

# Rapid organic matter mineralization coupled to iron cycling in intertidal mud flats of the Han River estuary, Yellow Sea

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**Abstract** Organic matter oxidation represents a transfer of elements to inorganic nutrients that support biological productivity and food web processes. Therefore, quantification of the controls of organic matter mineralization is crucial to understanding the carbon cycle and biogeochemical dynamics in coastal marine environments. We investigated the rates and pathways of anaerobic carbon (C) oxidation in an unvegetated mud flat (UMF) and a vegetated mud flat (VMF) of the Ganghwa intertidal zone of the macro-tidal Han River estuary, Yellow Sea. Analyses of geochemical constituents revealed relatively oxidized conditions and high reactive Fe(III) concentrations (40–100  $\mu\text{mol cm}^{-3}$ ) in the sediments. A pronounced depth stratification in Fe(III) was observed at the VMF site likely due to the lower number of infaunal burrows along with dense root formation by the macrophytes, *Suaeda japonica*. Depth-integrated rates of anaerobic C mineralization as

well as sulfate- and Fe(III) reduction at the VMF were consistently higher than those at the UMF, likely driven by the dense vegetation that supplied organic C substrates and electron acceptors to the rhizosphere. Sediment inventories revealed that solid Fe(III) was up to 17 times more abundant than pore water sulfate, and direct rate measurements showed that microbial Fe(III) reduction comprised an equal or larger percentage of C oxidation (36–66 %) in comparison to sulfate reduction (36–40 %) at both sites studied. Time-course experiments indicated that sulfate reduction rates were likely underestimated, especially in the VMF rhizosphere, due to the reoxidation of reduced S in the presence of high Fe(III). The high rates of C mineralization suggest that the Ganghwa intertidal mud flats are a significant sink against the external loading of organic compounds, and organic matter mineralization is enhanced by chemical exchange regulated by extreme tidal flushing and macro-microorganisms interactions.

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## Introduction

Intertidal marine ecosystems provide critical services to coastal human inhabitants. These environments provide nursery grounds for commercially important

fish and shellfish species, limit nutrient exchange at the land-sea boundary, and protect coastal municipalities from catastrophic storms (Pomeroy and Wiegert 1981). Benthic intertidal zones are hotspots of organic matter cycling and their contribution to the exchange of carbon at the land-sea boundary is dependent upon complex controls including primary productivity, extent of plant cover and macrofauna, tidal amplitude, and geomorphology of the estuarine landscape (Odum 2000). Due to these complexities, quantification of the contribution of intertidal zones to the carbon budget in estuaries remains challenging. The carbon budget is fundamental to our understanding of ecosystem services provided by the intertidal zone and essential for the management of estuarine ecosystems (Jensen et al. 1995; Giblin et al. 1997; Holmer et al. 2001; Nielsen and Andersen 2003). Organic matter oxidation represents a transfer of elements from organic matter to inorganic pools, thereby releasing inorganic nutrients to support biological productivity and food web processes. Therefore, quantification of the controls of organic matter mineralization is crucial to understanding the carbon cycle and biogeochemical dynamics in coastal marine environments.

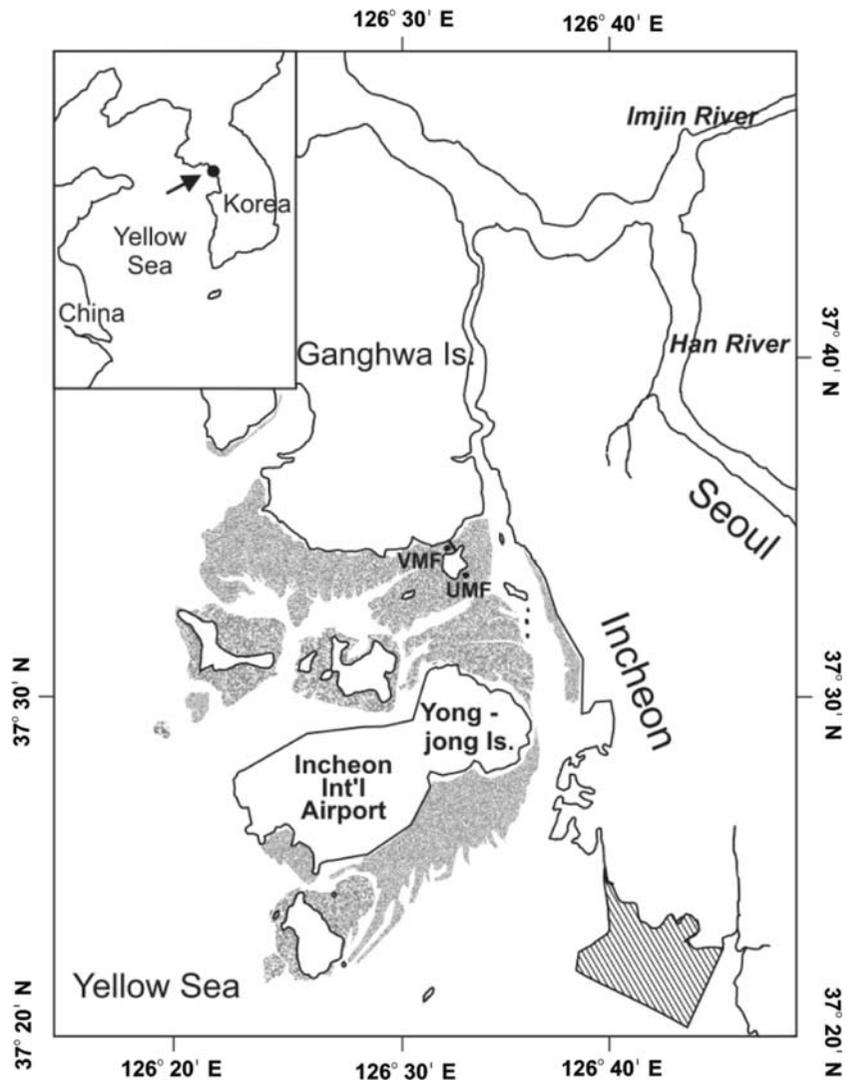
In organic-enriched intertidal sediments, rapid depletion of oxygen occurs within the top few millimeters of the sediment (King 1988; Furukawa et al. 2004), and thus most C oxidation occurs under anaerobic conditions (Howarth 1993; Alongi 1998). Anaerobic decomposition of organic matter in marine sediments is performed by a complex web of microbial processes, and the intensity of each process depends on the availability of organic substrates and terminal electron acceptors (Jørgensen 2000; Thamdrup and Canfield 2000). Because of the abundance of sulfate in seawater (ca. 25–28 mM), previous studies have shown that sulfate reduction dominates anaerobic C mineralization in shallow marine sediments (Jørgensen 1982; Howes et al. 1984; Capone and Kiene 1988; Howarth 1993). More recent studies have demonstrated that microbial Fe(III) reduction may outcompete sulfate reduction to comprise a substantial portion of carbon oxidation in marine sediments where concentrations of reactive Fe(III) exceed other electron acceptors (Lovley and Phillips 1987; Kristensen et al. 2000; Lowe et al. 2000; Kostka et al. 2002a; Canfield et al. 2005). Though microbial Fe(III) reduction has emerged as an important pro-

cess, few direct rate measurements of this process are available in the literature (Kostka et al. 2002a; Gribsholt et al. 2003).

Due to the abundance and reactive properties of S and Fe in the sediment, determining the significance of sulfate- and Fe(III) reduction in C oxidation is particularly important to understanding the role of benthic processes in regulating biogeochemical nutrient cycles in coastal environments (Jensen et al. 1995; Holmer et al. 2001; Koretsky et al. 2003; Dollhopf et al. 2005). The rate of C mineralization and the relative contribution of sulfate- and Fe(III) reduction in C oxidation processes are largely affected by a number of environmental controls, such as bioturbation, vegetation, frequency of tidal inundation, and geophysical properties of the sediment. Plant roots supply both electron donors for stimulating microbial metabolism and oxygen, which is responsible for the rapid regeneration of various electron acceptors (Hines et al. 1989, 1999; King and Garey 1999; Neubauer et al. 2005; Koretsky et al. 2008a, 2008b). At the same time, macrofaunal burrowing activity profoundly affects the mineralization of organic matter primarily through sediment reworking that supplies labile organic matter to the subsurface sediment and irrigation that expedites the exchange of solutes between the sediment and overlying water (Aller 1994, 2001; Kristensen 2001; Nielsen et al. 2003; Koretsky et al. 2005). The frequency of inundation by tidal waters also regulates gas exchange at the sediment-water interface, thereby determining the geochemical constituents and rates and pathways of mineralization in the sediment (Boudreau and Jørgensen 2001; Gribsholt and Kristensen 2002, 2003; Hyun et al. 2007).

The west coast of South Korea harbors an extensive intertidal wetland (area of approximately 2,000 km<sup>2</sup>), and Gyeonggi-do Province, including the study site (the Ganghwa intertidal mud flat), comprises 35% (ca. 840 km<sup>2</sup>) of the total coastal wetland in South Korea (ca. 2,400 km<sup>2</sup>) (MOMAF 1999). One of the most unique environmental properties characterizing this region is the large tidal range (average of >8 m) (OHA 1978). This enormous tidal range together with massive runoff from the eutrophic Han River affects the semidiurnal fluctuations of physico-chemical and microbiological factors in the water column (Hyun et al. 1999a, b). During low tide, the intertidal sediments are extensively exposed, further suggesting that the area may act as an important reservoir mineralizing

**Fig. 1** Study area and distribution of intertidal mud flats (*shaded area*) in the vicinity of Ganghwa. The *hatched area* indicates a recently reclaimed site for the construction of a new city (Song-do). The Incheon international airport and surrounding areas were once intertidal sediments



the external loading of organic matter from the Han River, which passes through the Seoul-Incheon metropolitan area with a population of over 20 million people (Hyun et al. 2004). This coastal area also serves as a major habitat for many intertidal fishes and invertebrates and thus provides a resting and feeding area for endangered domestic waterfowl and birds migrating between Australia and Siberia (MOMAF 1999; Lee and Kim 2006). However, due to the presence of a large human population and consequent industrial needs, a substantial portion of the intertidal wetland in the region is continuously being reclaimed for the construction of new cities and airports (Fig. 1) with relatively little concern for the

ecological and environmental impacts (MOMAF 1999). Despite its significant areal scale and environmental significance, we know of no studies examining the rates and pathways of organic matter mineralization in the intertidal wetlands of the macro-tidal Han River estuary. The objectives of our study were: (1) to characterize the geochemical conditions of the sediments, (2) to quantify the rates and pathways of anaerobic carbon oxidation through direct rate measurements, and (3) to elucidate the major environmental controls of C oxidation in two contrasting habitats, an unvegetated mud flat (UMF) and a vegetated mud flat (VMF) in the Ganghwa intertidal sediments during the summer.

## Materials and methods

### Study area

The Ganghwa intertidal mud flat is located at the mouth of the macro-tidal Han River estuary in South Korea and comprises a major portion (~340 km<sup>2</sup>) of the intertidal wetlands of Gyeonggi-do Province (Fig. 1). The majority of the mid- to upper intertidal zone is vegetated by *Suaeda japonica*, the dominant annual intertidal salt marsh plant that reaches heights of ~20 cm and flowers in September (Min 1998). Sampling was conducted in July 2003, during the active growing season of *S. japonica*. The rhizosphere of the *S. japonica* was visually identified by the orange-color between 3 and 7 cm depth of the VMF sediments. Sediment samples were collected from the UMF, which is a typical intertidal mud flat along the west coast of Korea, and the VMF, which was inhabited by *S. japonica*. Both sites, particularly the UMF, are highly bioturbated by crabs and polychaete worms (Koo et al. 2007).

### Sediment handling

Duplicate or triplicate sediment samples for geochemical analysis were collected using polycarbonate cores (6 cm i.d.). Cores were immediately sealed with butyl rubber stoppers, and cooled on ice until processed in the laboratory. Cores were transferred to a nitrogen filled glove bag, where the sediment was sectioned. The sediment was loaded into polypropylene centrifuge tubes in a N<sub>2</sub>-filled glove bag. The tubes were tightly-capped and centrifuged for 15 min. at 5,000×g. After reintroduction into the glove bag, pore waters were sampled and filtered through 0.2 μm cellulose acetate syringe filters. Sediments for solid-phase analysis were frozen for future analysis.

### Pore-water and solid-phase analysis

Pore-water for the determination of total CO<sub>2</sub> and NH<sub>4</sub><sup>+</sup> analyses was filtered into 1.8 ml glass vials that were capped with Teflon-coated butyl rubber septa, leaving no gas phase. The samples were stored at 4°C after adding 18 μl of HgCl<sub>2</sub> (125 mM) to eliminate the interference of hydrogen sulfide (Lustwerk and Burdige 1995), and analyzed within a few days of sampling by flow injection with conductivity

detection (Hall and Aller 1992). Dissolved Fe<sup>2+</sup> in pore water fixed with HCl (0.1N) was determined by colorimetry with a ferrozine solution (Stookey 1970). Dissolved sulfide was determined on filtered pore water after precipitation with Zn acetate using the methylene blue method (Cline 1969). Sulfate concentrations were measured in acidified pore water using ion chromatography (Metrohm 761).

For determination of solid phase Fe, wet chemical extraction was used to determine the poorly crystallized Fe(III) oxide minerals. Total Fe was extracted from air-dried sediment in a 0.2 M oxic oxalate solution (pH 3) for 4 h (Thamdrup and Canfield 1996), and Fe(II) was extracted in anoxic oxalate (Phillips and Lovley 1987). Total oxalate-extractable Fe and Fe(II) were determined with ferrozine as described above. Solid Fe(III) was defined as the difference between total Fe and Fe(II). Sediments that were fixed with Zn acetate at the end of the incubation for the SO<sub>4</sub><sup>2-</sup> reduction measurement were used for the determination of total reduced sulfur (TRS), which includes acid volatile sulfide (AVS = FeS + H<sub>2</sub>S) and chromium-reducible sulfur (CRS = S<sup>0</sup> + FeS<sub>2</sub>). The TRS was recovered using single-step distillation with cold 12 M HCl and boiling 0.5 M Cr<sup>2+</sup> solution (Fossing and Jørgensen 1989), and then the sulfide was determined according to the method of Cline (1969).

### Chlorophyll-a, organic carbon and nitrogen

Chlorophyll-a concentrations in the surface sediment (0–2 cm) were determined using spectrophotometry according to Parsons et al. (1984). The content of particulate organic carbon (POC) and nitrogen (PON) in the surface sediment were analyzed using a CHN analyzer (CE Instrument, EA 1110).

### Rates of total CO<sub>2</sub> production, sulfate- and Fe(III) reduction

For determination of the rates and pathways of anaerobic carbon mineralization, bulk sediment from 0 to 6 cm depth was collected using a trowel into a polypropylene bag that was immediately sealed with no head space (Hyun et al. 2007). Sediment was homogenized and loaded into 50 ml centrifuge tubes in a N<sub>2</sub>-filled glove bag. The tubes were incubated at in situ temperature in the dark. The tubes were then sacrificed at regular intervals, and

**Table 1** Physico-chemical properties of the Ganghwa intertidal sediments

Site	Porosity	Density (g cm <sup>-3</sup> )	Water content (%)	POC (% dry wt)	PON (% dry wt)	Chl <i>a</i> (mg m <sup>-2</sup> )
UMF	0.61 (±0.02)	1.59 (±0.05)	38.34 (±1.83)	0.849 (±0.118)	0.053 (±0.002)	24.39
VMF	0.60 (±0.04)	1.52 (±0.11)	40.05 (±5.52)	0.980 (±0.072)	0.058 (±0.003)	54.79

Values represent averages ±1 SD (*n* = 3)

the pore waters were extracted by centrifugation and filtered as described above. Anaerobic carbon respiration rates were determined from the accumulation of CO<sub>2</sub> in the pore water as described above. Another set of incubation experiments was further performed to elucidate the significance of organic substrates in controlling respiration rates. Sediment samples from 0 to 6 cm depth were collected as described above, and were amended with acetate (f.c., 5 mM) in the N<sub>2</sub> filled glove bag. Total CO<sub>2</sub> (TCO<sub>2</sub>) produced during the incubation was measured as described above.

After pore water retrieval from the C mineralization incubation experiment, the sediment was homogenized under a N<sub>2</sub> atmosphere, and Fe(II) was extracted in oxalate as described above. Fe(III) reduction rates were determined by the linear regression of Fe(II) concentration with time (Kostka et al. 2002a, Hyun et al. 2007). Sulfate reduction rates were determined using the radiotracer method of Jørgensen (1978). Triplicate intact cores (15 cm long with 2 cm i.d.) were collected at each site. Two μCi of <sup>35</sup>SO<sub>4</sub><sup>2-</sup> were injected into the injection port at 1 cm intervals, and cores were incubated for 2 h at *in situ* temperature. At the end of the incubation, the sediment was sliced into sections, fixed in Zn acetate (20%), and frozen until processed in the laboratory. The reduced <sup>35</sup>S was recovered using distillation with a boiling acidic Cr<sup>2+</sup> solution according to Fossing and Jørgensen (1989). The re-oxidation of the reduced sulfur compounds produced during the 2 h incubation may lead to the underestimation of sulfate reduction, especially in highly bioturbated surface sediments and in the rhizosphere of actively growing plants (Jørgensen 1994; Moeslund et al. 1994; Isakson and Finster 1996). Therefore, to evaluate the re-oxidation of reduced sulfur, we performed separate experiments using different incubation times (30 min, 1 h, and 2 h) in the sediments collected at both the surface (0–2 cm) and subsurface (4–6 cm) of the UMF and VMF.

## Results

### Ecological parameters

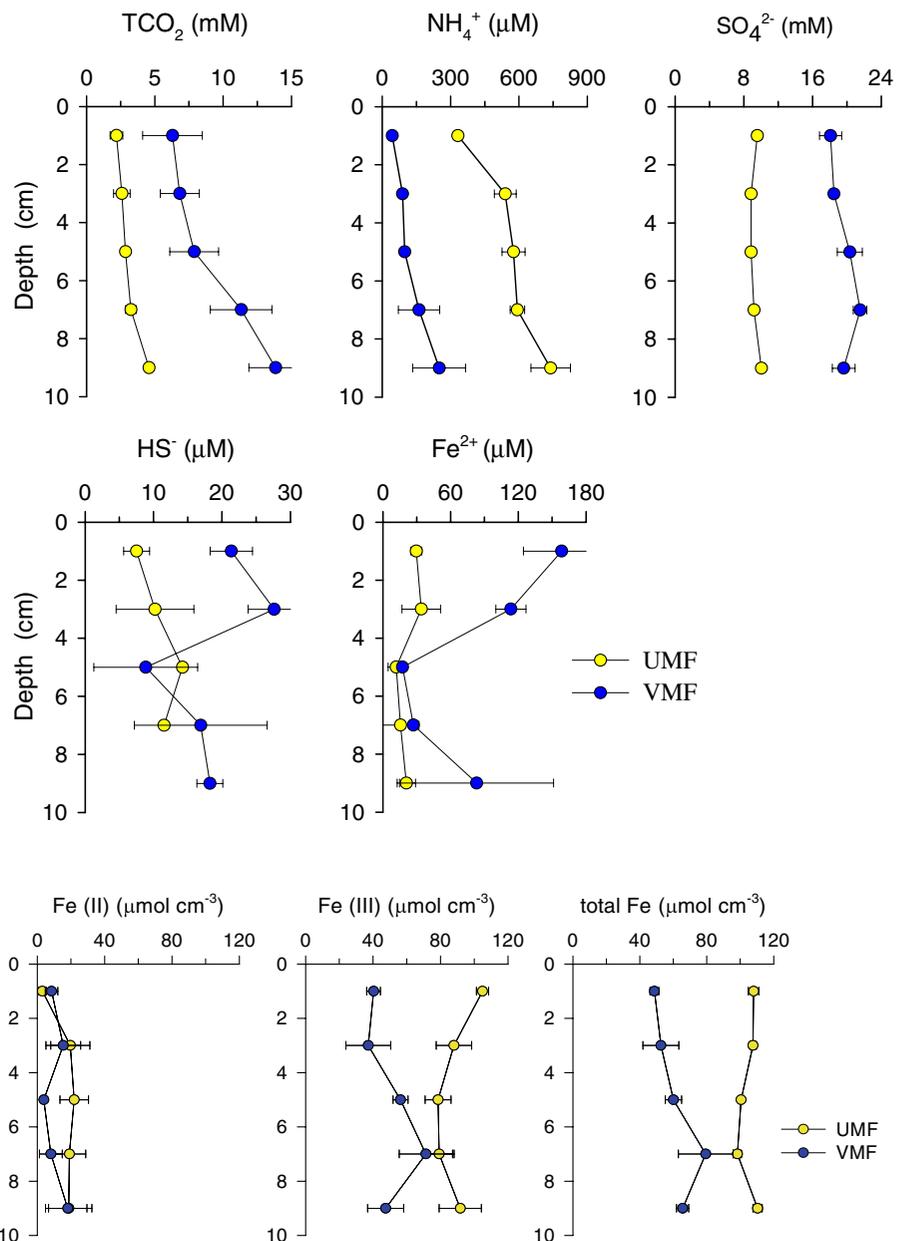
The sediment temperature at 0–2 cm depth was 30°C at both sites. The salinity at the UMF site (13 psu) was lower than that of the VMF site (27 psu). Oxygen was depleted from the top 1–2 mm of the surface sediment (Kim 2006). Both sites contained muddy sediments with a high organic matter content, ranging from 8.49 (UMF) to 9.80 mg g<sup>-1</sup> (VMF) (Table 1). The chlorophyll *a* concentration measured in the upper 2 cm was twice as high at the VMF (54.8 mg m<sup>-2</sup>) than at the UMF (24.4 mg m<sup>-2</sup>), indicating that the VMF provides more labile organic substrates to stimulate microbial metabolism in the summer.

### Pore-water and solid-phase geochemistry

Concentrations of TCO<sub>2</sub> were higher at the VMF than at the UMF (Fig. 2). Relatively high amounts of NH<sub>4</sub><sup>+</sup> and low concentrations of SO<sub>4</sub><sup>2-</sup> at the UMF were associated with high nutrient freshwater runoff (i.e., the Han River). The lower NH<sub>4</sub><sup>+</sup> concentration at the VMF may be associated with nitrogen uptake by actively growing plants and/or enhanced microbial ammonium nitrification via oxygen supplied from the plant roots (White and Howes 1994; Alongi 1998; Dollhopf et al. 2005).

The highly bioturbated UMF site was characterized by lower Fe<sup>2+</sup> and HS<sup>-</sup> (Fig. 2) but exceptionally higher reactive Fe(III) (>80 μmol cm<sup>-3</sup>) compared to the VMF (Fig. 3). Vertical distributions of the redox-sensitive Fe and S constituents were relatively homogenous with depth at the UMF, but exhibited marked differences with depth at the VMF. The rhizosphere of the VMF, that was visually identifiable by its orange-color, appeared to be the most oxidized with the lowest concentrations of Fe<sup>2+</sup> and HS<sup>-</sup> and the highest concentrations of reactive Fe(III), whereas the most reduced conditions were observed in the

**Fig. 2** Vertical distributions of pore water constituents at each site (UMF, unvegetated mud flat; VMF, vegetated mud flat)



**Fig. 3** Vertical distributions of total reduced sulfur (TRS), solid phase Fe(II) and Fe(III), and total Fe at each site

surface sediment of the VMF (Figs. 2, 3) because of decreased bioturbation resulting from dense root formation during active plant growth (Koo et al. 2007). The lowest concentrations of sulfide and Fe<sup>2+</sup> in the rhizosphere indicated that re-oxidation of reduced HS<sup>-</sup> and Fe<sup>2+</sup> occurs in this relatively oxidized subsurface rhizosphere (Emerson et al. 1999; Sobolev and Roden 2001; Weiss et al. 2003).

The concentrations of total reduced S (TRS = H<sub>2</sub>S + S<sup>0</sup> + FeS + FeS<sub>2</sub>) at both sites were relatively constant with depth (Fig. 3), and the depth-integrated amounts of TRS were also similar at both sites (Table 2). Both total Fe and Fe(III) in solid phase were 1.7 times higher at the UMF than at the VMF, and most solid phase Fe (>80%) occurred as reactive Fe(III) (Table 2). We observed a marked Fe(II)

**Table 2** Depth-integrated (0–8 cm) concentrations of S and Fe constituents in the pore water and sediments

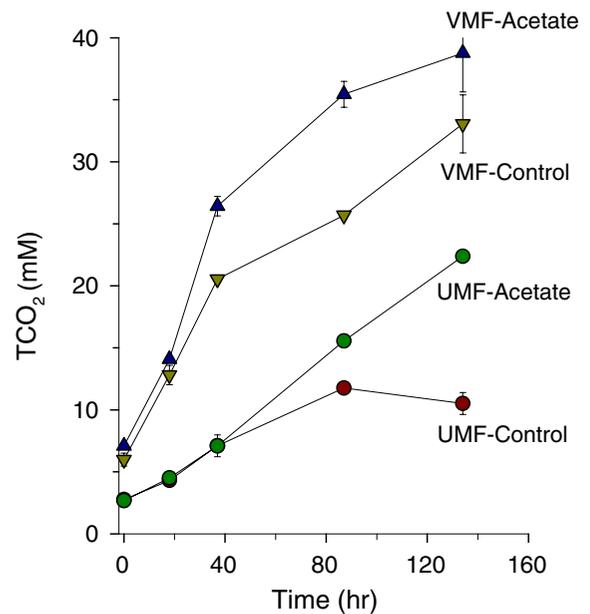
Site	Depth integration range (cm)	Pore water (mmol m <sup>-2</sup> )			Solid phase (mmol m <sup>-2</sup> )		
		SO <sub>4</sub> <sup>2-</sup>	H <sub>2</sub> S	Fe <sup>2+</sup>	TRS	Fe(II)	Fe(III)
UMF	0–4	225	0.25	0.78	958	453	3,860
	4–8	219	0.25	0.33	862	821	3,156
VMF	0–4	447	0.53	3.45	967	478	1,550
	4–8	510	0.26	0.51	909	238	2,552

minimum layer at the root zone (5–7 cm) of *Suaeda japonica* at the VMF, in which reactive Fe(III) exhibited a maximum value (Fig. 3).

#### Microbial metabolic rate measurements

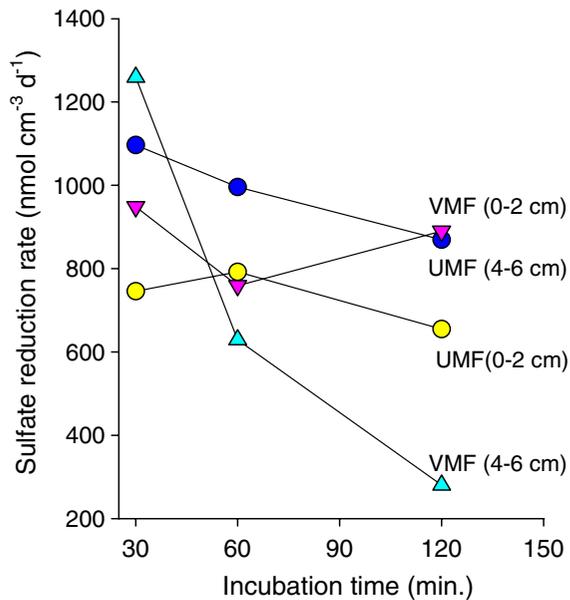
Anaerobic C respiration rates were determined from the accumulation of TCO<sub>2</sub> with time during sediment incubations. The concentrations of pore water TCO<sub>2</sub> generally linearly increased during anoxic incubation for 80 and 40 h at the UMF and VMF, respectively, (Fig. 4). Rates of TCO<sub>2</sub> production at the two sites indicated that anaerobic C respiration at the VMF (0.3932 mM h<sup>-1</sup>;  $r^2 = 0.9858$ ,  $n = 3$ ) exceeded those at the UMF (0.1040 mM h<sup>-1</sup>;  $r^2 = 0.987$ ,  $n = 3$ ) by a factor of 4. Respiration rates in sediments amended with acetate were 2.2 times higher than those in unamended sediments at the UMF, whereas only a small increase (1.2 times) was observed at the VMF after 134 h of incubation (Fig. 4).

Sulfate reduction rates (SRR) in sediments collected from the rhizosphere (4–6 cm) of the VMF decreased approximately 75% during 2 h incubations compared to values from 30 min incubations. In contrast, we observed less than a 20% difference in samples collected from 0 to 2 cm and 4–6 cm depth at the UMF and 0–2 cm depth at the VMF (Fig. 5). These results suggested that re-oxidation of reduced sulfur produced from sulfate reduction during 2 h incubations underestimated sulfate reduction by a factor of 4 in the rhizosphere of the VMF. Because the sulfate reduction rate measurements were primarily determined using 2 h incubations, the rates in the rhizosphere (4–6 cm) of the VMF (Fig. 6) have been re-calculated by multiplying by a factor of 4 to compensate for the underestimation of SRR due to the re-oxidation of reduced <sup>35</sup>S.



**Fig. 4** Anaerobic carbon respiration determined from the accumulation of total CO<sub>2</sub> in incubations of unamended sediments (controls) and acetate-amended sediments collected at the UMF and VMF sites

Both sulfate- and Fe(III) reduction rates were higher at the VMF than at the UMF. The SRR averaged across 10 cm of the sediment was three times higher at the VMF ( $871 \pm 645$  nmol S cm<sup>-3</sup> d<sup>-1</sup>) than at the UMF ( $291 \pm 67$  nmol S cm<sup>-3</sup> d<sup>-1</sup>). The highest SRR occurred in the rhizosphere of the VMF, whereas the SRR at the UMF was relatively low and constant with depth (Fig. 6). During the 40 h incubations, the concentrations of solid-phase Fe(II) linearly increased at both sites (Fig. 7a), with concomitant accumulations of dissolved Fe<sup>2+</sup> in the pore water of the VMF (Fig. 7b). The Fe(III) reduction rate, as estimated from the linear regression of the solid-phase Fe(II)



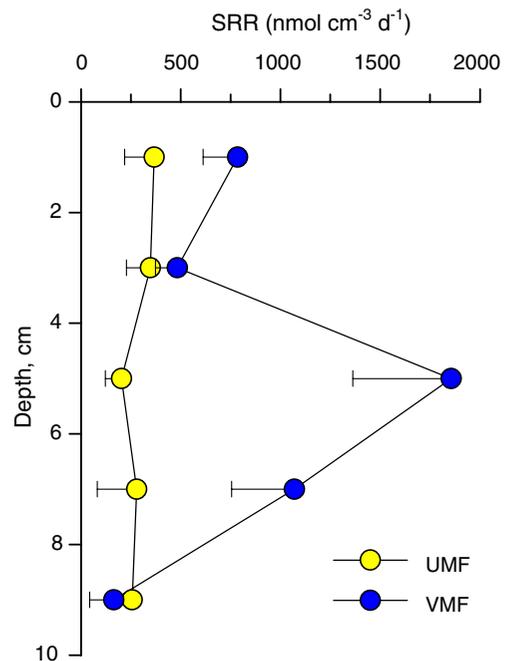
**Fig. 5** Variation in the rates of sulfate reduction with different incubation times (i.e., 0.5, 1, and 2 h)

accumulation, was 2.4 times higher at the VMF ( $0.272 \mu\text{mol g}^{-1} \text{h}^{-1}$ ,  $r^2 = 0.983$ ,  $n = 3$ ) than at the UMF ( $0.115 \mu\text{mol g}^{-1} \text{h}^{-1}$ ,  $r^2 = 0.975$ ,  $n = 3$ ).

## Discussion

### Geochemical characterization of the sediment

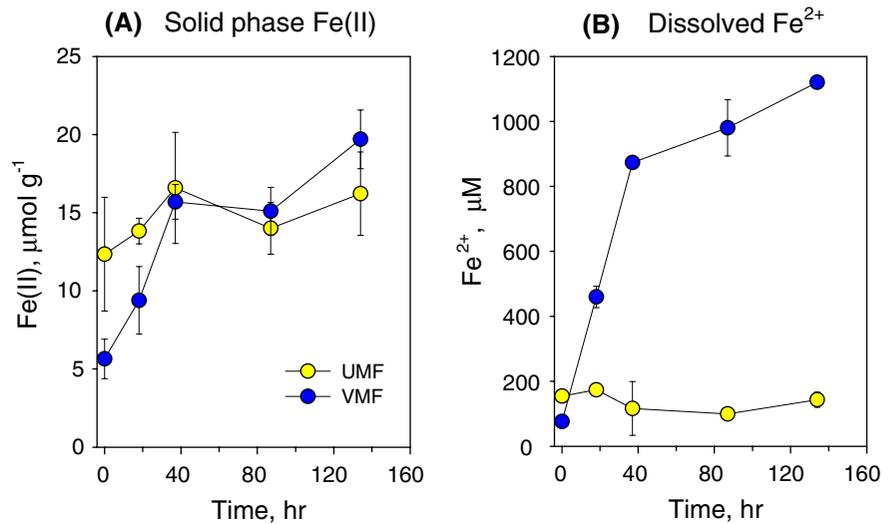
One of the remarkable features observed from the inventories of geochemical constituents was that the sediments of the UMF and VMF sites exhibited high amounts of reactive Fe(III) (Table 2). The observed concentrations of Fe(III) ( $40$  to  $100 \mu\text{mol cm}^{-3}$ ) were comparable to other coastal marine environments (Hansen et al. 1996; Kristensen et al. 2000; Kostka et al. 2002a; Hyun et al. 2007), with the exception of Amazon inner shelf muds (Aller et al. 1996). However in this study, Fe(III) was more abundant relative to sulfate (Fe(III): $\text{SO}_4^{2-}$  = from 3.44 to 17.16; Table 2) in comparison to previous studies carried out in the salt marsh (Fe(III): $\text{SO}_4^{2-}$  = from 1.38 to 2.94; Hyun et al. 2007). Most of the Fe deposited in marine sediments is supplied from river runoff (Poulton and Raiswell 2002). Because Fe(III) oxide exists primarily in the solid phase, high reactive Fe(III) concentrations in anoxic marine sediments are associated with sediment mixing either through bioturbation by



**Fig. 6** Vertical profiles of sulfate reduction rates (SRRs) at each site. SRRs in the rhizosphere (4–6 cm) of VMF were recalculated by multiplying by a factor of 4 to compensate for the 4-fold underestimation of SRRs by the re-oxidation of reduced  $^{35}\text{S}$  during 2 h incubations as shown in Fig. 5

macrofauna or sediment resuspension by waves and currents (Thamdrup 2000; Canfield et al. 2005). Kristensen and Kostka (2005) estimated that bioturbation due to the presence of various infaunal burrows increased the area of the sediment-water interface by 50–400%, which enhanced the exchange of solutes between sediments and overlying water, thereby increasing the supply of various electron acceptors (Aller 2001; Kristensen 2001). Because the Ganghwa intertidal zone is situated at the mouth of the Han River, its sediments are directly affected by freshwater inputs that transport most of the iron to the area. The UMF site is highly bioturbated by various macrofauna, such as crabs (*Cleistostoma dilatatum* and *Macrophthalmus japonicus*) and polychaete worms (*Perineris aibuhitensis* and *Periserrula leucophryna*), which construct burrows to escape physiological damage due to high temperatures and desiccation in the summer (Koo et al. 2005, 2007). Koo et al. (2007) demonstrated that these deep infaunal burrows increased the area of the sediment-water interface by up to 90% at the UMF. The high concentrations of Fe(III) in the study area may also be controlled by the

**Fig. 7** Reduction of Fe(III) determined from the accumulation of **a** solid-phase Fe(II) and **b** Fe<sup>2+</sup> during sediment incubations



particularly large tidal range of >8 m (OHA 1978), which results in extensive exposure of the sediments and draining of interstitial waters during low tide. We hypothesize that the relatively oxidized conditions and high Fe(III) concentrations of the Ganghwa intertidal zone sediments are due to the macro-tidal system of the Han River estuary, which regulates the renewal of iron and chemical exchange at the sediment-water interface (King et al. 1982). The comparable high solid Fe(III) content and low concentrations of CO<sub>2</sub>, HS<sup>-</sup>, and Fe<sup>2+</sup> in the pore waters at both sites are indicative of tidal flushing (Boudreau and Jørgensen 2001).

In contrast to the UMF, the distribution of geochemical constituents at the VMF showed clear depth gradients oriented around the rhizosphere (Figs. 2, 3). At the VMF, burrow dimensions were much smaller and the increase in the area of the sediment-water interface was only 21%, because the roots of the actively growing marsh plant *Suaeda japonica* in the summer were too dense for burrow construction by adult macrofauna (Bertness 1985; Leven and Talley 2000; Koo et al. 2007). Mesocosm studies have also demonstrated that dense growth of *Spartina anglica* has antagonistic effects on the polychaete *Nereis diversicolor* (e.g., Gribsholt and Kristensen 2002). The less bioturbated surface sediments at the VMF may dampen the effects tidal flushing, thereby generating relatively reduced conditions. Enhanced concentrations of reactive Fe(III) together with the relatively oxidized conditions in the rhizosphere of the VMF (Figs. 2, 3) were likely associated with O<sub>2</sub>

supply via plant roots. Consequently, the geochemical conditions of the two typical habitats of the Ganghwa intertidal sediments were largely determined by: (1) the intensity of sediment mixing by bioturbation in concert with tidal flushing at the UMF site, and (2) vegetation that inhibited the formation of infaunal burrows at the surface layer and provided O<sub>2</sub> to the rhizosphere of the VMF site.

#### Controls of C oxidation by sulfate- and Fe(III) reduction

The rates and pathways of C oxidation processes in the sediments are highly dependent on the availability of electron acceptors (i.e., sulfate and poorly crystalline Fe-oxides) and electron donors (i.e., labile organic substrates; Jørgensen 2000; Canfield et al. 2005). Macrophytes and benthic macrofauna act together with hydrology to control geochemical exchange in organic-enriched coastal sediments (Aller 1994, 2001; Hansen et al. 1996; Gribsholt and Kristensen 2002, 2003; Nielsen et al. 2003; Neubauer et al. 2005; Hyun et al. 2007; Koretsky et al. 2008a, 2008b). In the Ganghwa intertidal sediments, the presence of *Suaeda japonica* at the VMF had a clear stimulating effect on C oxidation processes (Figs. 4, 6, 7). Depth-integrated C mineralization rates were 3.8 times higher at the VMF compared to the UMF, and differences in rates measured in acetate-amended sediments suggested that the availability of labile carbon substrates was responsible for the elevated rates at VMF. Dissimilatory Fe(III) reduction rates

**Table 3** Partitioning of depth integrated (0–6 cm) sulfate- and Fe(III) reduction in rates of C oxidation (units, mmol m<sup>-2</sup> d<sup>-1</sup>)

Site	Anaerobic C oxidation rate	Sulfate reduction rate	Total Fe(III) reduction rate	Fe(III) reduction by		C oxidation by	
				Sulfide oxidation <sup>a</sup>	Fe(III) reducer <sup>a</sup>	Sulfate reduction <sup>a</sup>	Fe(III) reduction <sup>a</sup>
UMF	92	18	254	12 (4.7%) <sup>b</sup>	242 (95.3%) <sup>b</sup>	37 (39.9%) <sup>c</sup>	60 (65.7%) <sup>c</sup>
VMF	351	63	549	42 (7.7%) <sup>b</sup>	507 (92.3%) <sup>b</sup>	126 (35.9%) <sup>c</sup>	127 (36.1%) <sup>c</sup>

<sup>a</sup> Stoichiometric equations were used to estimate the partitioning of C mineralization: Abiotic reduction of Fe(III) by sulfide oxidation:  $3\text{H}_2\text{S} + 2\text{FeOOH} = 2\text{FeS} + \text{S}^0 + 4\text{H}_2\text{O}$ ; Microbial Fe(III) reduction = Total Fe(III) reduction – abiotic Fe(III) reduction; C oxidation by sulfate reduction:  $\text{SO}_4^{2-} + \text{CH}_3\text{COO}^- + 2\text{H}^+ = 2\text{CO}_2 + 2\text{H}_2\text{O} + \text{HS}^-$ ; C mineralization by microbial Fe(III) reduction:  $4\text{FeOOH} + \text{CH}_3\text{COO}^- + 8\text{H}^+ = \text{CO}_2 + 7\text{H}_2\text{O} + 4\text{Fe}^{2+}$

<sup>b</sup> Indicates relative contribution (%) of abiotic and microbial Fe(III) reduction in total Fe(III) reduction

<sup>c</sup> Indicates relative contribution (%) of sulfate reduction and Fe(III) reduction to total anaerobic C respiration

were also five times higher at the VMF compared to the UMF (Table 3). These results are consistent with previous studies that reported enhanced microbial metabolism during active plant growth in salt marshes and seagrass beds (Isaksen and Finster 1996; Hines et al. 1999; Holmer et al. 2001; Gribsholt and Kristensen 2002, 2003; Smith et al. 2004; Hyun et al. 2007).

Burrowing activity by macrofauna can either stimulate or suppress anaerobic C oxidation. Burrows generally promote oxidized conditions through the increased area of the sediment-water interface, thereby suppressing sulfate reduction (Holmer et al. 1997; Banta et al. 1999; Nielsen et al. 2003), whereas the introduction of labile organic matter through sediment reworking may stimulate microbial metabolism (Hines and Jones 1985; Hansen et al. 1996). In the intertidal sediments of the Ganghwa estuary, we hypothesize that electron acceptors such as Fe(III) and sulfate are rapidly replenished due to periodic drainage and the extremely active semidiurnal tides which enhance chemical exchange at the sediment-water interface. Therefore, the input of labile carbon from macrophytes is likely responsible for the higher rates of sulfate- and Fe(III) reduction at the VMF.

Because iron oxyhydroxide plaques routinely occur due to chemical and plant iron oxidation, aquatic macrophyte roots may act to recycle Fe (Weiss et al. 2003) and thus serve as an important habitat for iron reducers. Roden and Wetzel (1996) found relatively large pools of ferric iron and rapid rates of iron reduction in the rhizosphere sediments of *Juncus effuses*. King and Garey (1999) demonstrated that Fe(III) reduction occurs on marine macrophyte roots under conditions that inhibit sulfate reduction. The highly oxidized geochemical profile in the rhizo-

sphere of the VMF (Figs. 2, 3) indicated that FeOOH was quickly regenerated by O<sub>2</sub> penetration into sub-surface sediments via the rhizosphere. Indeed, the turnover rate of Fe(III), as calculated from the depth-integrated Fe(III) reduction rate (Table 3) divided by the depth-integrated (0–6 cm) concentrations of Fe(III), was 4.4 times faster at the VMF (0.205 d<sup>-1</sup>) than at the UMF (0.047 d<sup>-1</sup>). Further, the rapid re-oxidation of reduced S during our incubations of sediments from the VMF rhizosphere (Fig. 5) is likely associated with the rapid recycling (i.e., reduction) of FeOOH. Previous research demonstrated that actual sulfate reduction rates in the oxidized layer of sediments were underestimated several-fold due to a rapid re-oxidation of radioactive sulfide during incubation (Jørgensen 1994; Moeslund et al. 1994; Isaksen and Finster 1996). In a study of the root zone of seagrass bed sediments, Isaksen and Finster (1996) reported that the drop in <sup>35</sup>S-sulfide activity with incubation time must have been due to a re-oxidation of sulfide by oxidized inorganic compounds such as Fe(OH)<sub>3</sub> and MnO<sub>2</sub>, and possibly by oxygen excreted from the roots.

#### Partitioning of C oxidation by sulfate- and Fe(III) reduction

Few studies have quantified the contribution of microbial Fe(III) reduction to carbon oxidation in marine sediments through direct rate measurements of Fe(III) reduction (Canfield et al. 2005). This study of the Ganghwa intertidal zone revealed some of the most rapid rates of Fe(III) reduction and Fe turnover yet measured. Using a mass balance approach, we further showed that microbial Fe(III) reduction outcompeted sulfate reduction to comprise one-half or more of

overall anaerobic carbon oxidation (Table 3). At the UMF site, sulfate- and Fe(III) reduction added up to approximately 70% of total C oxidation (Table 3). This discrepancy in the mass balance may be due to the fermentation of organic substrates (Jørgensen 2000) or the coupling of carbon oxidation to other terminal electron accepting processes ( $O_2$ , nitrate, Mn(IV), or humic acid reduction). Using  $O_2$  microelectrode profiling, Kim (2006) recently observed that most  $O_2$  consumption occurred within the top 1–2 mm of the surface sediment and it was estimated that C oxidation by aerobic respiration accounted for less than 10% at the UMF. However, subsurface injection of oxygen via plant roots and burrow walls may enhance aerobic respiration to a certain extent. An (2005) also estimated that denitrification was responsible for less than 5% of C oxidation in unvegetated intertidal sediments near the UMF site. Although we considered the re-oxidation effect of reduced sulfur during 2 h incubations (Fig. 5) and recalculated the SRR based on 30 min incubations (Fig. 6), it is also possible that we have still underestimated the SRR when compared to 15 min incubations (Isaksen and Finster 1996).

At the highly bioturbated UMF site, microbial Fe(III) reduction was the most dominant process of C oxidation, accounting for 65.7% of total C oxidation (Table 3). The importance of Fe(III) reduction at the UMF was strongly associated with high reactive Fe(III) concentrations caused by bioturbation. Nielsen et al. (2003) found that sulfate reduction decreased on the walls of *Arenicola marina* (Polychaeta) burrows due to irrigation of oxygenated water, which suppressed the potential stimulating effect of the increase in organic C availability from mucus secretions of the worm. In contrast, irrigation and sediment reworking by *A. marina* increased the content of biologically reactive Fe(III) (Nielsen et al. 2003). A kinetic model based on field observations also revealed that dissimilatory Fe(III) reduction accounted for most C oxidation at high concentrations of poorly crystalline Fe(III) oxide ( $>40 \mu\text{mol cm}^{-3}$ ) in subtidal (Jensen et al. 2003) and salt marsh sediments (Kostka et al. 2002a; Gribsholt et al. 2003). Therefore, our observations of high Fe(III) reduction under high Fe(III) conditions coincide with previous research in other coastal and marine sediments.

Through rapid recycling of Fe(III) oxide, dissimilatory Fe(III)-reducing bacteria outcompete sulfate-reducing and methanogenic bacteria for organic C ox-

idation in the sediments (Lovley and Phillips 1987; Lovley 1991; Roden and Wetzel 1996). Despite the exceptionally higher concentration of amorphous Fe(III)-oxides (Table 2), the contribution of sulfate reduction to C oxidation (39.9% at the UMF and 35.9% at the VMF) was also substantial (Table 3). The presence of reduced S in the pore water and solid phase constituents also supports the high metabolic activity of sulfate-reducing bacteria (SRB; Table 2). Postma and Jakobsen (1996) suggested that, depending on the stability of the Fe oxide, the simultaneous occurrence of Fe(III)- and sulfate reduction is thermodynamically plausible, and sulfate reduction may even occur before Fe(III) reduction. The crystallinity of iron oxide, the surface area of iron oxides available for iron reducers, and/or the sorption of  $Fe^{2+}$  to iron oxide surfaces may affect competition between Fe(III)- and sulfate reduction as well as methanogenic processes (see Canfield et al. 2005). In addition, the active re-oxidation of reduced sulfur by  $O_2$  in the rhizosphere of the VMF (Fig. 5) alleviated the negative effect of  $O_2$  suppressing the activity of SRB. Therefore, high sulfate reduction can be maintained by the various groups of microorganisms responsible for the reduction of sulfur compounds in the organic-enriched rhizosphere. Simultaneous molecular phylogenetic analyses of 16S rRNA gene sequences in the same study areas revealed that diverse clones related to SRB, such as *Desulfobacterium*, Sva 0103, *Desulfobulbus*, and *Desulfosarcina* (Rooney-Varga et al. 1997; Ravenschlag et al. 1999, 2000; Bowman and McCuaig 2003) were identified in the rhizosphere of the VMF, whereas only one type of clone related to *Desulfobacterium* was identified at the same depth (5–6 cm) at the UMF site (Hyun et al. unpublished data).

#### Environmental role of the Ganghwa intertidal wetlands

The observed rates of C oxidation, sulfate-, and Fe(III) reduction (Table 4) were generally higher than or comparable to those observed previously in organic-enriched salt marsh sediments (Kostka et al. 2002a, b; Gribsholt and Kristensen 2002, 2003; Hyun et al. 2007), in mangrove forests (Holmer et al. 1999; Kristensen et al. 2000), and in seagrass beds (Holmer et al. 2001; Smith et al. 2004). Our results indicate that the Ganghwa intertidal sediments are a region of active mineralization of organic matter transported to

**Table 4** Summary of the rates ( $\text{mmol m}^{-2} \text{d}^{-1}$ ) of carbon (C) oxidation, sulfate reduction (SRR), and Fe(III) reduction (FeRR) from various coastal habitats

Habitat	Location	Station ID	Environmental description	Temp (°C)	Integrated Depth (cm)	C oxidation rate	SRR	FeRR	Reference
Tidal flat	Ganghwa, S. Korea	UMF	Unvegetated intertidal mud flat, highly bioturbated	30	0–6	92	18	242	This study
		VMF	Less bioturbated intertidal mud flat, vegetated by <i>Suaeda japonica</i>	30	0–6	351	63	507	
Salt marsh	Skidaway, Georgia, USA	SS (MM)	Inundated high marsh, less bioturbated, vegetated by short <i>Spartina</i>	28–31	0–6	54	25	Nd	Kostka et al. (2002a) Hyun et al. (2007)
		TS (BVL)	Well drained mid-marsh, bioturbated, vegetated by tall <i>Spartina</i>	28–31	0–6	80–300	46	346–427	
		CB (BUC)	Tidal creek bank, bioturbated, unvegetated	28–31	0–6	64	21	167	
		CB (NUC)	Tidal creek bank, non-bioturbated, unvegetated	28–31	0–6	49	20	nd	
	Westerschelde, Netherlands	1	Open mud flat, unvegetated	15	0–18	34–85	7–12		Gribsholt and Kristensen (2003)
		2, 3	Boundary between mud flat and vegetated marsh (marsh cliff)	15	0–18	100–824	106–167		
		4, 5, 6	Exposed high marsh, vegetated by <i>Spartina</i>	15	0–18	109–247	10–19		
Seagrass	Pensacola Bay, Florida, USA	–	Vegetated	25–30	0–10	–	53	–	Smith et al. (2004)
		–	Unvegetated	25–30	0–10	–	11	–	
	Phuket, Thailand	Bare	Unvegetated	–	0–16	–	2	–	Holmer et al. (2001)
		Cymodocea	Vegetated by <i>Cymodocea</i>	–	0–10	–	7	–	
		Thalassia	Vegetated by <i>Thalassia</i>	–	0–10	–	2	–	
Mangrove	Bangrong, Thailand	MA	Landward edge, Vegetated	28	0–16	46–48	1–23	–	Holmer et al. (1999)
		MB	Mid intertidal, Vegetated	28	0–16	25–95	4–8	36	Kristensen et al. (2000)
		MC	Main channel, Unvegetated	28	0–16	24–97	3–6	17	
		MD	Low intertidal, Unvegetated	28	0–16	12–72	5–10	5	

For a comprehensive comparison, papers using the same methods were selected

the area by the eutrophic Han River. Enhanced rates of C oxidation in sediment samples amended with acetate at the UMF site, together with the high rate of organic C mineralization, further imply that the primarily open and unvegetated Ganghwa intertidal mud flats are a significant sink against the external loading of organic compounds. Thus, this system may play a significant role as an environmental buffer between terrestrial and coastal environments.

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## References

- Aller RC (1994) Bioturbation and remineralization of sedimentary organic matter: effects of redox oscillation. *Chem Geol* 114:331–345. doi:[10.1016/0009-2541\(94\)90062-0](https://doi.org/10.1016/0009-2541(94)90062-0)
- Aller RC (2001) Transport and reactions in the bioirrigated zone. In: Boudreau BP, Jørgensen BB (eds) *The benthic boundary layer: transport processes and biogeochemistry*. Oxford University Press, Oxford, pp 269–301
- Aller RC, Mackin JE, Cox RT Jr (1996) Diagenesis of Fe and S in Amazon inner shelf muds: apparent dominance of Fe reduction and implications for the genesis of ironstones. *Cont Shelf Res* 6:263–289. doi:[10.1016/0278-4343\(86\)90064-6](https://doi.org/10.1016/0278-4343(86)90064-6)
- Alongi DM (1998) *Coastal Ecosystem Processes*. CRC Press, Boca Raton, p 419
- An S (2005) Seasonal variations of sediment oxygen demand and denitrification in Kanhwa tidal flat sediments. (The Sea). *J Kor Soc Oceanogr* 10:47–55 In Korean
- Banta GT, Holmer M, Jensen M, Kristensen E (1999) Effects of two polychaete worms, *Nereis diversicolor* and *Arenicola marina*, on aerobic and anaerobic decomposition in a sandy marine sediment. *Aquat Microb Ecol* 19:189–204. doi:[10.3354/ame019189](https://doi.org/10.3354/ame019189)
- Bertness MD (1985) Fiddler crab regulation of *Spartina alterniflora* production on a new England salt marsh. *Ecology* 66:1042–1055. doi:[10.2307/1940564](https://doi.org/10.2307/1940564)
- Boudreau BP, Jørgensen BB (2001) *The benthic boundary layer: transport processes and biogeochemistry*. Oxford Univ Press, Oxford
- Bowman JP, McCuaig RD (2003) Biodiversity, community structural shifts, and biogeography of prokaryotes within Antarctic continental shelf sediments. *Appl Environ Microbiol* 69:2463–2483. doi:[10.1128/AEM.69.5.2463-2483.2003](https://doi.org/10.1128/AEM.69.5.2463-2483.2003)
- Canfield DE, Thamdrup B, Kristensen E (2005) *Aquatic geomicrobiology*. Elsevier, Amsterdam, p 640
- Capone DG, Kiene R (1988) Comparison of microbial dynamics in marine and freshwater sediments: Contrasts in anaerobic carbon catabolism. *Limnol Oceanogr* 33:725–749
- Cline JD (1969) Spectrophotometric determinations of hydrogen sulfide in natural waters. *Limnol Oceanogr* 14:454–458
- Dollhopf SL, Hyun J-H, Smith AC, Adams HJ, O'Brien S, Kostka JE (2005) Quantification of ammonia-oxidizing bacteria and controls of nitrification in saltmarsh sediments. *Appl Environ Microbiol* 71:240–246. doi:[10.1128/AEM.71.1.240-246.2005](https://doi.org/10.1128/AEM.71.1.240-246.2005)
- Emerson D, Weiss JV, Megoñigal JP (1999) Iron-oxidizing bacteria are associated with ferric hydroxide precipitates (Fe-plaque) on the roots of wetland plants. *Appl Environ Microbiol* 65:2758–2761
- Fossing H, Jørgensen BB (1989) Measurement of bacterial sulfate reduction in sediments: evaluation of a single-step chromium reduction method. *Biogeochem* 8:205–222. doi:[10.1007/BF00002889](https://doi.org/10.1007/BF00002889)
- Furukawa Y, Smith AC, Kostka JE, Watkins J, Alexander CR (2004) Quantification of macrobenthic effects on diagenesis using a multicomponent inverse model in salt marsh sediments. *Limnol Oceanogr* 49:2058–2072
- Giblin AE, Hopkins CS, Tucker J (1997) Benthic metabolism and nutrient cycling in Boston harbor, Massachusetts. *Estuaries* 20:346–364. doi:[10.2307/1352349](https://doi.org/10.2307/1352349)
- Gribsholt B, Kristensen E (2002) Effects of bioturbation and plant roots on salt marsh biogeochemistry: a mesocosm study. *Mar Ecol Prog Ser* 241:71–87. doi:[10.3354/meps241071](https://doi.org/10.3354/meps241071)
- Gribsholt B, Kristensen E (2003) Benthic metabolism and sulfur cycling along an inundation gradient in a tidal *Spartina anglica* salt marsh. *Limnol Oceanogr* 48:2151–2162
- Gribsholt B, Kostka JE, Kristensen E (2003) Impact of fiddler crabs and plant roots on sediment biogeochemistry in a Georgia saltmarsh. *Mar Ecol Prog Ser* 259:237–251. doi:[10.3354/meps259237](https://doi.org/10.3354/meps259237)
- Hall PO, Aller RC (1992) Rapid small-volume, flow injection analysis for CO<sub>2</sub> and NH<sub>4</sub><sup>+</sup> in marine and freshwaters. *Limnol Oceanogr* 37:113–119
- Hansen K, King GM, Kristensen E (1996) Impact of the soft-shell clam *Mya arenaria* on sulfate reduction in an intertidal sediment. *Aquat Microb Ecol* 10:181–194. doi:[10.3354/ame010181](https://doi.org/10.3354/ame010181)
- Hines M, Jones GE (1985) Microbial biogeochemistry and bioturbation in the sediments of Great Bay, New Hampshire. *Estuar Coast Shelf Sci* 20:729–742. doi:[10.1016/0272-7714\(85\)90029-0](https://doi.org/10.1016/0272-7714(85)90029-0)
- Hines ME, Knollmeyer SL, Tugel JB (1989) Sulfate reduction and other sedimentary biogeochemistry in northern New England salt marsh. *Limnol Oceanogr* 34:578–590
- Hines ME, Evans RS, Genthner BRS, Willis SG, Friedman S, Rooney-Varga JN, Devereux R (1999) Molecular phylogenetic and biogeochemical studies of sulfate-reducing bacteria in the rhizosphere of *Spartina alterniflora*. *Appl Environ Microbiol* 65:2209–2216
- Holmer M, Forbes VE, Forbes TL (1997) Impact of the polychaete *Capitella sp.* I on microbial activity in an organic-rich marine sediment contaminated with the polycyclic aromatic hydrocarbon fluoranthene. *Mar Biol (Berl)* 128:679–688. doi:[10.1007/s002270050135](https://doi.org/10.1007/s002270050135)

- Holmer M, Andersen FØ, Holmboe N, Kristensen E, Thongtham N (1999) Transformation and exchange processes in the Bangrong mangrove forest-seagrass bed system, Thailand. Seasonal and spatial variations in benthic metabolism and sulfur biogeochemistry. *Aquat Microb Ecol* 20:203–212. doi:[10.3354/ame020203](https://doi.org/10.3354/ame020203)
- Holmer M, Andersen FØ, Nielsen SL, Boschker HTS (2001) The importance of mineralization based on sulfate reduction for nutrient regeneration in tropical seagrass sediments. *Aquat Bot* 71:1–17. doi:[10.1016/S0304-3770\(01\)00170-X](https://doi.org/10.1016/S0304-3770(01)00170-X)
- Howarth RW (1993) Microbial processes in salt-marsh sediments. In: Ford TE (ed) *Aquatic microbiology: An ecological approach*. Blackwell, Cambridge, pp 239–259
- Howes BL, Dacey JWH, King GM (1984) Carbon flow through oxygen and sulfate reduction pathways in salt marsh sediments. *Limnol Oceanogr* 29:1037–1051
- Hyun J-H, Choi JK, Chung JH, Yang EJ, Kim MK (1999a) Tidally induced changes in bacterial growth and viability in the macrotidal Han River estuary, Yellow Sea. *Estuar Coast Shelf Sci* 48:143–153. doi:[10.1006/ecss.1998.0421](https://doi.org/10.1006/ecss.1998.0421)
- Hyun J-H, Chung KH, Park YC, Choi JK (1999b) Variations in ammonium removal rate with tidal stage in the macrotidal Han River estuary: potential role of nitrification. *(The Sea). J Kor Soc Oceanogr* 4:33–39
- Hyun J-H, Mok JS, Cho HY, Cho BC, Choi JK (2004) Anaerobic mineralization of organic matter and sulfate reduction in summer at Ganghwa intertidal flat, Korea. *J Korean Wetlands Soc* 6:132 In Korean
- Hyun J-H, Smith AC, Kostka JE (2007) Relative contributions of sulfate- and iron(III) reduction to organic matter mineralization and process controls in contrasting habitats of the Georgia saltmarsh. *Appl Geochem* 22:2637–2651. doi:[10.1016/j.apgeochem.2007.06.005](https://doi.org/10.1016/j.apgeochem.2007.06.005)
- Isaksen MF, Finster K (1996) Sulphate reduction in the root zone of the seagrass *Zostera noltii* on the intertidal flats of a coastal lagoon (Arcachon, France). *Mar Ecol Prog Ser* 137:187–194. doi:[10.3354/meps137187](https://doi.org/10.3354/meps137187)
- Jensen HS, Mortensen PB, Andersen FØ, Rasmussen E, Jensen A (1995) Phosphorus cycling in a coastal marine sediment, Aarhus bay, Denmark. *Limnol Oceanogr* 40:908–917
- Jensen MM, Thamdrup B, Rysgaard S, Holmer M, Fossing H (2003) Rates and regulation of microbial iron reduction in sediments of the Baltic-North Sea transition. *Biogeochem* 65:295–317. doi:[10.1023/A:1026261303494](https://doi.org/10.1023/A:1026261303494)
- Jørgensen BB (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
- Jørgensen BB (1982) Mineralization of organic matter in the sea bed - the role of sulphate reduction. *Nature* 96:643–645. doi:[10.1038/296643a0](https://doi.org/10.1038/296643a0)
- Jørgensen BB (1994) Sulfate reduction and thiosulfate transformations in a cyanobacterial mats during diel oxygen cycle. *FEMS Microbiol Ecol* 13:303–312. doi:[10.1016/0168-6496\(94\)90068-X](https://doi.org/10.1016/0168-6496(94)90068-X)
- Jørgensen BB (2000) Bacteria and marine biogeochemistry. In: Schulz HD, Zabel M (eds) *Marine geochemistry*. Springer, Berlin, pp 173–207
- Kim DS (2006) Estimation of oxygen consumption rates using an oxygen microelectrode in Ganghwa intertidal flat. *Ocean Polar Res* 28:119–127 In Korean
- King GM (1988) Patterns of sulfate reduction and the sulfur cycle in a South Carolina salt marsh. *Limnol Oceanogr* 33:376–390
- King GM, Garey MA (1999) Ferric iron reduction by bacteria associated with the roots of freshwater and marine macrophytes. *Appl Environ Microbiol* 65:4393–4398
- King GM, Klug MJ, Wiegert RG, Chalmers AG (1982) Relation of soil water movement and sulfide concentration to *Spartina alterniflora* production in a Georgia Salt Marsh. *Science* 218:61–63
- Koo BJ, Kwon KK, Hyun J-H (2005) The sediment-water interface increment due to the complex burrows of macrofauna in a tidal flat. *Ocean Sci J* 40:221–227
- Koo BJ, Kwon KK, Hyun J-H (2007) Effect of environmental conditions on variation in the sediment-water interface created by complex macrofaunal burrows on a tidal flat. *J Sea Res* 58:302–312. doi:[10.1016/j.seares.2007.07.002](https://doi.org/10.1016/j.seares.2007.07.002)
- Koretsky CM, Moore CM, Lowe KL, Meile C, Dichristina TJ, Van Cappellen P (2003) Seasonal oscillation of microbial iron and sulfate reduction in saltmarsh sediments (Sapelo Island, GA, USA). *Biogeochem* 64:179–203. doi:[10.1023/A:1024940132078](https://doi.org/10.1023/A:1024940132078)
- Koretsky CM, Van Cappellen P, DiChristina TJ, Kostka JE, Lowe KL, Moore CM, Roychoudhury AN, Viollier E (2005) Salt marsh porewater geochemistry does not correlate with microbial community structure. *Estuar Coast Shelf Sci* 62:233–251. doi:[10.1016/j.ecss.2004.09.001](https://doi.org/10.1016/j.ecss.2004.09.001)
- Koretsky CM, Haveman M, Cuellar A, Beuving L, Shattuck T, Wagner M (2008a) Influence of *Spartina* and *Juncus* on saltmarsh sediments. I. pore water geochemistry. *Chem Geol* 255:87–99. doi:[10.1016/j.chemgeo.2008.06.013](https://doi.org/10.1016/j.chemgeo.2008.06.013)
- Koretsky CM, Cuellar A, Haveman M, Beuving L, Shattuck T, Wagner M (2008b) Influence of *Spartina* and *Juncus* on saltmarsh sediments. II. Trace element geochemistry. *Chem Geol* 255:100–113. doi:[10.1016/j.chemgeo.2008.06.014](https://doi.org/10.1016/j.chemgeo.2008.06.014)
- Kostka JE, Gribsholt B, Petrie E, Dalton D, Skelton H, Kristensen E (2002a) The rates and pathways of carbon oxidation in bioturbated saltmarsh sediments. *Limnol Oceanogr* 47:230–240
- Kostka JE, Roychoudhury A, Van Cappellen P (2002b) Rates and controls of anaerobic microbial respiration across spatial and temporal gradients in saltmarsh sediments. *Biogeochem* 60:49–76. doi:[10.1023/A:1016525216426](https://doi.org/10.1023/A:1016525216426)
- Kristensen E (2001) Impact of polychaetes (*Nereis* spp. and *Arenicola marina*) on carbon biogeochemistry in coastal marine sediment. A review. *Geochem Trans* 2:92–104. doi:[10.1186/1467-4866-2-92](https://doi.org/10.1186/1467-4866-2-92)
- Kristensen E, Kostka JE (2005) Macrofaunal burrows and irrigation in marine sediment: microbiological and biogeochemical interactions. In: Kristensen E, Haese RR, Kostka JE (eds) *Interaction between macro- and microorganisms in marine sediments*, vol 60. American Geophysical Union, Washington, DC, pp 125–157
- Kristensen E, Andersen FØ, Holmboe N, Holmer M, Thongtham N (2000) Carbon and nitrogen mineralization in sediments of the Bangrong mangrove area, Phuket, Thailand. *Aquat Microb Ecol* 22:199–213. doi:[10.3354/ame022199](https://doi.org/10.3354/ame022199)
- Lee K, Kim I (2006) Status and breeding biology of black-faced spoonbills in Korea. *Proceedings: Keeping Asia's spoonbills airborne*. International Symposium on research and

- conservation of the black faced spoonbill, Hong Kong, pp 56–62
- Leven LA, Talley TS (2000) Influence on vegetation and abiotic environmental factors on salt marsh invertebrates. In: Weinstein MP, Kreeger DA (eds) Concepts and controversies in tidal marsh ecology. Kluwer Academic Publishers, Dordrecht, pp 661–707
- Lovley DR (1991) Dissimilatory Fe(III) and Mn(IV) reduction. *Microbiol Rev* 55:259–287
- Lovley DR, Phillips EJP (1987) Competitive mechanisms for inhibition of sulfate reduction and methane production in the zone of ferric iron reduction in sediments. *Appl Environ Microbiol* 53:2636–2641
- Lowe KL, DiChristina TJ, Roychoudhury AN, Van Cappellen P (2000) Microbiological and geochemical characterization of microbial Fe(III) reduction in salt marsh sediments. *Geomicrobiol J* 17:163–178. doi:10.1080/01490450050023836
- Lustwerk RL, Burdige DJ (1995) Elimination of dissolved sulfide interference in the flow injection determination of ΣCO<sub>2</sub> by addition of molybdate. *Limnol Oceanogr* 40:1011–1012
- Min BM (1998) Vegetation on the west coast of Korea. *Ocean Res* 20:167–178
- Moeslund L, Thamdrup B, Jørgensen BB (1994) Sulfur and iron cycling in a coastal sediment: radiotracer studies and seasonal dynamics. *Biogeochem* 27:129–152
- MOMAF (1999) Our coastal wetland, tidal flat ‘Getbul’. Ministry of Maritime Affairs and Fisheries. p 38
- Neubauer SC, Valentine SK, Kim G, Megonigal JP (2005) Seasonal patterns and plant-mediated controls of subsurface wetland biogeochemistry. *Ecology* 86:3334–3344. doi:10.1890/04-1951
- Nielsen T, Andersen FØ (2003) Phosphorus dynamics during decomposition of mangrove (*Rhizophora apiculata*) leaves in sediments. *J Exp Mar Biol Ecol* 293:73–88. doi:10.1016/S0022-0981(03)00200-4
- Nielsen OI, Kristensen E, Holmer M (2003) Impact of *Arenicola marina* (polychaeta) on sediment sulfur dynamics. *Aquat Microb Ecol* 33:95–105. doi:10.3354/ame033095
- OHA (1978) Technical reports of hydrographic office of republic of Korea. Office of Hydrographic Affairs. Pub No 1101
- Odum EP (2000) Tidal marshes as outwelling/pulsing systems. In: Weinstein MP, Kreeger DA (eds) Concepts and controversies in tidal marsh ecology. Kluwer Academic Publishers, Dordrecht, The Netherlands, pp 3–7
- Parsons TR, Maita Y, Lalli CM (1984) A manual of chemical and biological methods for seawater analysis. Pergamon Press, Oxford, p 173
- Phillips EJP, Lovley DR (1987) Determination of Fe(III) and Fe(II) in oxalate extracts of sediment. *Soil Sci Soc Am J* 51:938–941
- Pomeroy LR, Wiegert RG (1981) The ecology of a salt marsh. Springer-Verlag, New York, p 271
- Postma D, Jakobsen R (1996) Redox zonation: equilibrium constraints on the Fe(III)/SO<sub>4</sub><sup>2-</sup> reduction interface. *Geochim Cosmochim Acta* 60:3169–3175. doi:10.1016/0016-7037(96)00156-1
- Poulton SW, Raiswell R (2002) The low-temperature geochemical cycle of iron: From continental fluxes to marine sediment deposition. *Am J Sci* 302:774–805. doi:10.2475/ajs.302.9.774
- Ravenschlag K, Sahn K, Perenthaler J, Amann R (1999) High bacterial diversity in permanently cold marine sediments. *Appl Environ Microbiol* 65:3982–3989
- Ravenschlag K, Sahn K, Knoblauch C, Jørgensen BB, Amann R (2000) Community structure, cellular rRNA content, and activity of sulfate-reducing bacteria in marine Arctic sediments. *Appl Environ Microbiol* 66:3592–3602. doi:10.1128/AEM.66.8.3592-3602.2000
- Roden EE, Wetzel RG (1996) Organic carbon oxidation and suppression of methane production by microbial Fe(III) oxide reduction in vegetated and unvegetated freshwater wetland sediments. *Limnol Oceanogr* 41:1733–1748
- Rooney-Varga JN, Devereux R, Evans R, Hines ME (1997) Seasonal changes in the relative abundance of uncultivated sulfate-reducing bacteria in salt marsh sediment and in the rhizosphere of *Spartina alterniflora*. *Appl Environ Microbiol* 63:3895–3901
- Smith AC, Kostka JE, Devereux R, Yates DF (2004) Seasonal composition and activity of sulfate-reducing prokaryotic communities in seagrass bed sediments. *Aquat Microb Ecol* 37:183–195. doi:10.3354/ame037183
- Sobolev D, Roden EE (2001) Suboxic deposition of ferric iron by bacteria in opposing gradients of Fe(II) and oxygen at circumneutral pH. *Appl Environ Microbiol* 67:1328–1334. doi:10.1128/AEM.67.3.1328-1334.2001
- Stookey LL (1970) Ferrozine—a new spectrophotometric reagent for iron. *Anal Chem* 42:245–252. doi:10.1021/ac60289a016
- Thamdrup B (2000) Bacterial manganese and iron reduction in aquatic sediments. *Adv Microb Ecol* 16:41–84
- Thamdrup B, Canfield DE (1996) Pathways of carbon oxidation in continental margin sediments off central Chile. *Limnol Oceanogr* 41:1629–1650
- Thamdrup B, Canfield DE (2000) Benthic respiration in aquatic sediments. In: Jackson RB, Sala OE, Mooney HA, Howarth RW (eds) Methods in ecosystem science. Springer, New York, pp 86–103
- Weiss JV, Emerson D, Backer SM, Megonigal JP (2003) Enumeration of Fe(II)-oxidizing and Fe(III)-reducing bacteria in the root zone of wetland plants: implications for a rhizosphere iron cycle. *Biogeochem* 64:77–96. doi:10.1023/A:1024953027726
- White DS, Howes BL (1994) Long-term <sup>15</sup>N-nitrogen retention in the vegetated sediments of a New England salt marsh. *Limnol Oceanogr* 39:1878–1892