Impact of fiddler crabs and plant roots on sediment biogeochemistry in a Georgia saltmarsh

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ABSTRACT: The influence of macrofauna and macrophytes on sediment biogeochemistry was quantified in a *Spartina alterniflora* (Loisel) saltmarsh, with emphasis on sulfur and iron cycling. Vertical profiles of sediment geochemistry and rates of microbial metabolism at 3 sites with different abundances of fiddler crab *Uca pugnax* burrows, vegetation coverage and hydrology were supplemented with high-resolution radial profiles around burrow walls and *S. alterniflora* roots. Carbon oxidation was measured as sulfate reduction using the ^{35}S technique, as total anaerobic CO_2 production, and as Fe(III) reduction by monitoring Fe(II) evolution. Depth-integrated (0 to 10 cm) sulfate reduction was 25% lower, while total Fe and Fe(III) concentrations were 1.5 and 6 times higher, respectively, in bioturbated than in nonbioturbated sediment. Low sulfate-reduction rates adjacent to burrow walls (3% of those in bulk sediment) were counteracted by very high Fe(III) reduction rates. Thus, Fe(III) reduction accounted for 54 to 86% of the total carbon oxidation within 4 cm distance of burrows, decreasing in importance with distance from the burrow wall. Overall, *S. alterniflora* roots showed a greater impact on sediment biogeochemistry than crab burrows. Sulfate reduction was almost absent in the rhizosphere, whereas Fe(III) reduction rates (6.2 µmol Fe cm^{-3} d^{-1}) were among the highest reported for marine sediments, accounting for >99% of carbon oxidation. Our results confirm the universal relationship between the contribution of Fe(III) respiration to total carbon oxidation and solid Fe(III) concentrations that has been suggested based on studies of subtidal marine sediments. The importance of Fe(III) respiration was strongly dependent on Fe(III) concentrations below levels of 30 µmol cm^{-3}, whereas above this level almost all anaerobic respiration was mediated by Fe(III) reduction in saltmarsh sediments.

KEY WORDS: Carbon oxidation · Bioturbation · Fe(III) reduction · Root oxidation · *Spartina alterniflora* · Sulfate reduction · *Uca pugnax*

INTRODUCTION

Salt marshes are areas of intense biogeochemical cycling driven by high rates of primary production (Mitsch & Gosselink 1993). The interactions between marsh plants and sediment biogeochemistry are complex, with several interrelated mechanisms and processes (Giblin & Howarth 1984, Hines et al. 1989). The majority of the production by the halophyte *Spartina alterniflora* in saltmarshes along the east coast of North America occurs below ground, and dead roots and

rhizomes are major sources of organic carbon for microbial metabolism (Howarth 1993). A large part of this organic carbon pool is relatively refractory, and thus inaccessible to many anaerobic bacteria. Living roots and rhizomes, however, also supply organic matter to the sediment through root excretion of dissolved organic carbon and fermentation products from anaerobic root metabolism (Hines et al. 1989). This labile pool can readily be utilized by anaerobic bacteria, such as sulfate reducers (Hines et al. 1999, Gribsholt & Kristensen 2002b). Sulfate reduction, which is considered

to be the dominant microbial respiration process in marshes (Hines et al. 1989, Alongi 1998), responds quickly to changes in root excretion of dissolved organic carbon (Hines et al.1999). Enhanced rates of sulfate reduction have been observed in the rhizosphere of various marine macrophytes (Isaksen & Finster 1996, Hansen et al. 2000, Nielsen et al. 2001, Gribsholt & Kristensen 2003).

In addition to acting as a source of organic matter to the sediment, *Spartina alterniflora* creates a mosaic of oxic and oxidized microniches rich in Fe(III) around roots via oxygen translocation across the root surface into the surrounding sediment (Sundby et al. 1998, Holmer et al. 2002). Microbial reduction of Fe(III) formed around roots may therefore contribute to the carbon cycling in saltmarsh sediments (Jacobson 1994, Kostka & Luther 1995, Kostka et al. 2002a). This has been confirmed by the presence of active iron-reducing bacteria associated with aquatic macrophytes, including *S. alterniflora* (King & Garey 1999, Lowe et al. 2000, Kostka et al. 2002a). Differentiated and enhanced benthic mineralization due to more oxidized redox conditions and increased substrate availability has been found recently in marsh sediments vegetated by *Spartina anglica* (Gribsholt & Kristensen 2002a, 2003) as well as in mangrove and seagrass areas (Holmer et al. 1999).

Sediment-dwelling infauna are a ubiquitous component of saltmarshes in North America, with fiddler crabs (*Uca* spp.) being the most abundant and conspicuous group in *Spartina alterniflora* marshes (Bertness 1985). The distribution of fiddler crabs within saltmarshes varies considerably, and they occur most frequently on creek banks and in 'tall' and 'medium' stands of *S. alterniflora.* Fiddler crabs excavate and maintain semi-permanent burrows in the marsh, which can potentially enhance sediment drainage and oxidation level (Howes et al. 1981, Montague 1982, Bertness 1985). The burrows generally extend from 3 to 25 cm into the sediment and may exceed abundances of 500 ind. m^{-2} (Taylor & Allanson 1993). The continuously changing spatial heterogeneity and physical conditions created by burrowing activities of fiddler crabs may affect the dynamics of organic matter decomposition in marshes. Sediment from oxic surface layers is buried into anoxic zones and vice versa during burrow excavation, transferring labile substrates to starved anaerobic bacteria and refractory substrates to efficient aerobic bacteria (Montague 1982, Kranzberg 1985, Kristensen & Holmer 2001).

Burrow structures enlarge the area of oxic interfaces of saltmarsh sediments by 20 to 60% or more (Montague 1982). The intrusion of oxygen enhances aerobic decomposition (Katz 1980), increases the volume of oxidized Fe(III)-containing sediment, and neutralizes toxic metabolites from anaerobic processes (e.g. sulfide). Fiddler crabs not only stimulate microbial activity and metabolism in the sediment (Taylor & Allanson 1993), they may also affect the partitioning between electron acceptors (e.g. sulfate vs Fe[III]) used by anaerobic bacteria in the terminal oxidation of organic carbon (Kostka et al. 2002a). Despite their high abundance in saltmarshes, little attention has been directed towards an understanding of the ecological role of fiddler crabs, including their effects on carbon oxidation within the sediments.

Here we further elucidate the impacts of fiddler crab burrows and plant roots on sediment biogeochemistry through radial profiling of the burrow wall and rhizosphere. The emphasis of our studies was on sulfate reduction and Fe(III) reduction since these 2 processes are considered most important for terminal carbon oxidation in saltmarsh sediments (Lowe et al. 2000, Kostka et al. 2002b). Sediment geochemistry as well as microbial rate measurements associated with macrobenthic structures were conducted in vertical and radial profiles at sites with variable abundances of macrobenthic organisms. Our high-resolution results document the dramatic effects burrows and roots have on saltmarsh sediment geochemistry. The Fe cycle is stimulated to such an extent that microbial Fe(III) reduction almost completely outcompetes sulfate reduction around crab burrows and in rhizospheres.

MATERIALS AND METHODS

Study area. The study was conducted at the Saltmarsh Ecosystem Research Facility (SERF) of the Skidaway Institute of Oceanography on Skidaway Island, Georgia (Fig. 1). The SERF marsh is dominated by monospecific stands of the halophyte *Spartina alterniflora* (Loisel). Short forms dominate the interior platform of the marsh, while the levees adjacent to creeks are vegetated by tall forms of *S. alterniflora.* The fiddler crab *Uca pugnax* is abundant throughout the marsh. The marsh is influenced by semidiurnal tides, with a maximum range of about 2 m.

Sediment samples were collected from 3 sites differing in abundance of macroorganisms: (1) an unvegetated creekbank without fiddler crabs (non-bioturbated unvegetated creek bank, NUC), (2) an unvegetated creekbank with fiddler crabs (bioturbated unvegetated creek bank, BUC) and (3) a vegetated levee with tall stands of *Spartina alterniflora* and fiddler crabs (bioturbated vegetated levee, BVL) (Fig. 1). NUC and BUC were selected at the same elevation, while BVL was located at about 0.5 m higher elevation, and consequently was air-exposed for longer periods of time. Since the crab burrows at BUC generally were

variable in size, shape and depth, care was taken to select burrows of approximately similar diameter. Only isolated burrows some distance from roots were sampled on the levee. Samples were collected during low tide on 2 sampling occasions, October 26 to 28, 1999 and August 1 to 5, 2000. Sediment temperature was ~20 and 30°C and the salinity of tidal creek water was 20 and 33 in October and August, respectively.

Flora and fauna. All fiddler crab burrows at the bio-turbated creek bank (BUC) and at the levee (BVL) were counted within 10 randomly chosen quadrats (25 × 25 cm) in August, and the burrow diameter at the sediment surface was measured. The maximum height of all plant shoots within 10 quadrats (25 × 25 cm) was measured in August. The below-ground plant biomass in the top 10 cm sediment was determined in October by washing 1 cm sediment sections over a 1 mm mesh. Root and rhizome dry weight (DW) was obtained after drying at 65°C for 24 h.

Sediment sampling. Triplicate sediment cores for determination of vertical profiles of solid-phase and porewater constituents were collected at each site by gently pushing Plexiglas tubes (i.d. = 4.8 cm) into the sediment. Simultaneously, 3 cores for determining sulfate reduction rates (SRR) were sampled by inserting smaller tubes (i.d. = 2.2 cm). All tubes were sealed with butyl rubber stoppers and dug out of the sediment. Care was taken to avoid coring too close to burrows or large roots. All sediment cores were kept cool (4°C) until processing (within 5 h).

Sediment for high-resolution radial profiles of solid-phase and porewater constituents, sulfate reduction and anaerobic CO_2 production (jars) near burrows were collected according to the technique of Hansen et al. (1996). After exposing a burrow wall, radial mini-cores (1.2 cm in diameter) were obtained 5 cm below the sediment surface by gently inserting a 10 cm^3 'cutoff' syringe 5 to 6 cm horizontally into the sediment. Cores for radial burrow sampling were obtained at the creek bank (BUC burrows) as well as on the levee (BVL burrows). Radial mini-cores of sediment in the root zone of tall *Spartina alterniflora* plants were collected in a similar manner to radial burrow samples after exposing a vertical section of the rhizosphere directly below a large plant.

Solid-phase iron and sediment characteristics. Vertical profiles of solid-phase iron were measured in the sediment remaining after porewater extraction, whereas separate mini-cores were used for iron analysis in the radial sampling. Wet chemical extractions were used to determine the poorly crystalline Fe-oxide minerals. Iron was extracted in 0.5 M HCl for 1 h (Kostka & Luther 1994). The oxidation state of Fe in the extract was further determined by analysis in (1) ferrozine buffer (50 mM HEPES, 0.1% ferrozine,
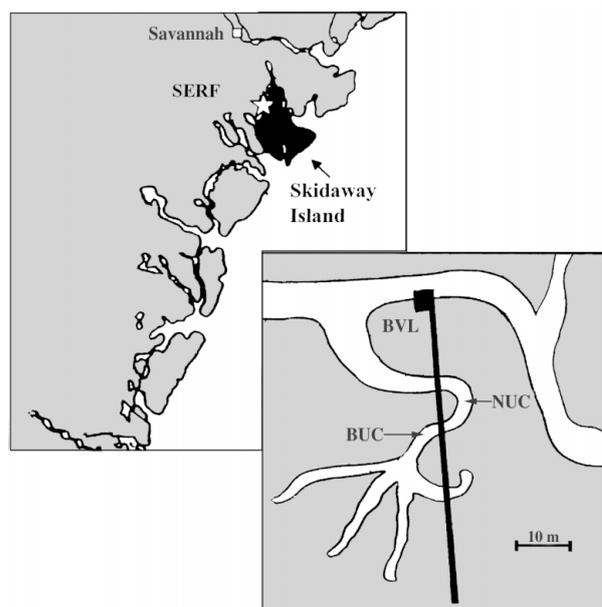

Fig. 1. Map of coast of Georgia, USA, showing Saltmarsh Ecosystem Research Facility (SERF study site (☆) and sampling stations (inset) along the boardwalk across the saltmarsh (NUC: non-bioturbated unvegetated creek bank; BUC: bioturbated unvegetated creek bank; BVL: bioturbated vegetated levee)

pH 7), and (2) ferrozine buffer + 1% (w/v) hydroxyl-amine hydrochloride (pH 7). Iron determined in the HCl extract with hydroxylamine addition is opera-tionally defined as the total HCl-extractable fraction (Fe[II] + Fe[III]), while Fe in the HCl extract without hydroxylamine addition is defined as the HCl-extractable Fe(II). Solid Fe(III) was determined by dif-ference between these 2 fractions. Calibration experi-ments with pure Fe phases have confirmed the selectivity of this extraction towards poorly crystalline or amorphous Fe-oxide minerals (Kostka & Luther 1994).

Sediment density was obtained from the wet weights of known sediment volumes. Water content and organic content (loss on ignition, LOI) was determined as weight loss after drying at 105°C and subsequent combustion at 520°C for 6 h, respectively. Particulate organic carbon (POC) and particulate organic nitrogen (PON) of dried samples were determined with a Carlo Erba Elemental Analyser EA 1100A after the method of Kristensen & Andersen (1987).

Radial profiles of temperature and pH from the bur-row walls and in the bulk sediment were measured *in situ* at BUC and BVL in August by inserting a temper-ature probe and a pH glass electrode calibrated with NBS standards (National Bureau of Standards, Gaithersburg, USA) directly into the sediment.

Porewater extraction and analysis. Sediment cores for porewater extraction were sectioned into 1 cm intervals to 10 cm depth for vertical profiles. Radial mini-cores from October were sectioned into 5 mm intervals to a distance of 10 mm, followed by 10 mm sections to a distance of 40 mm, whereas those from August were sectioned into 0–3, 3–6, 6–9, 9–12, 12–15, 15–20, 20–30 and 30–40 mm intervals from the burrow wall. Rhizosphere and bulk levee profiles were not sub-sectioned but were otherwise treated similarly. Porewater was obtained by centrifugation (10 min, 5000× g) and filtered through 13 mm Gelman acrodisc nylon filters before analysis of SO_4^{2-}, Fe^{2+}, H_2S, total CO_2, (TCO_2) and dissolved organic carbon (DOC). All sediment-sectioning, manipulation, and porewater sectioning was carried out under strictly anoxic conditions in a nitrogen-filled glove bag.

SO_4^{2-} in acidified (pH < 3 with HCl) porewater was analyzed using the turbidometric method of Tabatabai (1974). Dissolved Fe^{2+} was determined spectrophotometrically on HCl-acidified (pH ~2) samples after complexation with ferrozine (0.02% in 50 mM HEPES, pH 7) according to Stookey (1970). Sulfide was analyzed according to the method of Cline (1969). Porewater for the determination of TCO_2 were stored in 1.8 ml glass vials capped with Teflon-coated butyl rubber septa, to exclude any gas phase and to maintain anoxia. Samples were stored at 4°C and analyzed for TCO_2 within a few days by the flow injection/diffusion cell technique of Hall & Aller (1992). DOC was analyzed on a Shimadzu TOC-5000 total organic carbon analyzer after acidification with 2 M HCl (pH < 3) to remove dissolved inorganic carbon. Burrow and creek-water samples were treated in a similar manner to the porewater, except that no analysis of H_2S and DOC was performed.

Burrow-water sampling. Burrow water was sampled by withdrawing water into a 60 ml syringe via 3 mm silicone tubing gently pushed 4 to 6 cm into a burrow. Burrow water was sampled at 1 h intervals after exposure of the sediment during receding tides in October, and stored for later determination of dissolved SO_4^{2-}, Fe^{2+} and TCO_2 as described above. However, most burrows were rapidly drained of water at the onset of low tide, and only about 20% of the burrows at the levee (BVL) and even less at BUC contained sufficient water for sampling. Although burrow-water time series were available from the levee, the data was pooled as there was no significant difference over time for any of the parameters examined. At BUC, sufficient burrow water for analysis was obtained only once. Outgoing and incoming tidal water was collected directly from the main creek for comparative purposes.

Sulfate reduction assay. Vertical profiles of sulfate reduction rates (SRR) were determined by the core-

injection technique (Jørgensen 1978). Volumes of 2 µl radiolabeled sulfate (^{35}S-SO_4^{2-}, 60 kBq) were injected through silicone-filled ports at 1 cm intervals down to 10 cm depth. Cores were incubated for 2.5 h in the dark at *in situ* temperatures. The incubations were terminated and sulfide was preserved by slicing the sediment at 1 cm depth intervals directly into 50 ml screw-capped plastic centrifuge tubes containing 5 ml of 20% (w/w) zinc acetate solution. The tubes were vigorously shaken and stored frozen until analysis.

Radial profiles of SRR were made by line-injection of 10 µl radiolabeled sulfate (^{35}S-SO_4^{2}, 300 kBq) along the central axis of radial mini-cores. Samples were incubated for 2.5 h in the dark at 20 and 30°C in October and August, respectively. The incubations were terminated by transferring the syringes directly onto dry ice, which quickly froze the sediment. Sediment samples were later extruded while still frozen, and were sectioned as described above for the porewater extractions. The sediment slices were transferred directly into ZnAc (20% w/w). The reduced ^{35}S was recovered from the ZnAc preserved sediment from both vertical and radial profiles by distillation according to the 2-step procedure of Fossing & Jørgensen (1989) followed by radiocounting of subsamples from the distillation traps. The total reducible inorganic sulfur pools (TRS) was determined as sulfide in the distillation traps by the Cline method described above for porewater.

Anaerobic jar incubations. Anaerobic carbon mineralization rates in radial profiles from fiddler crab burrows at the creek bank (BUC) and in cross-sections at 5 cm sediment depth through the rhizosphere and the bulk levee sediment were determined in August. A total of 150 radial mini-cores were collected from burrows at the creek bank, while only 15 radial mini-cores were obtained from both the levee rhizosphere and the bulk levee sediment. All cores were stored cold on ice immediately after collection. Mini-cores from the creek bank burrows were sectioned under nitrogen as described above for the August porewater extraction, and the sediment from each interval was pooled and mixed thoroughly. Mini-cores from the rhizosphere and bulk levee were pooled and mixed after discarding 5 mm sediment at either end of the core. The homogenized sediment of each mixture was transferred into twelve 4 ml glass vials (jars) which were capped leaving no headspace, and incubated in the dark at 30°C. After 0, 12, 24, 48, 96 and 160 h centrifugation (5000× g, 10 min) for 2 jars of each type were sacrificed to obtain porewater. After filtration through 13 mm Gelman acrodisc nylon filters, 110 µl of the porewater was transferred to a 450 µl glass vial containing 330 µl distilled water and 10 µl saturated $HgCl_2$ solution and capped with Teflon-coated butyl rubber septa leaving no headspace. Samples were stored at

4°C and analyzed for TCO_2 within 1 mo as described above. The remaining porewater was acidified (HCl) for later determination of dissolved Fe^{2+} as described above. The sediment was then homogenized and solid-phase Fe(II) was extracted and analyzed as described above. All sediment and porewater handling associated with jars were done under N_2 atmosphere. Reaction rates in jars were calculated from a linear fit of concentration changes as a function of time.

RESULTS

Sediment and porewater properties

Sediment from the non-bioturbated creek bank (NUC) consisted of fine silt with an upper, 1 cm thick, brownish oxidized zone. Below this depth, the reduced sediment was homogeneously greyish-black. The infauna was sparse and consisted of occasional polychaetes of the genus *Nereis*. In the bioturbated creek bank site (BUC), the sediment between fiddler crab burrows was heterogeneous grey-brownish in appearance, whereas the burrows were coated by a several mm thick oxidized zone. Sediment from the levee (BVL) appeared oxidized, and was a brownish color deep down, but with many black spots. The sediment in the rhizosphere directly below large plants was highly oxidized and red iron-oxide coatings were evident on the roots.

Fiddler crab burrows were smaller and more abundant at BVL than at BUC (Table 1). Burrow density was not quantified in October but based on visual observations it appeared to be lower than in August. The 'tall' *Spartina alterniflora* at BVL was 138 ± 17 cm tall in October and occurred at a density of ~95 plants m^{-2}. The root and rhizome biomass at BVL (between plants) increased with depth to 10 cm, while no roots and rhizomes (living or dead) were observed in the creek-bank sediments (NUC and BUC).

Porosity and water content were similar at the 3 sites, but with an elevated trend at NUC (Table 2). Radial profiles showed that water content was 2 to 9% higher near the burrows than in sediment away from them (Fig. 2A). The water content at 5 cm depth in the rhizosphere, on the other hand, was 6 to 8% lower than in the bulk sediment between plants (data not shown). Particulate organic carbon and nitrogen content in bulk sediment was 25% lower at BUC than at the other sites, whereas BVL exhibited the highest molar C:N ratio. LOI at NUC and BUC

Table 1. Diameter (mm) and density (m^{-2}) of *Uca pugnax* burrows and *Spartina alterniflora* shoot density at the 3 sampling sites (NUC: non-bioturbated unvegetated creek bank; BUC: bioturbated unvegetated creek bank; BVL: bioturbated vegetated levee) in August 2000. Root biomass (g m^{-3}) was determined in October 1999 (mean ± SD, n = 10)

| Site | *Uca pugnax* burrows | | *S. alterniflora* | |
	Diameter	Density	Density	Root biomass
NUC	–	0	0	0
BUC	17.4 ± 9.9	280.8 ± 70.5	0	0
BVL	12.7 ± 7.7	342.9 ± 95.8	91.4 ± 33.7	96.9 ± 48.3

was similar at a level 10 to 30% lower than at BVL. A high variation in LOI at the innermost 1.5 cm of the radial burrow profiles (Fig. 2B) coincided with slightly elevated POC as well as the molar C:N ratio (10 to 20%) at BVL (Fig. 2C,D). Rhizosphere organic matter content, measured as POC and PON, was 25 to 30% lower than the bulk levels, whereas the molar C:N ratio was highest in the rhizosphere. Porewater pH was substantially lower (by ~1 pH unit) at the vegetated than at the unvegetated sites (Table 2). While pH was even further reduced in the rhizosphere, it appeared to be elevated around burrow walls compared to bulk sediment (Fig. 2F). Radial profiles of sediment temperature, on the other hand, increased with increasing distance from burrows (Fig. 2E).

Sulfate reduction

SRR was highest near the surface and gradually decreased with depth at NUC (Fig. 3A), whereas the 2 other sites had subsurface maxima at 1 to 3 cm depth followed by constant or slightly decreasing levels below this (Fig. 3B,C). Depth-integrated (0 to 10 cm) sulfate reduction rates showed an inverse relationship with abundance of macroorganisms in October. High-

Table 2. Sediment characteristics in vertical cores (0 to 10 cm) at non-bioturbated unvegetated creek bank (NUC), bioturbated unvegetated creek bank (BUC) and the bioturbated vegetated levee (BVL) and through the rhizosphere *Spartina alterniflora* at 5 to 6 cm depth in October 1999. pH was measured in August 2000 (mean ± SD, n = 3 to 5). LOI: loss on ignition

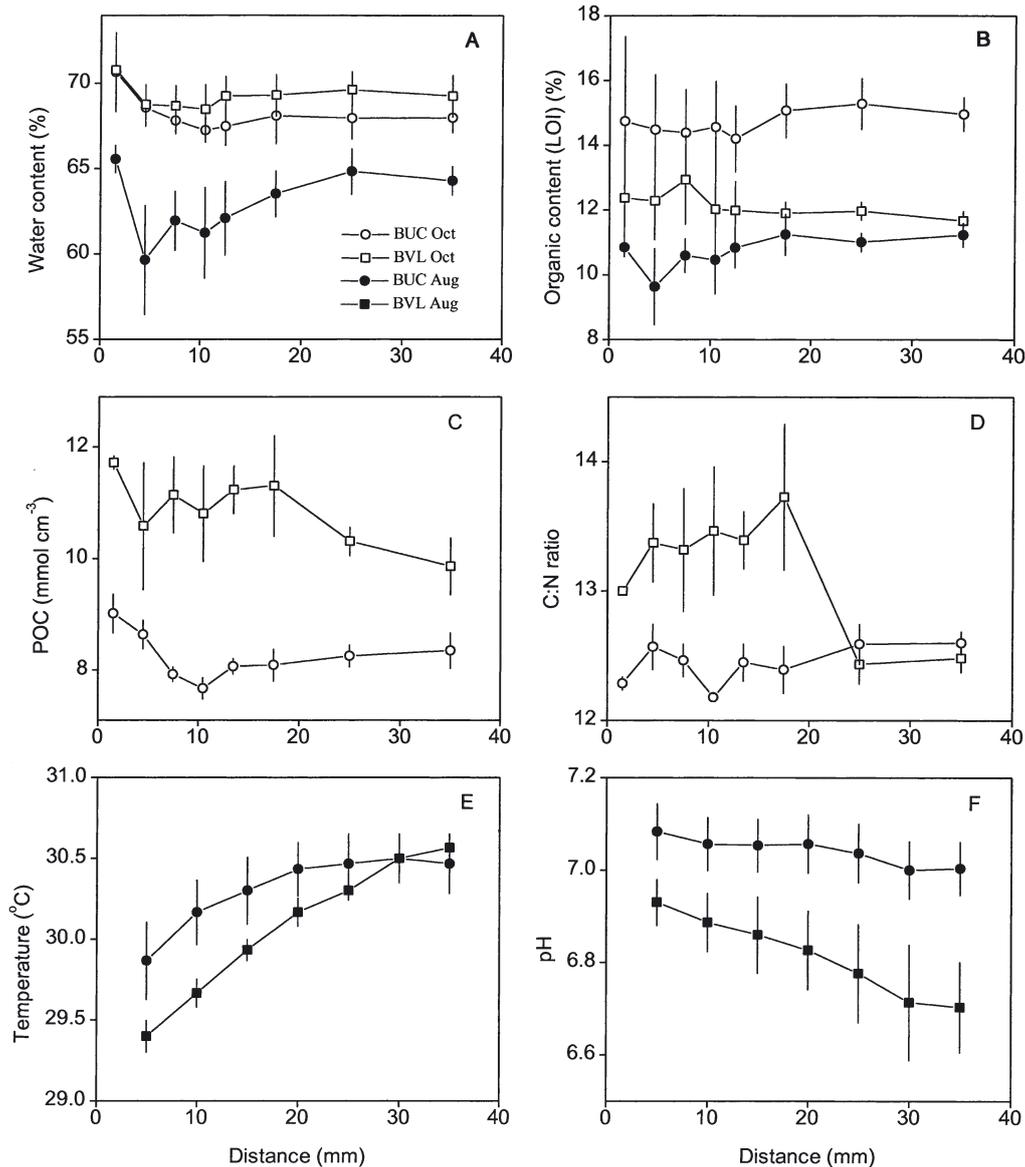|	NUC	BUC	BVL	Rhizosphere
Water content (%)	72.2 ± 1.0	67.3 ± 1.4	67.6 ± 0.8	63.1 ± 3.1
pH	7.2 ± 0.3	7.0 ± 0.1	6.4 ± 0.3	5.4 ± 0.0
Porosity	0.82 ± 0.01	0.78 ± 0.02	0.78 ± 0.01	–
LOI (%)	12.5 ± 0.4	12.2 ± 0.7	14.9 ± 0.6	12.8 ± 0.6
POC (mmol cm^{-3})	10.2 ± 1.1	7.4 ± 0.8	10.1 ± 0.4	7.5 ± 0.3
PON (mmol cm^{-3})	0.82 ± 0.07	0.60 ± 0.07	0.77 ± 0.04	0.53 ± 0.09
C:N	12.4 ± 0.6	12.4 ± 0.4	13.2 ± 0.4	14.0 ± 0.3

Fig. 2. Sediment characteristics in radial profiles from fiddler crab *Uca pugnax* burrow walls into bulk sediment at 5 cm depth (Distance = distance from burrow walls). Burrows were sampled at the levee (BVL) and creek bank (BUC) in October 1999 and August 2000 (Mean ± SD, n = 4 to 5). LOI: loss on ignition

est rates were observed at NUC, intermediate at BUC and lowest at BVL (Table 3). A seasonal difference was observed, with considerably lower (41%) rates at NUC in August.

SRR was 32 and 18 times higher in the bulk BUC and BVL sediment, respectively, than adjacent (3 mm) to the burrow walls in October, while the difference at BUC in August only was 4 times (Fig. 4A). The slope of increase along the radial profiles was highest within 1 to 2 cm of the burrow wall, approaching bulk sediment levels at 3 to 4 cm distance. Sulfate reduction was greatly reduced in the rhizosphere (25 to 130 nmol SO_4^{2-} cm^{-3} d^{-1}) compared to the bulk levee sediment (380 to 460 nmol SO_4^{2-} cm^{-3} d^{-1}) (Fig. 5B). However, the rhizosphere rates were >400% higher in October than in August, while an opposite trend (21%) was observed for the bulk levee sediment (data not shown).

Reaction rates in anoxic jars

The concentration of porewater TCO_2 and solid-phase Fe(II) generally increased in a linear fashion in all jar incubations during the anoxic incubation, with a con-

comitant accumulation of dissolved Fe^{2+} (Fig. 6). The data obtained within the first 24 h were not included in the regressions used for TCO_2 and Fe(II) rate determination due to disturbance of the sediment during homogenization (Kristensen et al. 2000). Total carbon mineralization rate (TCO_2 production) decreased with increasing distance within the first 2 cm from burrow

walls, followed by a slight increase 3 to 4 cm away (Fig. 5A). The Fe(III) reduction rate, determined as the inverse of the Fe(II) accumulation rate was highest (up to 6 µmol cm^{-3}) 0 to 1 cm adjacent to the burrow wall, and decreased substantially (40%) further away (Fig. 5A). The accumulation of dissolved Fe^{2+} in the bulk levee sediment was similar to the increase observed at BUC, while
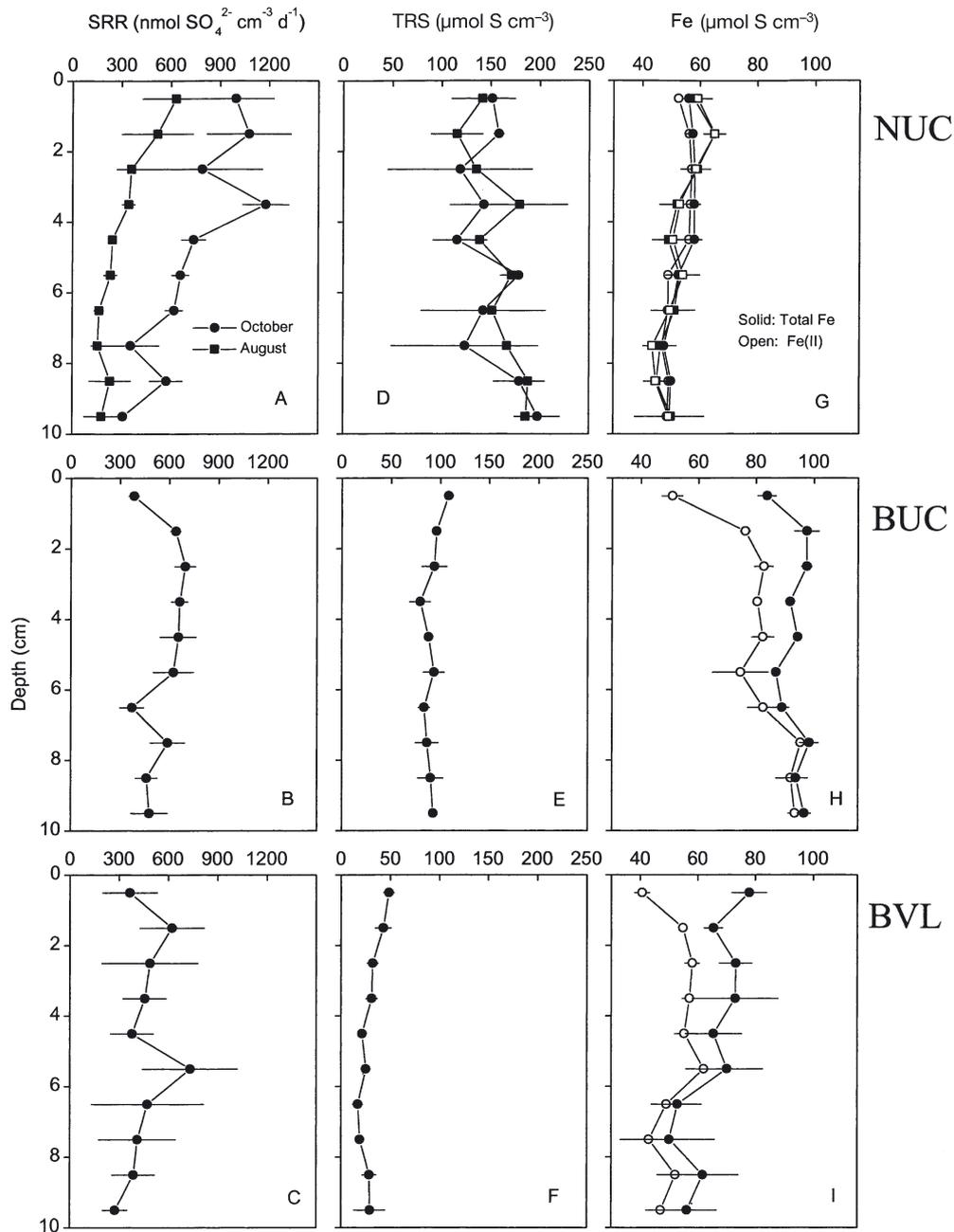

Fig. 3. Vertical profiles of (A–C) sulfate reduction rates (SRR) (D–F) total reducible sulfur (TRS) and (G–I) total Fe (●, ■) and Fe(II) (O, □) at nonbioturbated creek bank (NUC) in October 1999 and August 2000, and at bioturbated creek bank (BUC) and bioturbated vegetated levee (BVL) in October 1999 (Mean ± SD, n = 3). Values from October and August sampling periods are represented by circles and suares, respectively

Table 3. Depth-integrated (0 to 10 cm) sulfate reduction rates (SRR) and pools of total reducible sulfur (TRS) and reactive Fe(III) at non-bioturbated unvegetated creek bank (NUC), bioturbated unvegetated creek bank (BUC) and bioturbated vegetated levee (BVL) (mean ± SD, n = 3); nd: not detected

Parameter	October 1999			August 2000
	NUC	BUC	BVL	NUC
SRR (mmol SO_4^{-2} m^{-2} d^{-1})	73.0 ± 5.5	55.8 ± 1.1	45.0 ± 19.5	30.5 ± 9.6
TRS (mol S m^{-2})	15.1 ± 2.2	9.1 ± 0.6	2.9 ± 0.6	15.7 ± 2.2
Reactive Fe(III) (mol m^{-2})	0.17 ± 0.10	1.19 ± 0.48	1.27 ± 0.50	nd

Fe^{2+} accumulated to much higher (2.5 times) concentrations in the rhizosphere. The Fe(III) reduction rate was 4 times higher in the rhizosphere (6.2 ± 0.4 µmol Fe cm^{-3} d^{-1}) than in the bulk levee sediment (1.7 ± 0.5 µmol Fe cm^{-3} d^{-1}) (Fig. 5B).

Solid-phase sulfur and iron

TRS was comprised almost completely of chromium-reducible sulfide (95 to 100%) at all sites (data not shown). TRS concentrations increased irregularly with increasing depth in the sediment at NUC, whereas a slight decrease was observed at BUC and BVL (Fig. 3D–F). Depth-integrated (0 to 10 cm) TRS pools showed a pattern similar to SRR, with highest (15 mol m^{-2}) levels at NUC, intermediate levels (9 mol m^{-2}) at BUC and lowest (3 mol m^{-2}) at BVL (Table 3). Total Fe decreased slightly with increasing depth at NUC and BVL, but increased at BUC. The concentration of amorphous Fe(III) oxides (total Fe–Fe[II]) exhibited the opposite picture, with highest concentrations at BVL (19 ± 5% of total Fe), intermediate levels at BUC (13 ± 5%) and lowest levels at NUC (3 ± 2%) (Table 3). The concentration of Fe(III) gradually decreased with increasing depth from 15–20 to <5 µmol cm^{-3} (Fig. 3H,I). At NUC, where almost all iron (>97%) occurred as reduced Fe(II) (Fig. 3G), the total iron concentration was 17 and 42% lower than at BVL and BUC, respectively.

The TRS pool appeared relatively unaffected by the presence of burrows, resulting in a very slow sulfur turnover near burrow walls (Fig. 4C,D). Thus, turnover
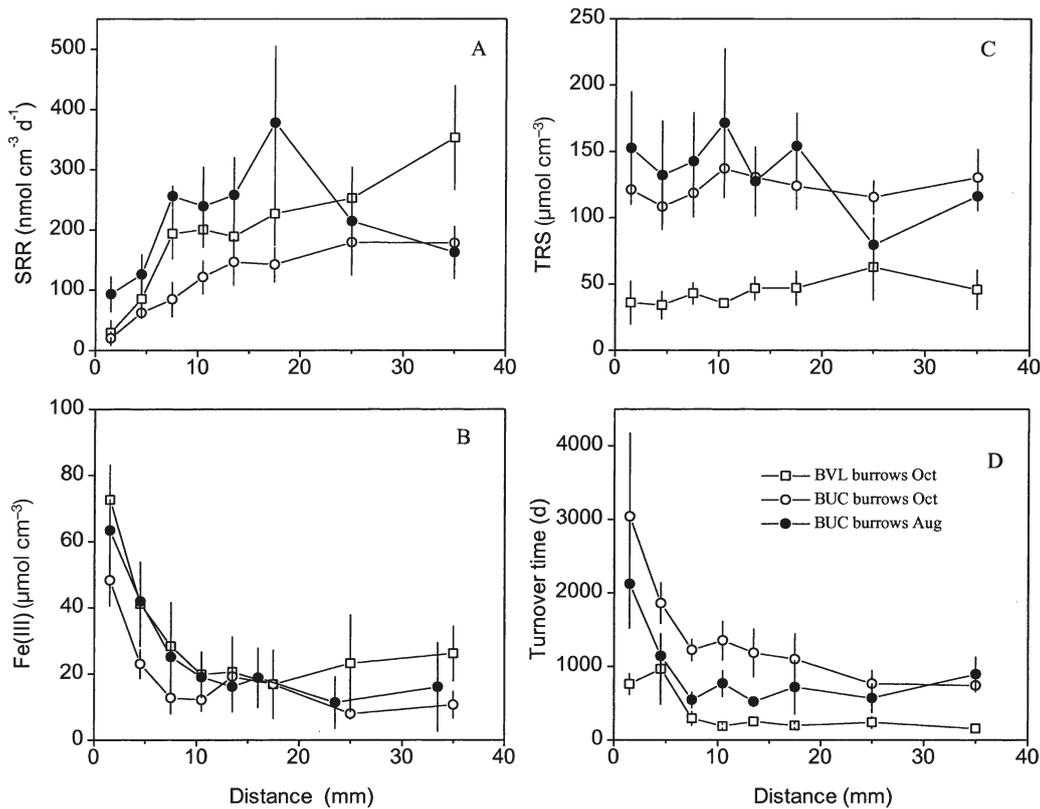

Fig. 4. Radial profiles of (A) sulfate reduction rates (SRR), (B) Fe(III) concentrations, (C) total reducible sulfur (TRS) and (D) turnover time of sulfur from *Uca pugnax* burrow walls into bulk sediment at 5 cm depth. Burrows were sampled at levee (BVL) in October 1999 and creek bank (BUC) in October 1999 and August 2000 (Mean ± SD, n = 5), Distance = distance from burrow walls
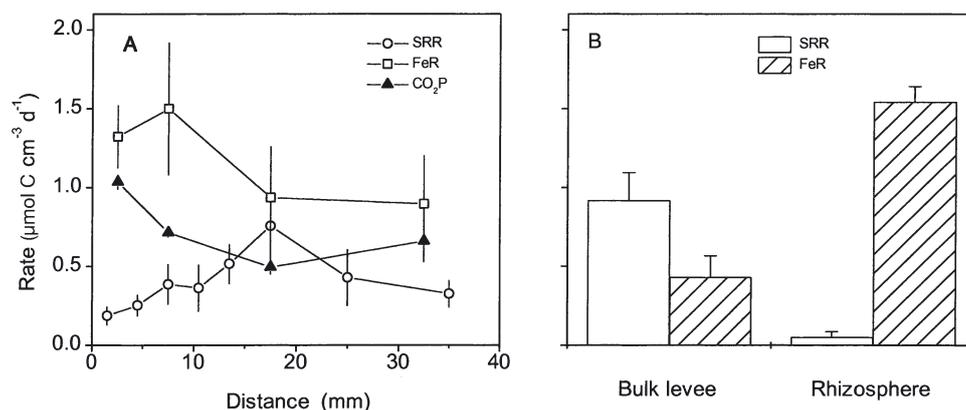
Fig. 5. (A) CO_2 production rates (CO_2P), SO_4^{2-} reduction rates (SRR) and Fe(III) reduction rates (FeR) as a function of distance from *Uca pugnax* burrow walls at the creek bank; (B) SO_4^{2-} reduction rates (SRR) and Fe(III) reduction rates (FeR) in the bulk levee and through the rhizosphere in August 2000. CO_2P and FeR were obtained from jar incubations (standard error determined from regression) while SRR was from ^{35}S whole-core incubations (values are means ± SD; n = 3). Rates are converted to C units by C:S ratio of 2:1 and Fe:C ratio of 4:1

time was 6 to 8 yr adjacent to BUC burrows, and about 2 yr around BVL burrows compared with 2 and 0.2 yr, respectively, at a distance of 3 to 4 cm. Total HCl-extractable Fe around burrows was similar to that in the bulk sediment at BVL, except for 30% higher values immediately adjacent to burrow walls (data not shown). Fe(III), on the other hand, was high around burrow walls at both sites and on both sampling occasions (Fig. 4B), and decreased rapidly with increasing distance from the walls. The Fe(III) content adjacent to the burrow walls was 2 to 3 times higher than 1 to 4 cm away from the walls and about 2 times higher than in surface sediment.

The TRS pool was low in the rhizosphere compared to bulk levee sediment. The total Fe content, on the other hand, was not significantly different from bulk sediment levels at the same depth, but almost all of the iron (89%) in the rhizosphere was oxidized Fe(III) compared to only 19% in the bulk sediment (Table 4).

Porewater chemistry

Vertical profiles of SO_4^{2-} ranged from 15 to 23 mM at all sites in October with no specific depth pattern (Fig. 7A). However, a clear depth gradient from 28 to 30 to 18 mM SO_4^{2-} was observed in the 4 to 7 cm depth interval at NUC in August. Fe^{2+} decreased rapidly with increasing depth at NUC and was not detectable below 3 cm depth (Fig. 7B), where dissolved sulfide started to accumulate (Fig. 7C). The Fe^{2+} gradient was steepest in October, while sulfide

evolved most dramatically in August. At the 2 bioturbated sites, BUC and BVL, Fe^{2+} increased to subsurface maxima of ~450 and ~570 µM, respectively, at 1 to 2 cm depth in October and remained high (>130 µM) throughout the entire depth interval. No dissolved sulfide was detected at these sites. DOC increased gradually with increasing depth from 0.4 to 1.9 mM (Fig. 7D), and was slightly but consistently higher at BVL than at the other sites. TCO_2 accumulated with depth at all sites (Fig. 7E), with highest TCO_2 concentrations observed at NUC in August and lowest at BUC in October.

While sulfate concentrations varied from 18 to 22 mM with no specific pattern with distance from burrow walls (data not shown), dissolved Fe^{2+} showed low concentrations immediately adjacent to burrow walls, increasing to ~100 µM (October) and ~350 µM (August) with increasing distance (Fig. 8). The radial TCO_2 profiles were almost similar at BUC and BVL (1 to 2 mM), showing a slight increase with distance from burrows walls (data not shown). All porewater

Table 4. Porewater and solid-phase concentrations in cross-sections through rhizosphere directly below *Spartina alterniflora* and through the bulk levee sediment between plants at 5 cm depth in October 1999 and August 2000 (mean ± SD, n = 5)

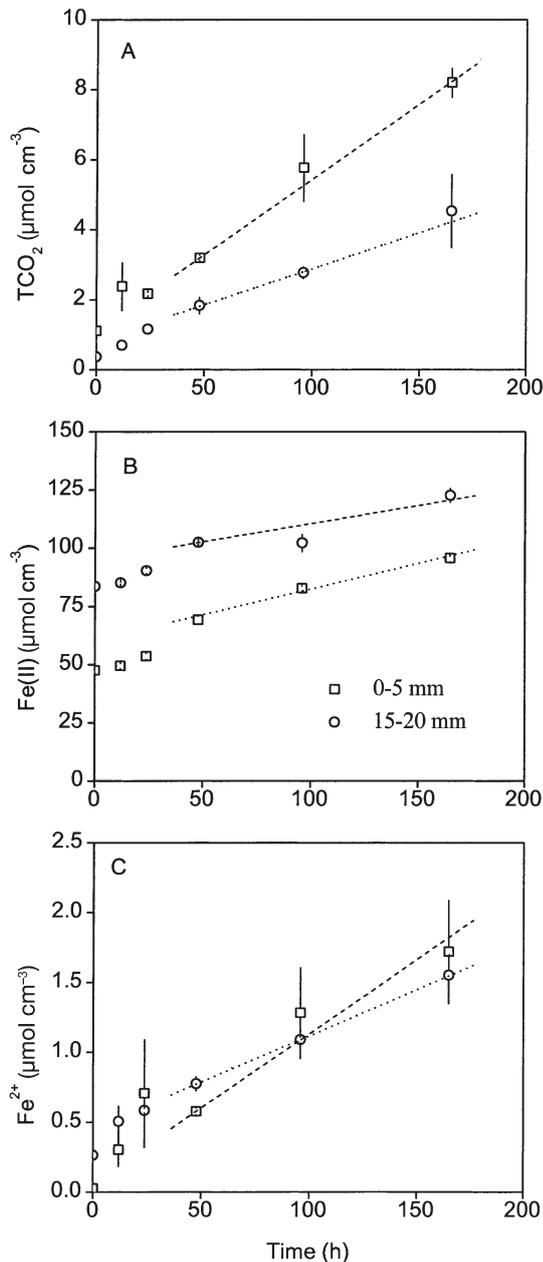| Parameter	Rhizosphere		Levee bulk	
	October	August	October	August
CO_2 (mM)	0.7 ± 0.5	0.9 ± 0.1	4.3 ± 0.8	2.9 ± 0.6
SO_4^{2-} (mM)	20.5 ± 2.1	30.6 ± 2.2	18.9 ± 0.8	26.8 ± 1.3
Fe^{2+} (µM)	196.0 ± 171.9	55.7 ± 28.5	493.7 ± 137.9	656.9 ± 136.1
Total Fe (µmol cm^{-3})	85.6 ± 35.2	130.8 ± 8.0	70.1 ± 21.8	86.6 + 8.6
Fe(III) (µmol cm^{-3})	86.4 ± 30.7	113.7 + 12.7	8.0 ± 10.9	5.1 + 3.3
TRS (µmol cm^{-3})	13.5 ± 20.0	3.7 ± 1.4	21.5 ± 7.8	51.1 ± 26.9

Fig. 6. Representative examples of changes in rates of (A) CO$_2$ production, (B) Fe(II) accumulation and (C) dissolved Fe^{2+} accumulation from anaerobically incubated sediment sampled at 0 to 5 and 15 to 20 mm distance from creek-bank burrows of *Uca pugnax* in August. Results represent mean ± range of duplicate samples sacrificed at each time point. Lines are drawn according to least-squares linear regression of the last 3 time points

respectively. Porewater Fe^{2+} in the rhizosphere reached 40 and 8% of the concentrations in bulk sediment. Dissolved sulfide was not detectable by analysis or odor in any radial burrow and rhizosphere samples.

The average concentrations of most solutes in the burrow water were intermediate to those of creek water and sediment porewater. Thus, the SO$_4^{2-}$ concentration was ~17 mM in burrow water compared to ~16 mM for incoming and ~20 mM for outgoing creek water and sediment porewater (Table 5). Dissolved Fe^{2+} in burrows varied from 0 to 110 µM at BUC and 0 to 86 µM at BVL, with most replicates near the lower limit. The level of TCO$_2$ in burrow water was within the range of that observed in the sediment porewater near burrow walls. Free sulfide was not detectable by odor in burrow water.

DISCUSSION

Previous research indicated that Fe(III) reduction and sulfate reduction should be considered the predominant microbial respiration processes coupled to organic carbon oxidation in saltmarsh sediments (Kostka et al. 2002a,b). This previous work also showed the drastic effects that plant roots and crab burrows can have on sediment geochemical parameters (Kostka et al. 2002a,b). In this study, we have further elucidated the effects of macrobenthic organisms on sediment biogeochemistry through radial profiling of the burrow wall and rhizosphere. Thus we confirm that the Fe cycle in saltmarsh sediments is stimulated by macrobenthic activity, leading to an increased supply of reactive Fe(III) which causes Fe(III) reduction to outcompete sulfate reduction during carbon oxidation.

Many previous studies have suggested that macrofauna and macrophytes substantially affect the geochemical cycles of S and Fe in marine sediments (e.g. Hines 1991, Kostka & Luther 1995, Kostka et al. 2002b), but few experimental studies in saltmarshes have directly determined the biogeochemical effects of these macroorganisms in general, and their impact on the partitioning of the predominant carbon oxidation pathways (microbial Fe[III] reduction and sulfate reduction) in particular. In this study a spatial gradient in sulfate reduction activity was observed with macroorganism abundance, with highest rates at the uninhabited site, intermediate rates at the bioturbated site and lowest rates at the bioturbated, vegetated site. Solute and particle-mixing, mediated by rooted macrophytes and bioturbating macrofauna, enhance the Fe cycle in saltmarsh sediments. Rapid Fe cycling supports increased reactive Fe(III) concentrations thereby allowing Fe(III)-reducing bacteria to outcompete sulfate-reducing bacteria during carbon oxidation.

constituents, except for SO$_4^{2-}$, were considerably lower in the rhizosphere than in the ambient sediment (Table 4). TCO$_2$ in the rhizosphere only attained 16 and 31% of the bulk level in October and August,
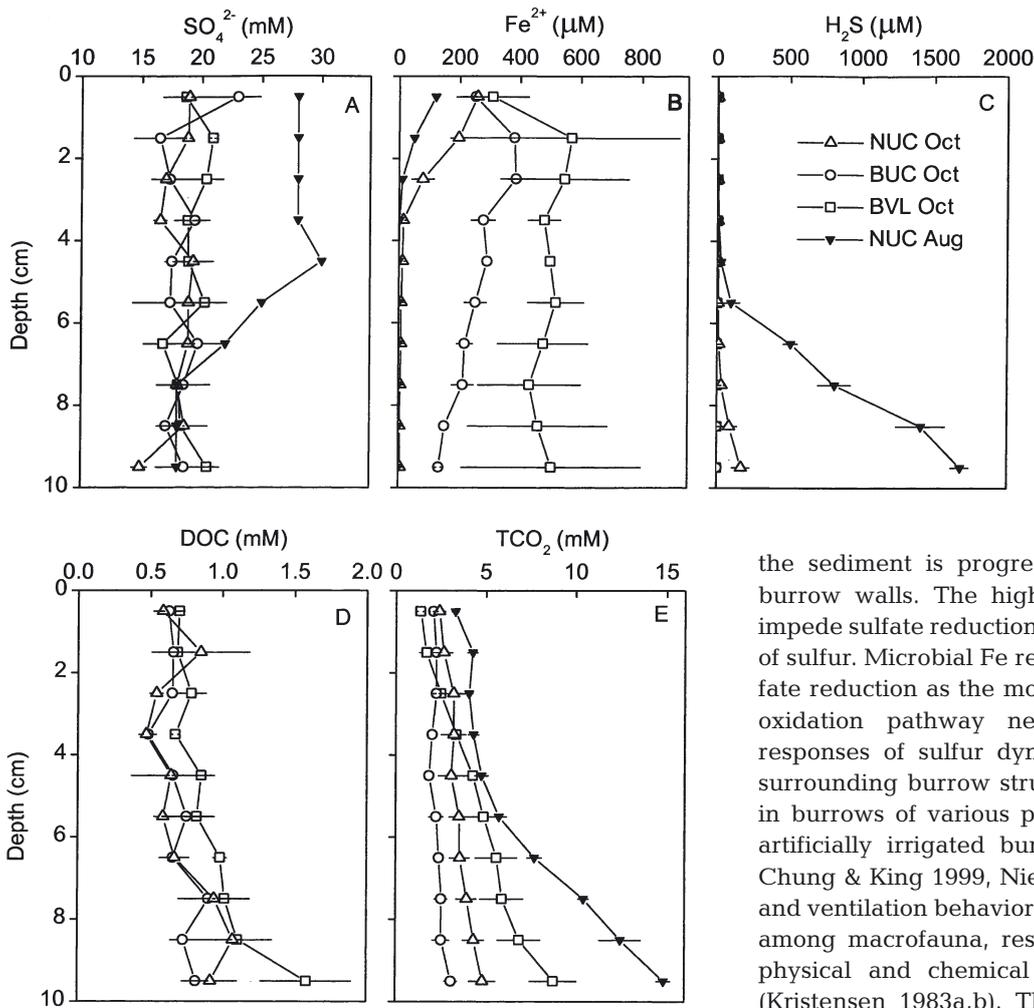
Fig. 7. Vertical profiles of porewater constituents at non-bioturbated creek bank (NUC) in October 1999 and August 2000, and at bioturbated creek bank (BUC) and bioturbated, vegetated levee (BVL) in October 1999 (Mean ± SD, n = 3). TCO_2 = total carbon dioxide

the sediment is progressively more oxidized near burrow walls. The high redox conditions strongly impede sulfate reduction and slow down the turnover of sulfur. Microbial Fe reduction clearly replaces sulfate reduction as the most important organic carbon oxidation pathway near burrow walls. Similar responses of sulfur dynamics in sediment directly surrounding burrow structures have been observed in burrows of various polychaetes, molluscs and in artificially irrigated burrows (Hansen et al. 1996, Chung & King 1999, Nielsen et al. 2003). Burrowing and ventilation behavior, however, vary considerably among macrofauna, resulting in differences in the physical and chemical characteristics of burrows (Kristensen 1983a,b). Thus, enhanced SRR around

Given the high density of fiddler crabs in the Georgia marsh and their impact on sediment biogeochemistry, the potential influence on overall saltmarsh productivity and carbon dynamics is obvious. High-resolution radial profiles provide evidence that the direct impact of burrows is focused in a zone of 1 to 2 cm from the burrow wall. The radial profiles of porewater and solid phase constituents clearly show that

Table 5. *Uca pugnax*-burrow and creek-water chemistry October 1999. (n): number of replicates (mean ± SD). TCO_2: total carbon dioxide

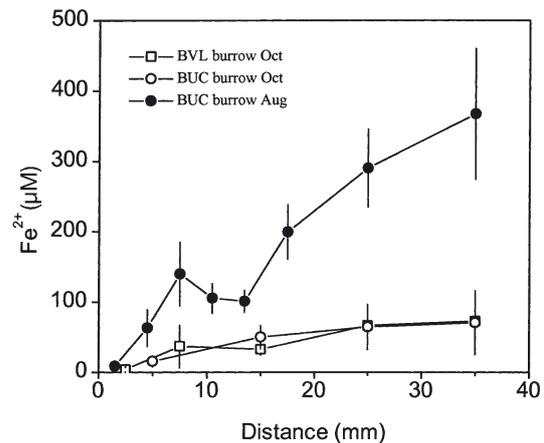| Site	(n)	SO_4^{2+} (mM)	Fe^{2+} (µM)	TCO_2 (mM)
BUC burrows	(5)	17.0 ± 1.8	38.6 ± 19.7	1.8 ± 0.7
BVL burrows	(20)	17.1 ± 1.9	7.1 ± 21.3	3.6 ± 1.1
Incoming creek	(5)	15.9 ± 1.8	1.1 ± 0.6	2.0 ± 0.7
Outgoing creek	(5)	20.2 ± 0.6	1.1 ± 0.7	1.8 ± 0.3

Fig. 8. Radial profiles of porewater Fe^{2+} from *Uca pugnax* burrow walls into bulk sediment at 5 cm depth. Burrows were sampled at levee (BVL) in October 1999 and creek bank (BUC) in October 1999 and August 2000 (Mean ± SD, n = 4 to 5). Distance = distance from burrow walls

Table 6. Dissimilatory sulfate reduction rates (SRR), partitioning of chemical and biotic (dissimilatory) Fe reduction rates (FeR), Fe:C stoichiometry in jar incubations, and importance of Fe reduction to total carbon oxidation in sediment incubations from BUC *Uca pugnax* burrows, *Spartina alterniflora* rhizosphere and bulk levee (BVL) in August 2000. To facilitate direct comparison, rates are presented in C units assuming the theoretical stoichiometry of C:S = 2:1 and Fe:C = 4:1. SRR = ^{35}S whole core incubations assuming C:S = 2:1; Chemical FeR = potential Fe reduction due to abiotic reaction with H_2S from SRR, assuming H_2S:FeOOH = 3:2; Total FeR = Fe reduction rates from regression (Fig. 6B) assuming Fe:C = 4:1; Biotic FeR = proportion of Fe reduction ascribed to bacterial processes; C-oxidation = jar C-oxidation rates from regression (Fig. 6A); Fe:C ratio = estimated Fe:C stoichiometry from jar rates when chemical FeR is subtracted; C-oxidation = estimated C-oxidation through biotic SO_4^{2-} and Fe(III) reduction; C-oxidation via FeR = C-oxidation through Fe reduction (total FeR) in% of total

Distance from burrow wall (mm)	SRR (nmol cm^{-3} d^{-1})	Chemical FeR (nmol cm^{-3} d^{-1})	Total FeR (nmol cm^{-3} d^{-1})	Biotic FeR (%)	Measured C-oxidation (nmol cm^{-3} d^{-1})	Estimated Fe:C ratio	Estimated C-oxidation (nmol cm^{-3} d^{-1})	Estimated C-oxidation via FeR (%)
0–5	219	18	1323	98.6	1034	5.0	1524	86
5–10	387	32	1500	97.9	714	8.2	1854	79
15–20	756	63	935	93.3	495	7.1	1628	54
30–35	377	31	895	96.5	659	5.2	1241	70
Rhizosphere	60	5	1544	99.7	456	13.5	1599	96
Levee bulk	920	77	432	82.2	367	3.9	1275	28

Mya arenaria burrows (Hansen et al. 1996) has been ascribed to substrate enrichment due to organic excretion from *M. arenaria* rather than to any ventilation or behavioral response. Chung & King (1999) further substantiated that parameters other than ventilation determines the microbial activity in *M. arenaria* burrows. The limited or no change in particulate organic carbon and nitrogen content in *Uca pugnax* burrow walls, on the other hand, suggests that the increase in sediment surface area (controlling the flux of oxygen) is the driving force behind the specific geochemistry around *U. pugnax* burrows, while passive or active addition of carbon to the burrow wall (as mucus or particle displacement) is of minor importance.

The effect of fiddler crabs is also evident from the average sediment biogeochemistry in the upper 10 cm sediment column, although cores were taken at some distance from burrows. The higher oxidation level caused by fiddler crabs at BUC resulted in 25% lower average sulfate reduction compared to NUC. The corresponding higher average total Fe concentration and lower TRS at BUC than at NUC indicates enhanced pyrite oxidation at BUC due to translocation and/or formation of Fe(III) into anoxic sediment. Thus, solid Fe(III) was observed at all depths at BUC, while most Fe was reduced at NUC. A similar pattern of net re-oxidation of TRS pools has been reported previously for other highly bioturbated sediments (Hansen et al. 1996, Banta et al. 1999, Kostka et al. 2002b).

Roots of marsh plants are efficient conduits of oxygen to the interior of the sediment because their well-developed aerenchyma system allows oxygen to diffuse from leaves to roots (Sundby et al. 1998, Holmer et al. 2002). Locally, *Spartina alterniflora* appears to have greater impact on the sediment biogeochemistry than
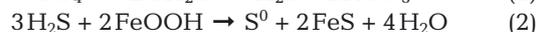
fiddler crabs. All the extractable Fe in the rhizosphere comprised amorphous Fe-oxides, and Fe reduction rates were among the highest reported for marine sediments (Thamdrup 2000), whereas sulfate reduction was almost absent. A high content of iron oxides in the rhizosphere and massive iron-oxide coatings around roots has been described for other aquatic macrophytes (Sundby et al. 1998). On a marsh-wide scale, the relative importance of *S. alterniflora* roots versus fiddler crab burrows for sediment biogeochemistry depends on the relative size of sediment volume influenced by each macroorganism. At the SERF marsh, where roughly 10 and 25% of the marsh surface is occupied by creek bank and tall *S. alterniflora* zones, respectively (Kostka et al. 2002a), quantification of the sediment zones influenced by macroorganisms is currently being addressed. Fiddler crabs increase the marsh surface area by as much as 60% (Katz 1980); hence the effects of fiddler crabs on S and Fe cycles may, on a marsh-wide scale, potentially match or even exceed those of *S. alterniflora*.

Fe(III) reduction

The lack of detectable H_2S in the upper 3 cm of the sediment at NUC or to 10 cm depth at the 2 other sites despite extensive sulfate reduction indicates rapid sulfide immobilization through reaction with dissolved iron in the sediment (Thamdrup & Canfield 1996). Fe(III) reduction in the saltmarsh has long been considered an almost exclusively abiotic reaction with dissolved sulfide (Howarth 1993). However, recent studies have shown that microbial Fe(III) reduction coupled to carbon oxidation can be important in saltmarsh

sediments (Luther et al. 1992, Jacobsen 1994, Kostka & Luther 1995). In accordance with this, we found that Fe(III) reduction rates greatly exceeded the reduction potential of H_2S produced by sulfate reduction (Table 6). These results are in accordance with those of Kostka et al. (2002a), who found that microbial Fe reduction accounted for all carbon mineralization in bioturbated vegetated sediments at the same location. Using treatments with molybdate, formalin and pasteurization, Kostka et al. (2002a) confirmed that Fe(III) reduction is primarily a biologically catalyzed process.

Dissimilatory reduction of 1 mol SO_4^{2-} produces 1 mol H_2S, which potentially can reduce $^2/_3$ mol Fe(III) according to Eqs. (1) & (2) below (Thamdrup & Canfield 1996, Jørgensen 2000):

$$SO_4^{2-} + 2\,CH_2O \rightarrow H_2S + 2\,HCO_3^- \qquad (1)$$
$$3\,H_2S + 2\,FeOOH \rightarrow S^0 + 2\,FeS + 4\,H_2O \qquad (2)$$

Accordingly, H_2S produced by SRR near BUC burrows can only account for <7% of the total Fe(III) reduction. The accumulation of Fe^{2+} in the present jar-incubations supports the contention that H_2S production by SRR is well below the oxidation capacity of Fe(III). More than 99% of the Fe(III) reduction in the rhizosphere and 82% in the bulk levee must therefore be ascribed to dissimilatory microbial reduction.

Dissimilatory reduction of 4 mol of Fe(III) is coupled to 1 mol of C oxidation according to:

$$4\,FeOOH + CH_2O + 7\,H^+ \rightarrow 4\,Fe^{2+} + HCO_3^- + 6\,H_2O \qquad (3)$$

By correcting the total Fe(III) reduction for the potential chemical reduction and total carbon oxidation for the contribution by SRR, the stoichiometry of dissimilatory Fe reduction coupled to carbon oxidation (Fe:C) in burrow profiles at BUC was 5.0 to 8.2, while ratios of 13.5 and 3.9 were observed in the rhizosphere and bulk levee, respectively at BVL (Table 6). The small size of the jars used, and consequently the limited volume of porewater obtained for analysis may have affected the precision of the method due to loss of CO_2 during handling of samples, preferentially in the low pH rhizosphere sediment at BVL. The Fe:C ratios may also have been affected by the abiotic reduction of Fe(III) by organic ligands (Luther et al. 1992, 1996), particularly close to burrow walls and in the rhizosphere. The predicted 4:1 stoichiometry of Fe reduction was, however, confirmed in simultaneous incubations of larger sediment volumes from the rhizosphere by Kostka et al. (2002a).

Dependence on Fe(III) concentrations

Dissimilative Fe reduction in sediments is highly dependent on the presence of poorly crystalline Fe-oxides

(Thamdrup 2000) and the availability of labile organic carbon. Reoxidation of Fe(II) mediated by bioturbation and root action in iron-rich saltmarsh sediments can sustain very high rates of microbial Fe reduction. If all carbon oxidation around burrow walls is driven by sulfate and Fe(III) reduction, and the theoretical stoichiometries of S:C = 0.5 and Fe:C = 4 are valid, dissimilatory reduction of amorphous Fe(III) (16 to 53 µmol cm^{-3}) is responsible for 54 to 86% of the total C-oxidation (Table 6). In the rhizosphere, where Fe(III) concentrations are extremely high (114 µmol cm^{-3}), virtually all the microbial carbon mineralization is due to Fe(III) reduction, while only 28% can be ascribed to Fe(III) reduction in the less Fe(III)-rich (5 µmol cm^{-3}) bulk levee sediment (Table 6). The contribution of Fe(III) reduction to the total C-oxidation in the marsh sediment is closely related to the concentration of amorphous Fe(III) (Fig. 9). The observed relationship agrees closely with the patterns previously observed for a range of subtidal marine sediments (Thamdrup 2000, Jensen et al. 2003), and described by Jensen et al. (2003) by the empirical function:

$$\%FeR = 100\% \times (1 - e^{-([Fe(III)] \times 0.056)}) \qquad (4)$$

where %FeR is the carbon oxidation through iron reduction in% of total carbon oxidation and Fe(III) is the concentration of poorly crystalline Fe oxides, suggesting this to be a universal relationship. Thus, the importance of Fe(III) respiration is strongly dependent on Fe(III) concentrations below levels of 30 µmol cm^{-3}, while almost all anaerobic carbon oxidation at higher Fe(III) concentrations is mediated by Fe(III) reduction.
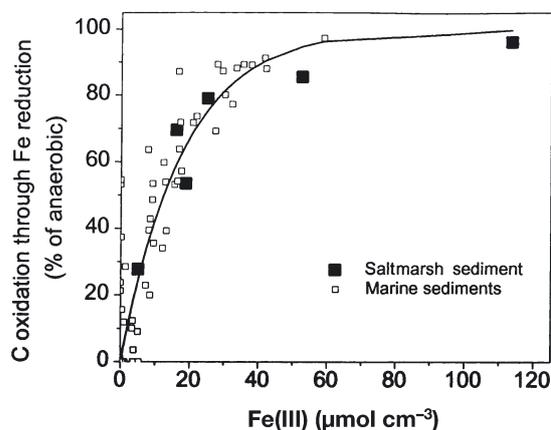

Fig. 9. Relative contribution of dissimilatory Fe(III) reduction to carbon oxidation as a function of the concentration of amorphous Fe(III) in the saltmarsh sediment incubations and in several marine locations (after Thamdrup 2000 and Jensen et al. 2003). Curve represents function %FeR = 100% × $(1-e^{-([Fe(III)] \times 0.056)})$. Sulfate reduction accounts for remaining carbon oxidation. (■) Data from present study

Other C-oxidation pathways

It must be emphasized that the importance of electron acceptors other than S and Fe has been ignored in the above discussion. The utilization of oxidized manganese as an electron acceptor for bacterial respiration in saltmarsh sediments is considered negligible, because manganese oxides are readily reduced chemically by (e.g.) Fe(II) and are therefore not available to bacteria (Howarth 1993). Denitrification due to nitrate limitation in saltmarsh sediments is also considered negligible. Nitrate concentrations never exceeded 10 to 12 μM at the SERF location in October (J. E. Kostka unpubl.). It is not possible, however, to measure rates of aerobic respiration directly in saltmarsh sediments, since oxygen is utilized both in aerobic respiration and for oxidation of reduced metabolites like sulfide and Fe(II). Both bioturbation and oxygen leakage from roots clearly injects oxygen into the marsh sediment, and aerobic respiration must be of some importance, especially when the sediment is exposed to air at low tide. However, recent microelectrode profiles in the SERF marsh indicated that oxygen is absent within the first few millimeters depth of the sediment surface or next to macrofaunal burrows (Y. Furukawa et al. unpubl. results), and the quantitative importance of oxygen for total carbon oxidation has been found to be relatively low in other intertidal sediments. Thus, Kristensen et al. (2000) estimated that aerobic respiration is responsible for 6 to 65% of the carbon oxidation in vegetated and bioturbated mangrove sediments, while Mackin & Swider (1989) found less than 15% in Long Island saltmarsh sediment. Thus, based on the existing evidence, anoxic mineralization processes must predominate in SERF marsh sediments.

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