to 30 cm depth) as compared to mid-marsh sites (to 6 cm depth) through profiling of particle-reactive radionuclides (Sharma et al. 1987).

Microbial respiration pathways in the saltmarsh

To date, the partitioning of anaerobic respiration pathways coupled to C oxidation in saltmarsh sediments has been based solely on information from the mid-marsh or environments vegetated by short stands of *Spartina*. In the few studies which have been carried out, 50 to 70% of C oxidation was attributed to sulfate respiration and the remainder to aerobic respiration (Howes et al. 1984, 1985; Howarth 1993).

Considering the 3 different sites during the summer for which C oxidation rates were obtained in this study, we concur with previous studies that sulfate reduction is the most important anaerobic microbial respiration pathway in saltmarsh sediments overall. Using the average ratios of C equivalents oxidized (0–5 + 10–15 cm depth intervals; Table 1), sulfate reduction measured by the radiotracer technique comprised approximately 69 to 87% of total C oxidation and no difference in the ratio was observed between sites. Though SRR was also determined from the depletion of sulfate in sediment incubations (data not shown), we have used the radiotracer SRR to partition the carbon oxidation pathways since the accuracy of our sulfate concentration determinations was called into question.

At 0 to 5 cm depth, it is clear that sulfate reduction in the predominant respiration pathway, comprising close to 100% of carbon oxidation (Table 1). However at 10 to 15 cm depth, where less carbon oxidation occurs (13 to 31% of 0 to 5 cm

depth interval; see Table 1), the partitioning of respiration pathways is less clear. At this depth, oxygen and nitrate have been most likely used up by sediment microbes with Fe(III), sulfate, and bicarbonate remaining as potential oxidants. No Fe(III) reduction was detected in sediment incubations at 10 to 15 cm depth and no extractable solid Fe(III) was present (Figure 6, Table 1). Methanogenesis could play an important role for carbon oxidation at this sediment depth, especially in the mid-marsh where solid Fe(III) and sulfate concentrations were relatively low. Also, though parallel cores were sampled in July within a few meters distance for all of the measurements used to partition the carbon oxidation pathways, considerable spatial heterogeniety (> 20%) was observed in parallel cores (Figure 7). Therefore, we cannot rule out the importance of sulfate and Fe(III) reduction as carbon oxidation pathways deeper in the sediment column at this time.

In surface sediments (0 to 5 cm depth), extremely rapid FeRR (568 to 783 mmol m^{-2} d^{-1}) were observed at the more heavily bioturbated sites (BUC and BVL; Table 1), which were 5 to 10 times higher than measured SRR (Table 1). To our knowledge, only one other study in a marine environment observed such rapid Fe(III) turnover rates (300 to 600 mmol m^{-2} d^{-1}) in the Amazon delta, where sediments are exposed to extreme physical mixing by bottom currents and reactive Fe(III) concentrations are similarly high (Aller et al. 1996). In contrast, at the less bioturbated MM site of our study, where the Fe(III) inventory was 10 times lower (Figure 6), no detectable Fe(III) reduction was observed (Figure 10, Table 1). Using our measured FeRR (Figure 10, Table 1) and the inventory of reactive Fe(III) minerals (Figure 6) present in the sediment, we calculate a residence time of 2 to 3 days for reactive Fe(III) at the heavily bioturbated sites. These residence times are among the shortest reported in marine sediments (Aller et al. 1996; Canfield et al. 1993b; Hines et al. 1997) and indicate an extremely rapid turnover of reactive Fe in bioturbated saltmarsh sediments.

Our measured FeRR should incorporate both abiotic and biotic (microbial) reduction of Fe(III) minerals. Calculation of the carbon equivalents oxidized from the SRR data (radiotracer methods) indicate that microbial Fe(III) reduction is not substantially coupled to carbon oxidation in these surface sediments (Table 1). Thus, we conclude that most of this rapid Fe(III) reduction is catalyzed by abiotic, chemical reaction with dissolved sulfide or organic ligands. Though a few past studies have suggested that microbial Fe(III) reduction may be coupled to carbon oxidation in saltmarsh sediments (Luther et al. 1992; Kostka and Luther 1995), most Fe(III) reduction was believed to be catalyzed abiotically though reaction of Fe(III) oxyhydroxides with dissolved sulfides produced by sulfate reduction (Pyzik and Sommer 1981; Giblin and Howarth 1984; Jacobson 1994). In addition, Luther et al. (1992) suggested that Fe(III) minerals may be solubilized and reduced by organic ligands (i.e. catecholates, humic acids) containing oxygen as the ligating atom. The potential role of organic ligands in Fe(III) reduction was further supported by the detection of Fe(III) organic complexes in saltmarsh pore waters using spectroscopic and microelectrode methods (Luther et al. 1996). We propose that the high Fe reduction rates we observe in the Sapelo marsh are supported by a combination of these abiotic mechanisms.

Hines and co-workers have observed that *Spartina* species enhance sulfate reduction activity by transporting primarily dissolved oxidants and organic matter into saltmarsh sediments (Hines et al. 1989; Hines 1991). Hines (1991) also observed that though the mechanisms may differ, both macrofauna and macrophyte plant activities result in the stimulation of subsurface Fe and S cycling, decreased dissolved sulfide and increased dissolved iron concentrations. Our results corroborate this previous work and further demonstrate the stimulation of the Fe cycle by providing direct measurements of solid Fe turnover. We conclude that the rapid Fe cycling we have observed in bioturbated sediments is stimulating higher rates of anaerobic respiration, mainly sulfate reduction, by decreasing sulfide concentrations through reoxidation and thereby increasing sulfate levels.

Alternatively, based on the high Fe(III) reduction rates we have measured, one could conclude that microbial Fe(III) reduction is driving a substantial portion of carbon oxidation in the Sapelo marsh. However, we believe that SRR determined via radiotracer methods is the most robust measurement of microbial activity, and therefore we have attributed this rapid Fe reduction to abiotic mechanisms. The discrepancies observed in the partitioning of anaerobic respiration pathways at 10 to 15 cm depth (Tables 1 and 2; above discussion) suggest that more data is needed to completely and accurately partition the microbial respiration pathways coupled to C oxidation.

Aerobic respiration may be operative at depth in the presence of macrofaunal burrows and *Spartina* roots. The latter may inject O_2 into subsurface sediment via evapotranspiration (Dacey and Howes 1984; Morris and Whiting 1985) or passive diffusion (Teal and Kanwisher 1961). Since our incubations were carried out anoxically, we may have underestimated the importance of aerobic respiration. However, King (1988) showed that oxygen was not present below the first 2 to 4 mm in sediments from a nearby South Carolina marsh during the summer, and a similar O_2 distribution was observed in Sapelo marsh sediments (W.J. Cai, unpublished data). Further, assuming that aerobic respiration is half the rate of oxygen uptake, and using the entire range of O_2 consumption rates measured in saltmarsh sediments (Howarth 1993), we obtain a maximum contribution of 26% of C oxidation, which is in the range of our estimates of C oxidation by respiration pathways other than sulfate respiration measured using the radiotracer technique (13 to 31%).

Controls of microbial respiration in saltmarsh sediment

In this study, gradients in sediment geochemistry between sites closely followed with those of microbial activity. During the summer sampling period when extensive sediment incubations were carried out, all rate measurements indicate that microbial activity was highest at the BVL, intermediate at the BUC, and lowest at the MM (Figures 7, 8, 9 and 10, Tables 1 and 2). Therefore, anaerobic microbial respiration, mainly sulfate reduction, appears to be stimulated in more heavily bioturbated saltmarsh sediments. The influence of bioturbation is specifically indicated by the following observations at more heavily bioturbated sites in the saltmarsh: higher solid phase reactive Fe concentrations, more oxidized Fe(III), more rapid

turnover rates of Fe(III), a lack of sulfate depletion, and less accumulation of solid phase sulfides (AVS + CRS) (Figures 2, 3, 5, 6 and 10). Microbial respiration processes have been shown to be limited by reoxidation reactions which replenish electron acceptors of respiration, and these reoxidation reactions are driven by physical and biological mixing (bioturbation) (Jørgensen 1977, 1978; Canfield et al. 1993a, 1993b; Thamdrup and Canfield 1996; Kostka et al. 1999). Thus, the most important factors which we hypothesize are limiting microbial respiration in Georgia saltmarsh sediments include: tidal flushing, bioturbation by *Uca*, and processes mediated by the roots of *Spartina*. Since sediment geochemistry was similar at both heavily bioturbated sites, only 1 of which was vegetated by macrophytes, we suggest that bioturbation by *Uca* is the most important factor controlling anaerobic microbial respiration at the sites we studied.

Through irrigation of burrows, radial diffusion, and reworking of surface sediments, macrofauna like *Uca* increase the intrusion of oxidants into sediments, producing 3 dimensional redox gradients which enhance the recycling of redox sensitive elements like Fe and S (Aller 1980; Hines and Jones 1985; Hines et al. 1997). In our study, rapid Fe(III) turnover appeared to be supported by intense bioturbation near tidal creeks. Rapid reoxidation of anaerobic respiration products (FeII, sulfide) would maintain the increased supply of oxidants (FeIII, sulfate) needed to support high Fe(III) and sulfate reduction rates. Further, sulfate reduction is actually more thermodynamically favorable when dissolved sulfide concentrations are kept low from reoxidation (Howarth and Giblin 1983). We concur with previous studies (King et al. 1982) that the abundance of Fe oxide limits anaerobic respiration pathways in saltmarsh sediments. However, we further suggest that it is not the external input of Fe oxide that controls Fe oxide abundance, but rather an enhanced turnover of sedimentary Fe supported by a greater rate and depth of bioturbation at the creekbank sites where *Uca* burrows are more abundant.

In the less bioturbated MM, sulfate limitation was evidenced as dissolved sulfate was depleted throughout a majority of the season (Figures 2 and 3) (Roychoudhury 1999)). Sulfate limitation may be exacerbated by oxygen depletion which forces the plant roots into anaerobic respiration making belowground plant production less efficient and thereby reducing organic matter turnover, including the supply of labile carbon substrates for respiration (Mendelssohn et al. 1981). The higher accumulation of dissolved sulfide we observed in the MM at Sapelo (Figures 2 and 3) has also been shown to inhibit root respiration completely leading to reduced growth and carbon turnover (Koch et al. 1990).

All measured rates of microbial activity were intermediate at the BUC site, though no roots were present to inject C into the sediment. The intermediate rates observed at BUC can be explained by the input of labile C from benthic microalgae which is mixed down into the sediment by *Uca*. Diatom mats were observed to cover the surface of the creekbank during much of the year in the Sapelo marsh, and benthic microalgal production has been shown to be equivalent to 43% of *Spartina* production in a nearby South Carolina marsh (Pinckney and Zingmark 1993).

Carbon substrates for anaerobic respiration

Acetate is an important electron donor for sulfate-reducing bacteria (SRB) (Widdel and Bak 1992) and the use of molecular probes has shown that acetate-utilizing SRB dominate over other SRB groups in saltmarsh sediments (Rooney-Varga et al. 1998; Hines et al. 1999; King et al. 2000). In this study, acetate concentrations in vegetated sediments were positively correlated to the SRR measured in the same sediment, with higher concentrations observed closer to the sediment surface at the MM and a deeper subsurface maximum observed at the BVL (Figure 4). Though only 2 sampling periods were available, we did observe lower acetate concentrations in the fall when root activity should be less relative to the summer (Figure 4).

Previous work observed that acetate oxidation rates were small in comparison to sulfate reduction rates in marsh sediment, and it was therefore concluded that sulfate-reducing bacteria were utilizing C substrates other than acetate (Hines et al. 1994). To determine if other C substrates were available for sulfate reduction, we chose a versatile HPLC method which detects organic acids in the C_1 to C_5 size range. Though present at much lower concentrations, we have identified another potential C source, malonate, available to bacteria in the Georgia marsh (Figure 4). To our knowledge, this compound has not been detected in marine sediments previously, although it was detected in association with plant roots in agricultural soils (Szmigielska et al. 1997). Further, malonate was shown to be produced from the oxidation of malate, an important constituent of root exudates, coupled to the reduction of Fe or Mn oxides (Jauregui and Reisenauer 1982). Malate has been measured in Louisiana marsh sediments vegetated by *Spartina* (Mendelssohn et al. 1981). We suggest that the accumulation of malonate results from rapid chemical or biological Fe reduction coupled to the oxidation of malate released from roots.

Hines et al. (1994) carried out an extensive study of the effects of coring and root disturbance on the measurement of acetate concentrations in saltmarsh sediment pore waters. Substantial artifacts were observed during coring and pore water removal in rooted sediments, and the effect was largest during the summer growing season because the acetate was thought to come from inside living roots. Through a comparison of destructive and nondestructive pore water sampling methods similar to the Hines et al. study, we observed no such artifacts during the November sampling period at MM. Such artifacts cannot be ruled out for our vegetated sites and further study is needed to determine whether acetate is released during coring/centrifugation when sampling in the summer growing season. However, we conclude that the organic acid concentrations we reported are not dominated by coring artifacts for the following reasons. The BUC site contained no living roots, intermediate SRR, and yet the acetate concentrations were still high (> 100 μM). We also observed high acetate (ave = 80 μM) and malonate (ave. = 20 μM) concentrations, equimolar in concentration to surface sediment pore waters, in duplicate seawater samples from small tidal creeks (where coring artifacts are not possible) within the MM site at slack tide. These observations were made in November when roots are thought to be less active.

72

Conclusions

Our study provides new insight into the spatial and temporal variability of anaerobic respiration rates, and we show that rapid Fe cycling, stimulated by higher organisms, enhances sulfate respiration activity in saltmarsh sediments. Solid phase and pore water geochemistry indicated enhanced sediment oxidation at more heavily bioturbated sites (BUC and BVL) relative to less bioturbated (MM). Iron(III) reduction rates were directly determined in saltmarsh sediments for the first time and this reduction was determined to be primarily driven by abiotic mechanisms. Solid phase reactive Fe and Fe(III) concentrations were higher and the turnover of Fe(III) was extremely rapid at the more heavily bioturbated BUC and BVL sites. An unexpected result was the fact that SRR varied nearly as much between sites as it did with temperature or season. Integrated sulfate reduction rates were higher throughout the growth season and by up to a factor of 3 at the BVL site inhabited by tall *Spartina* as compared to the MM site vegetated by short *Spartina*. Carbon oxidation rates paralleled those of sulfate reduction and Fe(III) reduction to show that organic matter remineralization follows a similar spatial variability. High sulfate reduction rates persisted deeper into the sediment column at BUC and BVL sites than in any other marine sediment studied to date. High SRR deep in the sediment column at the BUC site cannot be explained by the release of dissolved organic carbon from roots but must be due to downward mixing of organic matter by bioturbation. Acetate was the most abundant fermentation product observed in marsh porewaters but another organic acid, malonate, was detected at significant concentrations. Finally, results from sediment geochemistry and microbial rate measurements are combined to indicate that bioturbation is probably more important than roots in driving chemical reoxidation/ recycling which limits microbial respiration in Georgia saltmarsh sediments.

References

Aller R.C. 1980. Diagenetic processes near the sediment-water interface of Long Island Sound, II. Fe and Mn. In: Saltzman B. (ed.), Estuarine Physics and Chemistry Studies in Long Island Sound. Academic,, pp. 351–415.

Aller R.C., Blair N.E., Xia Q. and Rude P.D. 1996. Remineralization rates, recycling, and storage of carbon in Amazon shelf sediments. Cont. Shelf Res. 16: 753–786.

Alongi D.M. 1998. Coastal Ecosystem Processes. CRC Press, NY.

Basan P.B. and Frey R.W. 1977. Actual paleontology and neoichnology of salt marshes near Sapelo Island, Georgia. In: Crimes T.P. and Harper J.C. (eds), Trace Fossils 2. Steel House Press, London, pp. 41–70.

Bertness M.D. 1985. Fiddler crab regulation of Spartina alterniflora production on a New England salt-marsh. Ecology 66: 1042–1055.

Canfield D.E. 1988. Sulfate reduction and the diagenesis of iron in anoxic marine sediments. PhD Dissertation, Yale University, USA.

Canfield D.E. 1989. Reactive iron in marine sediments. Geochim. Cosmochim. Acta 53: 619–632.

Canfield D.E., Jorgensen B.B. and other 1993a. Pathways of organic carbon oxidation in three coastal sediments. Mar. Geol. 113: 27–40.

Canfield D.E., Thamdrup B. and Hansen J.W. 1993b. The anaerobic degradation of organic matter in Danish coastal sediments. Geochim. Cosmochim. Acta 57: 3867–3883.

Cline J.D. 1969. Spectrophotometric determination of hydrogen sulfide in natural waters. Limnol. Oceanogr. 14: 454–458.

Dacey J.W.H. and Howes B.L. 1984. Water uptake by roots controls watertable movement and sediment oxidation in a short Spartina marsh. Science 224: 487–489.

Dame R.F. and Kenny P.D. 1986. Variability of Spartina alterniflora primary production in the euhaline North Inlet estuary. Mar. Ecol. Prog. Ser. 32: 71–80.

Fossing H. and Jørgensen B.B. 1989. Measurement of bacterial sulfate reduction in sediments: evaluation of a single-step chromium reduction methods. Biogeochemistry 8: 223–245.

Fossing H. 1995. ^{35}S-Radiolabeling to probe biogeochemical cycling of sulfur. In: Vairavamurthy M.A. and Schoonen M.A.A. (eds), ACS Symposium Series. American Chemical Society, Washington, DC, pp. 348–364.

Gallagher J.L. and Plumley F. 1979. Underground biomass profiles and productivity in Atlantic coastal marshes. J. Bot. 66: 156–161.

Gallagher J.L., Reimold R.J., Linthurst R.A. and Pfeiffer W.J. 1980. Aerial production, mortality, and mineral accumulation-export dynamics in Spartina alterniflora and Juncus roemerianus plant stands in a Georgia salt marsh. Ecology 61: 303–312.

Gardner L.R. 1973. The effect of hydrologic factors on the pore water chemistry of intertidal marsh sediments. Southeast Geol. 15: 17–28.

Gardner L.R. 1980. Simulation of diagenesis of carbon, sulfur, and dissolved oxygen in saltmarsh sediments. Ecological Monographs 60: 91–111.

Giblin A.E. and Howarth R.W. 1984. Porewater evidence for a dynamic sedimentary iron cycle in salt marshes. Limnol. Oceanogr. 29: 47–63.

Hall P.O.J. and Aller R.C. 1992. Rapid, small-volume, flow injection analysis for CO_2 and NH_4^+ in marine and freshwaters. Limnol. Oceanogr. 37: 113–119.

Hines M.E. 1991. The role of certain infauna and vascular plants in the mediation of redox reactions in marine sediments. In: Berthelin J. (ed.), Diversity of Environmental Biogeochemistry. Elsevier,, pp. 275–286.

Hines M.E. and Jones G.E. 1985. Microbial biogeochemistry in the sediments of Great Bay, New Hampshire. Est. Coast. Shelf Sci. 20: 729–742.

Hines M.E., Knollmeyer S.L. and Tugel J.B. 1989. Sulfate reduction and other sedimentary biogeochemistry in a northern New England salt marsh. Limnol. Oceanogr. 34: 578–590.

Hines M.E., Banta G.T., Giblin A.E., Hobbie J.E. and Tugel J.T. 1994. Acetate concentrations and oxidation in salt marsh sediments. Limnol. Oceanogr. 39: 140–148.

Hines M.E., Faganeli J. and Planinc R. 1997. Sedimentary anaerobic microbial biogeochemistry in the Gulf of Trieste, northern Adriatic Sea: influences of bottom water oxygen depletion. Biogeochemistry 39: 65–86.

Hines M.E., Evans R.S., Sharak-Genthner B.R., Willis S.G., Friedman S., Rooney-Varga J.N. et al. 1999. Molecular phylogenetic and biogeochemical studies of sulfate-reducing bacteria in the rhizosphere of Spartina alterniflora. Appl. Environ. Microbiol. 65: 2209–2216.

Howarth R.W. 1993. Microbial processes in salt-marsh sediments. In: Ford T.E. (ed.), Aquatic Microbiology: An Ecological Approach. Blackwell Scientific Publications, Cambridge, MA.

Howarth R.W. and Hobbie J.E. 1982. The regulation of decomposition and heterotrophic microbial activity in salt marsh soils: a review. In: Kennedy V.S. (ed.), Estuarine Comparisons. Academic Press, NY.

Howarth R.W. and Giblin A. 1983. Sulfate reduction in the salt marshes at Sapelo Island, Georgia. Limnol. Oceanogr. 28: 70–82.

Howarth R.W. and Teal J.M. 1979. Sulfate reduction in a New England salt marsh. Limnol. Oceanogr. 24: 999–1013.

Howes B.L. and Teal J.M. 1994. Oxygen loss from Spartina alterniflora and its relationship to salt marsh oxygen balance. Oecologia 97: 431–438.

Howes B.L., Howarth R.W., Valiela I. and Teal J.M. 1981. Oxidation-reduction potentials in a salt marsh: spatial patterns and interactions with primary production. Limnol. Oceanogr. 26: 350–360.

Howes B.L., Dacey J.W.H. and King G.M. 1984. Carbon flow through oxygen and sulfate reduction pathways in salt marsh sediments. Limnol. Oceanogr. 29: 1037–1051.

Howes B.L., Dacey J.W.H. and Teal J.M. 1985. Annual carbon mineralization and belowground production of Spartina alterniflora in a New England salt marsh. Ecology 66: 595–605.

Howes B.L., Dacey J.W.H. and Goehringer D.D. 1986. Factors controlling the growth form of Spartina alterniflora: feedbacks between above-ground production, sediment oxidation, nitrogen and salinity. J. Ecol. 74: 881–898.

Jacobson M.E. 1994. Chemical and biological mobilization of Fe(III) in marsh sediments. Biogeochemistry 25: 41–60.

Jahnke R.A. and Craven D.B. 1995. Quantifying the role of heterotrophic bacteria in the carbon cycle: a need for respiration rate measurements. Limnol. Oceanogr. 40: 436–441.

Jauregui M.A. and Reisenauer H.M. 1982. Dissolution of oxides of manganese and iron by root exudate components. Soil Sci. Soc. Am. J. 46: 314–317.

Jørgensen B.B. 1977. The sulfur cycle of a coastal marine sediment (Limfjorden, Denmark). Limnol. Oceanogr. 5: 814–832.

Jørgensen B.B. 1978. A comparison of methods for the quantification of bacterial sulfate reduction in coastal marine sediments. 1. Measurement with radiotracer techniques. Geomicrobiol. J. 1: 11–28.

King G.M. 1988. Patterns of sulfate reduction and the sulfur cycle in a South Carolina salt marsh. Limnol. Oceanogr. 33: 376–390.

King G.M. and Wiebe W.J. 1980. Regulation of sulfate concentrations and methanogenesis in salt marsh soils. Est. Coastal Mar. Sci. 10: 215–223.

King G.M. and Garey M.A. 1999. Ferric iron reduction by bacteria associated with the roots of freshwater and marine macrophytes. Appl. Environ. Microbiol. 65: 4393–4398.

King G.M., Klug M.J., Wiegert R.G. and Chalmers A.G. 1982. Relation of soil water movement and sulfide concentration to Spartina alterniflora production. Science 218: 61–63.

King J.K., Kostka J.E., Frischer M.E. and Saunders F.M. 2000. Sulfate-reducing bacteria methylate mercury at variable rates in pure culture and in marine sediments. Appl. Environ. Microbiol. 66: 2430–2437.

Koch M.S., Mendelssohn I.A. and McKee K.L. 1990. Mechanism for the hydrogen sulfide-induced growth limitation in wetland macrophytes. Limnol. Oceanogr. 35: 399–408.

Kostka J.E. 1993. Biogeochemical cycling of Fe in anoxic environments: the importance of Fe speciation and bacterial Fe reduction. PhD Dissertation, University of Delaware, USA.

Kostka J.E. and Luther G.W. 1994. Partitioning and speciation of solid phase iron in saltmarsh sediments. Geochimica et Cosmochimica Acta 58: 1701–1710.

Kostka J.E. and Luther G.W. 1995. Seasonal cycling of Fe in saltmarsh sediments. Biogeochemistry 29: 159–181.

Kostka J.E., Thamdrup B., Glud R.N. and Canfield D.E. 1999. Rates and pathways of carbon oxidation in permanently cold Arctic sediments. Marine Ecol. Prog. Ser. 180: 7–21.

Lowe K., DiChristina T., Roychoudhury A. and Van Cappellen P. 2000. Microbiological and geochemical characterization of microbial Fe(III) reduction in salt marsh sediments. J. Geomicrobiol. 17: 163–176.

Lustwerk R.L. and Burdige D.J. 1995. Elimination of dissolved sulfide interference in the flow injection determination of ΣCO_2 by addition of molybdate. Limnol. Oceanogr. 40: 1011–1012.

Luther G.W., Kostka J.E., Church T.M., Sulzberger B. and Stumm W. 1992. Seasonal iron cycling in the salt-marsh sedimentary environment: the importance of ligand complexes with Fe(II) and Fe(III) in the dissolution of Fe(III) minerals and pyrite, respectively. Marine Chemistry 40: 81–103.

Luther G.W., Shellenbarger P.A. and Brendel P.J. 1996. Dissolved organic Fe(III) and Fe(II) complexes in salt marsh porewaters. Geochimica et Cosmochimica Acta 60: 951–960.

Mendelssohn I.A., McKee K.L. and Patrick W.H. 1981. Oxygen deficiency in Spartina alterniflora roots: metabolic adaptation to anoxia. Science 214: 439–441.

Montague C.L. 1982. The influence of fiddler crab burrows and burrowing on metabolic processes in saltmarsh sediments. In: Kennedy V.S. (ed.), Estuarine Comparisons. Academic Press, NY, pp. 283–301.

Morris J.T. and Whiting G.J. 1985. Gas advection in sediments of a South Carolina salt marsh. Mar. Ecol. Prog. Ser. 27: 187–194.

Nuttle W.K. and Hemond H.F. 1988. Salt marsh hydrology: implications for biogeochemical fluxes to the atmosphere and estuaries. Global Biogeochemical Cycles 2: 91–114.

Pinckney J. and Zingmark R.G. 1993. Biomass and production of benthic microalgal communities in estuarine habitats. Estuaries 16: 887–897.

Pomeroy L.R. and Wiegert R.W. 1981. Ecology of a salt marsh. Springer.

Pyzik A.J. and Sommer S.E. 1981. Sedimentary iron monosulfides: kinetics and mechanism of formation. Geochim. Cosmochim. Acta 45: 687–698.

Rooney-Varga J.N., Sharak-Genthner B.R., Devereux R., Willis S.G., Friedman S.D. and Hines M.E. 1998. Phylogenetic and physiological diversity of sulphate-reducing bacteria isolated from a salt marsh sediment. System. Appl. Microbiol. 21: 557–568.

Roychoudhury A. 1999. Biogeochemical dynamics in aquatic sediments: novel laboratory and field-based approaches. PhD Dissertation, Georgia Institute of Technology, Atlanta, USA.

Sharma P., Gardner L.R., Moore W.S. and Bollinger M.S. 1987. Sedimentation and bioturbation in a salt marsh as revealed by 210Pb, 137Cs, and 7Be studies. Limnol. Oceanogr. 32: 313–326.

Schubauer J.P. and Hopkinson C.S. 1984. Above- and belowground emergent macrophyte production and turnover in a coastal marsh ecosystem, Georgia. Limnol. Oceanogr. : 1052–1065.

Skyring G.W., Oshrain R.L. and Wiebe W.J. 1979. Assessment of sulfate reduction rates in Georgia marshland soils. Geomicrobiol. J. 1: 389–400.

Szmigielska A.M., Van Rees K.C.J., Cieslinski G. and Huang P.M. 1997. Comparison of liquid and gas chromatography for analysis of low molecular weight organic acids in rhizosphere soil. Commun. Soil Sci. Plant Anal. 28: 99–111.

Stookey L.L. 1970. Ferrozine – a new spectrophotometric reagent for iron. Analytical Chemistry 43: 779–781.

Tabatabi M.A. 1974. A rapid method for determination of sulfate in water samples. Environmental Letters 7: 237–243.

Teal J.M. 1962. Energy flow in the salt marsh ecosystem of Georgia. Ecology 43: 614–624.

Teal J.M. 1958. Distribution of fiddler crabs in Georgia salt marshes. Ecology 39: 185–193.

Teal J.M. and Kanwisher J. 1961. Gas exchange in a Georgia salt marsh. Limnol. Oceanogr. 6: 388–399.

Thamdrup B., Fossing H. and Jorgensen B.B. 1994. Manganese, iron, and sulfur cycling in a coastal marine sediment, Aarhus Bay, Denmark. Geochim. Cosmochim. Acta 58: 5115–5129.

Thamdrup B. and Canfield D.E. 1996. Pathways of carbon oxidation in continental margin sediments off central Chile. Limnol. Oceanogr. 41: 1629–1650.

Viollier E., Inglett P., Hunter K., Roychoudhury A. and Van Cappellen P. 2000. The ferrozine method revisited: Fe(II)/Fe(III) determination in natural waters. Appl. Geochem. 15: 121–126.

Widdel F. and Bak F. 1992. Gram negative mesophilic sulfate reducing bacteria. In: Balows A., Truper H.G., Dworkin M., Harder W. and Schleifer K.W. (eds), The Prokaryotes 2nd Edition. A Handbook on the biology of Bacteria: Ecophysiology, Isolation, Identification, and Applications. Vol. 2. Springer-Verlag, New York.