

Temporal Behavior of Manganese and Iron in a Sandy Coastal Sediment Exposed to Water Column Anoxia

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ABSTRACT: The influence of bottom water anoxia on manganese (Mn), iron (Fe), and sulfur (S) biogeochemistry was examined in defaunated sandy sediment from Kærby Fed, Denmark, under controlled laboratory incubations. The initial narrow peaks and steep gradients in solid Mn(IV) and Fe(III) as well as porewater Mn²⁺ and Fe²⁺ observed in the upper 2–5 cm of the sediment indicate rapid metal reduction-oxidation cycles under oxic conditions in the overlying water. The Fe zones were generally displaced about 0.5 cm downward compared with the Mn zones due to differences in reactivity. Mn(IV) was reduced and gradually disappeared first (within 10 d) when the sediment was exposed to anoxia followed by reduction and disappearance of Fe(III) (day 7 to 18). The associated loss of Mn²⁺ to the overlying water was most rapid during the first 15 d, whereas the Fe²⁺ efflux initiated around day 10, and after a few days with modest rates the efflux peaked around day 20. A considerable portion of the total Mn (26%) and Fe (23%) inventory initially present in the sediment was lost by efflux after about 1 mo of anoxia. The ability of the sediment to retain upward diffusion of H₂S gradually disappeared in a temporal pattern closely related to the changes in pool size of the reactive Mn and Fe present. The total metal pool in Kærby Fed sediment prevented H₂S release to the overlying water for at least a month of anoxia. It is speculated that external supplies from the overlying water allows a rapid refuelling of surface Mn and Fe oxides in the field when oxic conditions returns between periods of anoxia.

Introduction

Manganese (Mn) and iron (Fe) are among the most dynamic and geochemically important elements on earth. They are involved in a variety of important reduction-oxidation processes. In aquatic sediments they act as the major redox intermediates between oxygen and reduced compounds. Mn and Fe are found in a number of forms, ranging from amorphous, poorly ordered, and various crystalline oxide structures (Thamdrup 2000) to dissolved, adsorbed, and precipitated reduced forms (Berner 1981; Burdige 1993; van Cappellen and Wang 1996; Friedl et al. 1997). Oxidized surface sediments are usually enriched in amorphous or poorly crystalline Mn and Fe (Mn(III–IV), hereafter referred to as Mn(IV), and Fe(III)) oxides with low solubility (Burdige 1993; Thamdrup and Canfield 1996). The reduced forms, Mn(II) and Fe(II), found deeper in sediments are more soluble, although the concentrations of dissolved Mn²⁺ and Fe²⁺ usually are low and regulated by adsorption equilibria or precipitation-dissolution reactions (Canfield et al. 1993; Thamdrup 2000).

The balance between reduction rates and internal oxidation rates as well as external supply rates controls the steady state concentration of Mn(IV) and Fe(III) oxides in sediments. Both metal oxides

are readily reduced when buried into anoxic sediment by infauna or wave action, either as electron acceptors in microbial mediated respiratory oxidation of organic carbon (Lovley 1991; Thamdrup 2000) or reduced chemically by hydrogen sulfide (H₂S; Thamdrup et al. 1994a; Yao and Millero 1994). Reduced Mn may precipitate as carbonates, adsorb to clay minerals, carbonates, and metal oxides, or remain mobile as dissolved Mn²⁺ (Middelburg et al. 1987; Aller 1994). Although reduced Fe may behave similarly, it preferably precipitates as stable Fe sulfides (Coleman 1993). The supply of Mn(IV) and Fe(III) is maintained by internal Mn²⁺ and Fe²⁺ reoxidation within the sediment or externally by deposition of oxides from the water column (Slomp et al. 1997). Mn²⁺ and Fe²⁺ may be oxidized abiologically by oxygen (Burns and Burns 1975; Murray 1979), but microbially mediated oxidation generally occurs much faster (e.g., Thamdrup et al. 1994b).

Mn and Fe biogeochemistry in marine sediments have almost exclusively been studied in fine-grained continental shelf deposits with high capacity to adsorb or precipitate both oxidized and reduced metals (Hines et al. 1991; Aller 1994; Thamdrup et al. 1994a). Almost nothing is known about metal biogeochemistry in sandy sediments from shallow coastal and intertidal areas. These sediments are usually low in reactive Mn and Fe avail-

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able for biogeochemical transformations due to the coarse structure, high quartz, and low clay content. The internal cycling of Fe and Mn in any sediment depends on redox conditions and is tightly linked to the supply of oxygen from above. Oxygen deficiency at the sediment surface, as frequently observed for continental shelf sediments underlying a stratified water column (Sundby and Silverberg 1985; Aller 1994; Thamdrup et al. 1994a; Slomp et al. 1997), is usually considered unlikely in shallow areas. Coastal sediments periodically experience massive coverage of floating macroalgae (e.g., *Ulva lactuca* and *Chaetomorpha linum*; Neira and Rackemann 1996; Viaroli et al. 1996; Krause-Jensen et al. 1999), and the sediment may turn completely anoxic with subsequent reduction of Mn and Fe oxides leading to a release of Mn^{2+} , Fe^{2+} , and H_2S to bottom waters. The reactive Mn and Fe pools may actually delay the release of toxic H_2S and limit any damage on the aerobic benthic community (Dauer et al. 1992; Heip 1995). Kristiansen et al. (2002) found that organic-poor and metal-poor sandy sediment in an oligotrophic coastal lagoon has the capacity to prevent H_2S from reaching the surface after about 14 d of anoxia.

We examined effects of anoxia in the overlying water on vertical and temporal behavior as well as fluxes of Mn, Fe, and H_2S in sandy sediment from the eutrophic Odense Fjord, Denmark. The area frequently experiences periods of sediment anoxia due to coverage of macroalgal mats during late summer. Results from laboratory incubations, where complete sediment anoxia is simulated for 28 d, are related to the general knowledge on Mn and Fe biogeochemistry in marine sediments. The ability of these metals to trap upward diffusing H_2S within the sediment, and thus the capacity to prevent release of H_2S to the overlying water, is evaluated.

Materials and Methods

LOCATION AND SAMPLING

The sediment used for the experiment was collected in a shallow area, Kærby Fed, in the western and innermost part of Odense Fjord on the island of Fyn, Denmark (Fig. 1). Odense Fjord is a shallow (mean depth 2.25 m) eutrophic estuary with variable, and at times significant, freshwater influence from nearby river discharge (County of Fyn 2001). Salinity normally varies between 10‰ and 15‰ in the inner part, but may occasionally be as low as 3‰. Water temperature varies from 2°C in winter to 18°C in summer. The nearshore sediment is composed of well-sorted sand with a median particle size of about 200 μm and relatively high or-

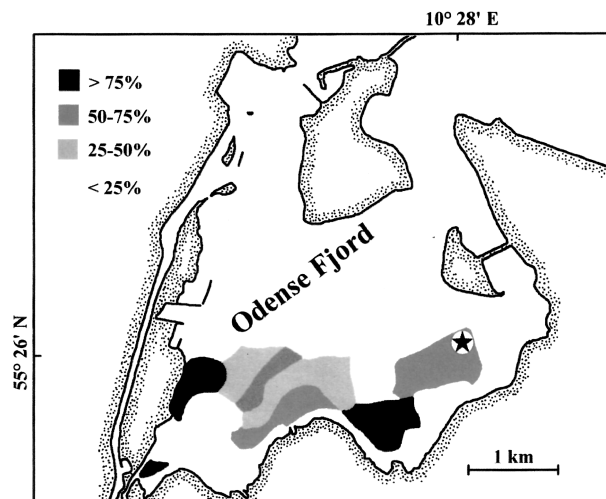


Fig. 1. Map of Odense Fjord, Denmark, with indication of the sampling site at Kærby Fed (star). The distribution and coverage of floating mats of *Ulva lactuca* in August 2000 is shown (redrawn after County of Fyn 2001).

ganic content (2–3% loss on ignition; County of Fyn 2001). The vegetation is dominated by the seagrass, *Ruppia maritima*, but massive occurrence of drifting sea lettuce (*U. lactuca*) is frequently observed in large areas from May to October. The macrofauna is dominated by high numbers of *Nereis diversicolor*, *Corophium volutator*, and *Hydrobia neglecta*.

The Kærby Fed area along the southeastern shore is open to the north and west, and under continuous and strong northwestern winds (the predominant wind direction in the area) *U. lactuca* may accumulate in the south and eastern part of the inner fjord (Fig. 1). As a consequence, the underlying sediment experience periods of complete anoxia with detrimental effects on aerobic organisms located near the bottom (Jørgensen et al. 1996).

Twelve sediment cores were collected from Kærby Fed in spring when no algal cover was present. The undisturbed sediment cores (18–20 cm long) were collected by hand at about 1 m water depth using 25 cm long and 8 cm inner diameter core liners. The salinity was ~13‰ and water temperature was 4–5°C. After return to the laboratory, the overlying water of the 12 cores was purged with N_2 for a few minutes to induce anoxia. The cores were then sealed and placed in darkness for 24 h at room temperature to force burrowing macrofauna out of the sediment (Andersen and Kristensen 1988). After removing emerged animals, the length of all sediment cores was adjusted to 18 cm by removing excess sediment from the bottom. No visible macrofauna was observed in any of the cores after defaunation. The cores were then al-

lowed 24 h to reacclimate with an oxic water column. Subsequently, 4 cores were sectioned to 15 cm depth (see below) and extracted for initial oxic parameter values (day 0).

EXPERIMENTAL SET-UP

The remaining four sets of duplicate cores were placed in a continuous-flow system (Binnerup et al. 1992) with an anoxic water phase to simulate the impact of prolonged anoxia due to algal coverage. The system was immersed in a water bath at a constant temperature of 15°C, which is comparable to the in situ water temperature at Kærby Fed when algal mats occur in summer and early fall (the temperature range from May to October is 12–18°C with a median of 15°C). For each pair of cores the flow system was composed of a reservoir containing 20 l of artificial 10‰ seawater. The reservoirs were made of diffusion retardant plastic bags (Ril-O-Ten 80/100 X), which were able to deform allowing the water to leave the reservoirs without replacement. Anoxia was obtained by pre-flushing the water with N₂ before sealing the reservoirs. A peristaltic pump maintained a continuous and constant flow rate of about 1 l d⁻¹ through the system via glass tubes with a gas trap inserted before the water entered the sealed core tubes 0.5 cm above the sediment surface. The volume of water above the sediment was 250 ml. A Teflon coated magnet (1 cm long), receiving momentum from an external rotating magnet (50 rpm), kept the water in the core tubes stirred well below the resuspension limit. The outlet from the core tubes was placed 0.5 cm under the lid and kept at the same vertical level as the reservoir to avoid pressure differences in the system. The lids were equipped with sampling ports, which were sealed with butyl rubber stoppers when not in use. Flux incubations were initiated after a 30 h acclimation period and repeated frequently during the 28-d experiment. The anoxic cores were sacrificed in pairs for porewater and solid phase analysis after 9, 14, 18, and 28 d.

FLUX MEASUREMENTS

Fluxes of dissolved Mn²⁺, Fe²⁺, and H₂S across the water-sediment interface were determined at daily intervals in 2 randomly selected cores for each incubation series. Water samples were siphoned from 2.5 cm above the sediment via glass tubings inserted through the sampling ports in the lids. Samplings were done before and after a 5 h incubation period during which the water flow was temporarily halted. Subsamples of 4 ml were preserved in 1 ml of 1 M HNO₃ and analyzed for Mn²⁺ by flame atomic absorption spectrometry (Perkin Elmer). Samples of 1 ml for Fe²⁺ were analyzed

spectrophotometrically at 562 nm after transfer to 0.1% (wt:vol) Ferrozine in 50 mM HEPES buffer (pH adjusted to 7.0; Stookey 1970). Samples of 1 ml for H₂S analysis were preserved in 100 µl of 5% (wt:vol) zinc acetate and analyzed spectrophotometrically by the methylene blue method (Cline 1969). Fluxes are presented as cumulative release for the ease of interpretation and are calculated as the sum of daily rate estimates.

SEDIMENT PARAMETERS

Cores were sectioned into 0.3–0.5 cm (0–2 cm), 1 cm (2–5 cm), and 2 cm (5–15) depth intervals in a nitrogen atmosphere for porewater and solid phase characteristics. Porewater was extracted and simultaneously filtered through GF/F and 0.45 µm cellulose-acetate filters from subsamples of each sediment slice by centrifugation in split centrifuge tubes at 1500 rpm for 10 min (Andersen and Kristensen 1988). Porewater samples for Mn²⁺, Fe²⁺, and H₂S were treated in the glove bag as previously described for flux samples.

Sediment for solid phase extractions were rapidly transferred to N₂ flushed centrifuge tubes and sealed with gas impermeable screw caps. The sediment was extracted at room temperature on a shaker for 1 h at 300 rpm. Extractions were terminated by centrifugation at 4500 rpm for 10 min and decantation. Solid phase Fe was extracted with HCl: 0.1–0.5 g fresh sediment was extracted anaerobically in 5 ml of 0.5 M HCl (Lovley and Phillips 1987). Extractable reduced Fe, Fe(II), was analyzed by mixing 50 µl of extractant with 2 ml of 0.02% Ferrozine in 50 mM HEPES buffer (Lovley and Phillips 1987). Total extractable Fe (total Fe = Fe(II) + Fe(III)) was determined by the Ferrozine reagent with 1% hydroxylamine-hydrochloride added as reducing agent. Oxidized Fe, Fe(III), was calculated as the difference between total Fe and Fe(II).

Solid phase Mn was extracted by anaerobic sequential extraction in three steps. The sediment pellets were resuspended and washed twice in 8 ml of milli-Q water between extractions and centrifugations. Adsorbed Mn(II): 0.5–1.0 g fresh sediment was extracted in 8 ml of 1 M MgCl₂ (pH adjusted to 7.0). Carbonate bound Mn(II): further extraction in 8 ml of 1 M sodium acetate (adjusted to pH 5.0 with acetic acid). Oxidized Mn: further extraction in 8 ml of ammonium oxalate dissolved in 0.5 M H₂SO₄ (pH 0.3). Residual Mn: the remaining sediment pellet was boiled in 2 ml of concentrated HNO₃ until near dryness and resuspended in 5 ml of 0.5 M HCl (Freeman and Chapman 1971; Tessier et al. 1979). All retrieved Mn fractions were analyzed by flame atomic absorption spectrometry as mentioned above. The obtained Mn and Fe frac-

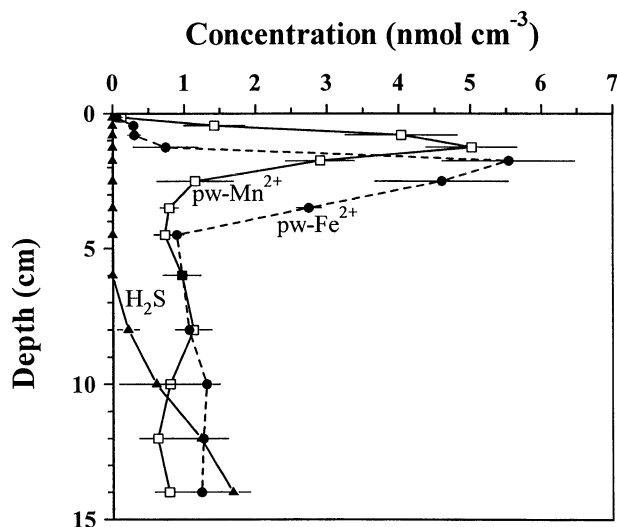


Fig. 2. Initial (day 0) porewater distribution of Mn^{2+} , Fe^{2+} , and H_2S in Kærby Fed sediment. Values are given as nmol cm^{-3} sediment and presented as mean \pm SE ($n = 4$).

tions are not unambiguously defined, but rather operationally defined by the chosen extraction methods (Thamdrup 2000).

Sediment porosity used for conversions between weight and volume of the sediment was calculated from wet density and water content. Sediment density was determined from the weight of a known volume. Water content was determined as weight loss after drying at 105°C for 24 h. All dissolved and solid phase concentrations in the sediment are for comparison given per cm^3 sediment.

Results

VISUAL OBSERVATIONS

The brown oxidized surface layer of Kærby Fed sediment was 8–10 mm initially, but gradually disappeared during the 28-d anoxic incubation period. The underlying sediment was initially characterized by scattered black spots that gradually extended to most of the sediment column in all treatments.

POREWATER CHEMISTRY

Porewater profiles in day 0 sediment showed that Mn^{2+} reached a maximum of 5 nmol cm^{-3} at 1–1.5 cm depth with a steep gradient ($4.7 \text{ nmol cm}^{-3} \text{ cm}^{-1}$) reaching almost zero Mn^{2+} at the sediment-water interface (Fig. 2). The Fe^{2+} maximum of 5.5 nmol cm^{-3} occurred 0.5 cm below the Mn^{2+} peak, but with an almost identical gradient to the surface. The concurrent presence of H_2S and dissolved metals (Mn^{2+} and Fe^{2+}) in deeper layers at both locations was probably a result of spatial inhomogeneity (e.g., macrofauna burrows) of the

sediment or low reactivity of the metal ions present. The variability of dissolved constituents among day 0 cores was modest with standard errors (SEM) generally less than 20% of the mean.

Dissolved Mn^{2+} increased with time of anoxia in the upper 10 cm of the Kærby Fed sediment and reached peak levels around day 14 (Fig. 3). The highest Mn^{2+} concentrations ($40\text{--}50 \text{ nmol cm}^{-3}$) in the upper 6 cm of the sediment column were up to an order of magnitude higher than found initially. Dissolved Mn^{2+} became gradually depleted at all depths within the next 14 d. Porewater Fe^{2+} increased slowly and irregularly in the upper 10 cm during the first 12 d with a distinct peak maintained at about 2 cm depth, but increased rapidly after Mn^{2+} had reached its maximum. The highest Fe^{2+} concentration (50 nmol cm^{-3}) was evident at 1–2 cm depth around day 18. A rapid decline occurred in Fe^{2+} and at day 28 it was almost depleted. In concert with the disappearance of metals, H_2S gradually accumulated from below reaching concentrations of about 30 nmol cm^{-3} in the deeper strata. The range of all dissolved constituents in the duplicate sets of cores always remained below 20% of the mean concentration.

SOLID PHASE

Initially, the solid pools showed peaks of Mn(IV) ($6.4 \mu\text{mol cm}^{-3}$), Fe(III) ($8.7 \mu\text{mol cm}^{-3}$), and Fe(II) ($13.5 \mu\text{mol cm}^{-3}$), in that sequence with depth, in the upper 2.5 cm (Fig. 4). The peak of Fe(II) occurred at the interface between brown oxidized and gray reduced sediment, just between the Fe(III) and the porewater Fe^{2+} peaks. There were no significant changes with depth in the adsorbed Mn(II) ($0.1\text{--}0.2 \mu\text{mol cm}^{-3}$) fraction, whereas the carbonate bound Mn(II) fraction was 5–10 times higher in concentration, and exhibited a broad peak in the upper 2 cm with a concentration twice as high as below. The among core variability of the particulate Mn constituents were generally low with SEM rarely exceeding 10%, except in the transition zone between oxidized and reduced sediment (1–2 cm depth) where SEM increased to levels between 20% and 50%. The intercore Fe(III) variability was high at all depths (SEM between 20% and 80%), whereas Fe(II) appeared similar among cores (SEM < 5%).

Mn(IV) became almost depleted and carbonate bound Mn(II) concentrations reduced by 50% in the upper 2 cm during the first 14 d of anoxia. This was associated with a simultaneous, but not quantitatively equivalent, build-up of adsorbed Mn(II) (Fig. 5). Solid Fe(II) remained high in the upper 1–2 cm until the peak in Fe^{2+} had evolved followed by a gradual decrease to a background level of $6\text{--}7 \mu\text{mol cm}^{-3}$ at day 28 (Fig. 6). Fe(III)

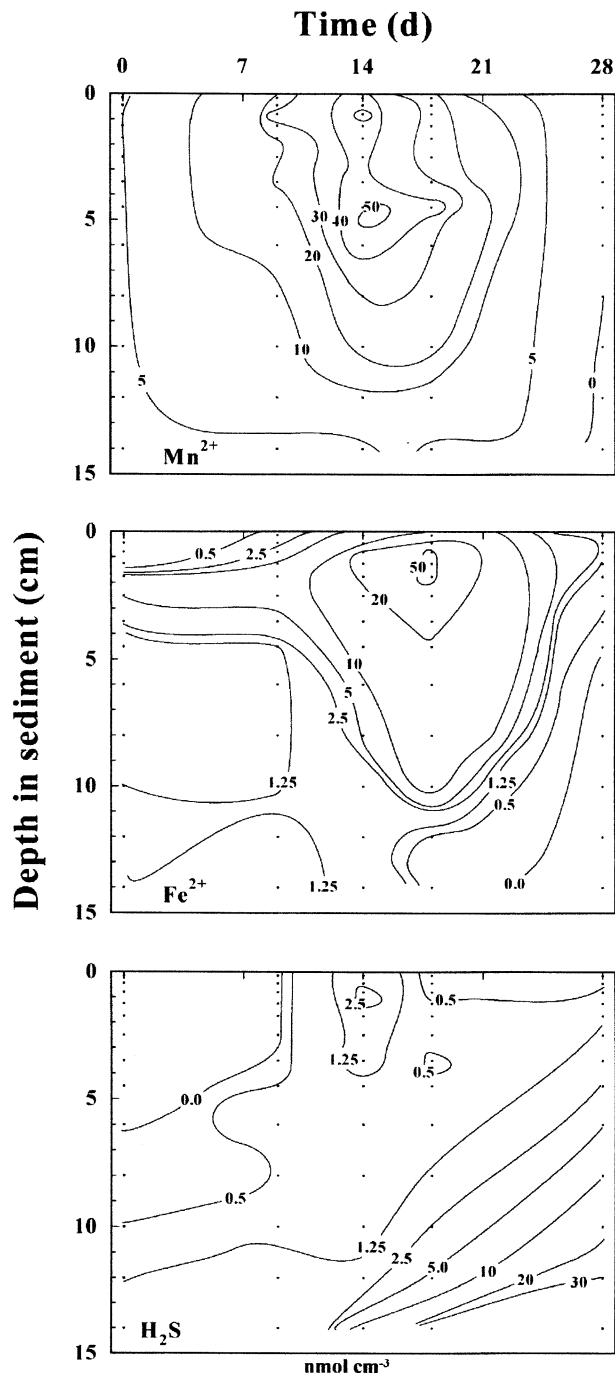


Fig. 3. Changes in the vertical distribution of dissolved Mn^{2+} , Fe^{2+} , and H_2S as a function of time in anoxic Kærby Fed sediment. Values are given as nmol cm^{-3} sediment.

remained unaffected by anoxia initially, but after 9 d when Mn(IV) was exhausted, Fe(III) decreased rapidly and reached almost zero at the end. The range between duplicate cores sacrificed after day 0, remained comparable to the SEM levels found at day 0 for all solid constituents.

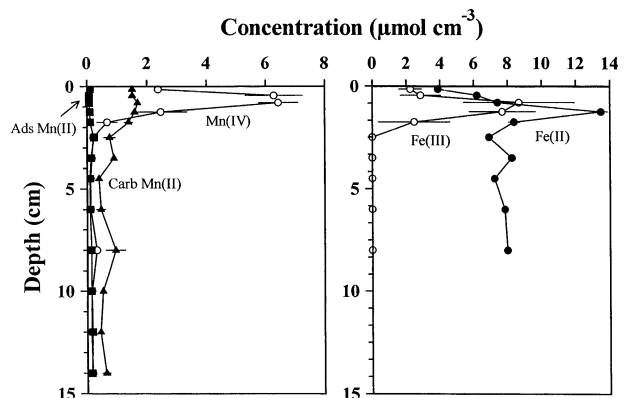


Fig. 4. Initial (day 0) distribution of solid phase Mn (Mn(IV) = oxidized Mn, Carb Mn(II) = carbonate bound Mn(II), Ads Mn(II) = adsorbed Mn(II), and Fe (Fe(III) and Fe(II)) fractions in Kærby Fed sediment. Values are given as $\mu\text{mol cm}^{-3}$ and presented as mean \pm SE ($n = 4$).

FLUXES

The release of Mn^{2+} from the anoxic sediment initiated at day zero and had a maximum rate from day 3 to 10 ($3.6 \pm 0.6 \text{ mmol m}^{-2} \text{ d}^{-1}$). After day 10 the flux gradually declined to $\sim 0.2 \text{ mmol m}^{-2} \text{ d}^{-1}$ at day 28 (Fig. 7). The efflux of Fe^{2+} started when the Mn^{2+} flux diminished and peaked at day 18–23 ($\sim 20 \text{ mmol m}^{-2} \text{ d}^{-1}$) followed by a rapid decline to $2.4 \pm 0.4 \text{ mmol m}^{-2} \text{ d}^{-1}$ at day 28. No release of H_2S was observed at any time during the 28-d anoxic incubation.

Discussion

INITIAL CONDITIONS

The initial depth distribution of dissolved and solid Mn and Fe in the sandy Kærby Fed sediment (Figs. 2 and 4) is consistent with observations from other marine sediments underlying an oxic water column (Sørensen and Jørgensen 1987; Thamdrup et al. 1994a; Thamdrup 2000). The level of all metal pools is generally 1–2 orders of magnitude lower than found in most fine grained continental shelf sediments (Canfield et al. 1993; Aller 1994; Thamdrup et al. 1994a; Slomp et al. 1997). Although the sediment in the eutrophic Kærby Fed appears sandy, it is about 4–5 times richer in organic matter and contains 2 times more of the various Mn and Fe pools than sandy sediment from the nearby oligotrophic Fællesstrand lagoon (Kristiansen et al. 2002). These differences are also reflected in the biogeochemical activities at the two sites. The average oxygen uptake measured at 15°C ($64 \text{ mmol m}^{-2} \text{ d}^{-1}$; County of Fyn 2001) as well as the role of sulfate reduction (equivalent to 63% of the oxygen uptake) at Kærby Fed is about 50% higher than at Fællesstrand (Kristensen 1993).

The typical stratification with Fe(III) extending

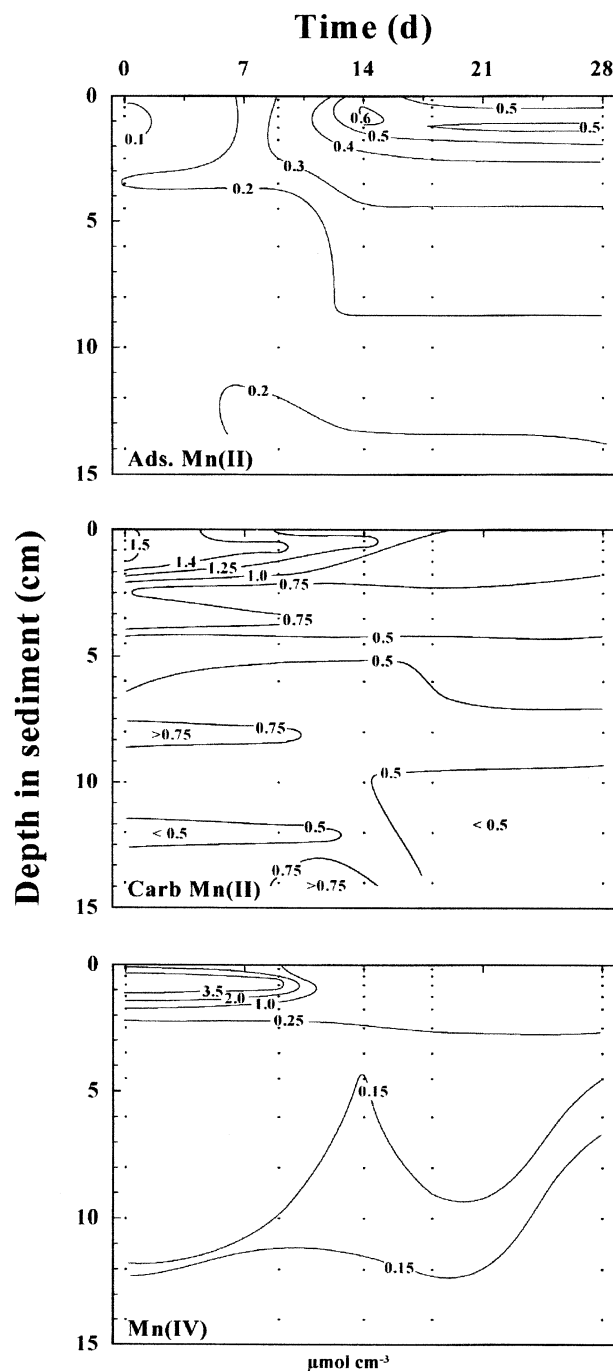


Fig. 5. Changes in the vertical distribution of solid phase manganese: adsorbed Mn(II), carbonate Mn(II), and oxidized manganese as a function of time in anoxic Kærby Fed sediment. Values are given as $\mu\text{mol cm}^{-3}$ sediment.

deeper than Mn(IV) is largely controlled by differences in reaction kinetics and thermodynamics, i.e., slower oxidation rates of Mn^{2+} compared to Fe^{2+} (Stumm and Morgan 1981; Lovley and Phillips 1988), and different solubility of the reduced

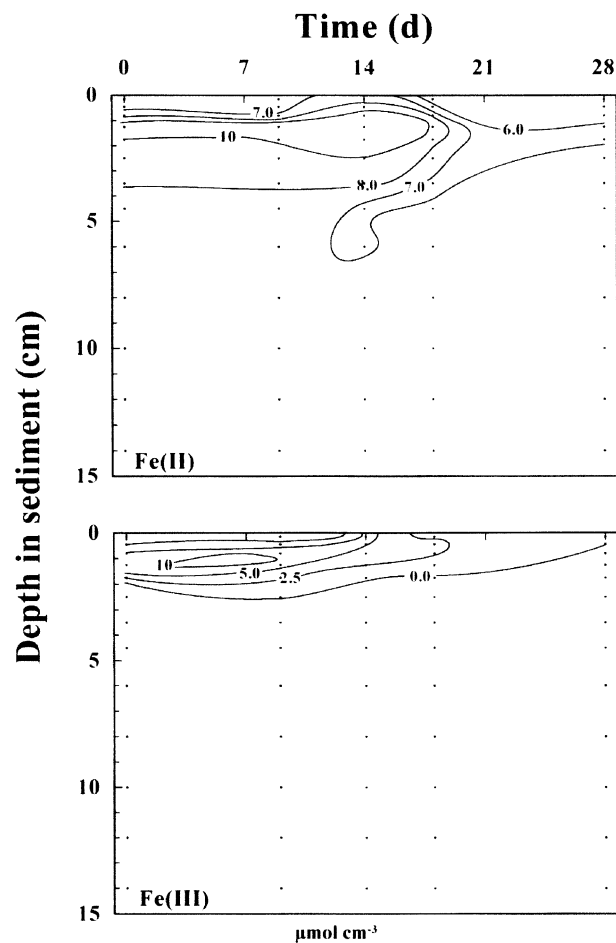


Fig. 6. Changes in the vertical distribution of solid phase iron: Fe(II) and Fe(III) as a function of time in anoxic Kærby Fed sediment. Values are given as $\mu\text{mol cm}^{-3}$ sediment.

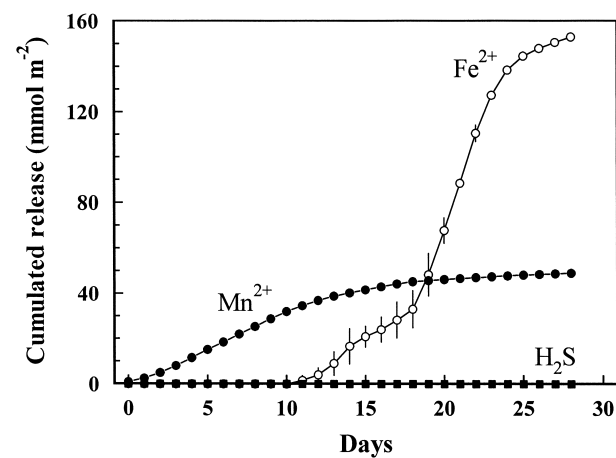


Fig. 7. Cumulative efflux of Mn^{2+} , Fe^{2+} , and H_2S through time from Kærby Fed sediment exposed to anoxia (given as mean \pm range, $n = 2$).

TABLE 1. Depth integrated manganese and iron pools in the top 15 cm of sediment from Kærby Fed (mmol m^{-2}) and cumulative flux (mmol m^{-2}) through time (d) after introduction of anoxia. Numbers in parentheses are standard deviations.

Time	0	9	14	18	28
Manganese					
Dissolved Mn^{2+}	0 (0)	1 (0)	5 (0)	4 (0)	0 (0)
Adsorbed Mn(II)	24 (0)	31 (8)	44 (2)	42 (6)	42 (2)
Carbonate Mn(II)	110 (3)	103 (9)	96 (7)	82 (3)	78 (1)
(Hydr)oxide Mn(IV)	91 (5)	61 (35)	25 (1)	32 (2)	29 (0)
Total sediment	225 (9)	195 (39)	170 (7)	160 (2)	149 (1)
Sum Mn^{2+} flux		29 (11)	42 (2)	47 (1)	51 (0)
Total recovery	225	224	212	207	200
Iron					
Dissolved Fe^{2+}	0 (0)	0 (0)	1 (0)	2 (1)	0 (0)
Reduced Fe(II)	713 (4)	692 (93)	726 (18)	622 (129)	568 (1)
Oxidized Fe(III)	101 (13)	90 (2)	61 (28)	20 (4)	0 (0)
Total sediment	814 (9)	782 (95)	787 (157)	644 (125)	569 (1)
Sum Fe^{2+} flux		0 (0)	17 (18)	33 (35)	172 (54)
Total recovery	814	782	804	677	741

and oxidized forms of Mn and Fe (Froelich et al. 1979). The steep gradients of the various pools in the upper 2–5 cm of the sediment indicate rapid diffusion of dissolved species coupled with oxidation-reduction reactions driven by redox oscillations (e.g., diurnal cycles). The turnover of the dissolved pools, which in reality acts as intermediates between oxidized and reduced solids, is much faster than for solid oxides as indicated by 3 orders of magnitude higher concentrations of the latter.

While much of the downward diffusing Mn^{2+} is immobilized in the sediment matrix due to adsorption or precipitation as carbonates (Canfield et al. 1993; Friedl et al. 1997), most of the downward diffusing Fe^{2+} is immobilized as sulfides (FeS or FeS_2 ; Canfield 1989). Fe(II) extracted with HCl largely represents the FeS pool (Lovley and Phillips 1986; Canfield 1989), which in the present case is equivalent to most Fe(II) present in the sediment as only a minor fraction occurs in the form of FeS_2 . Thus, the total reduced inorganic sulfur pool ($\text{FeS} + \text{FeS}_2 = 5\text{--}20 \mu\text{mol cm}^{-3}$, Kristensen unpublished results) below 4 cm depth at Kærby Fed is comparable to the presently measured Fe(II) pool. A substantial part of the distinct Fe(II) peak located between the Fe(III) and the Fe^{2+} zones at 2–3 cm depth (Fig. 4), probably consists of non-sulfur (S) bound Fe(II) as reported by Thamdrup et al. (1994a). They found a similar near surface peak of non-S- Fe(II) and argued that it not originated from silicates, but rather is formed authigenically in connection with Fe(III) reduction. The speciation of non-S- Fe(II) is generally not known (Thamdrup 2000). It has been argued that Fe(II) -containing sheet silicates are readily formed from solutions of Fe^{2+} (Michalopoulos and Aller 1995; Haese et al. 1997). Other potential candidates for non-S- Fe(II) are mixed

Fe(II)/Fe(III) hydroxides, loosely bound adsorbed Fe(II) and Fe(II) precipitated as phosphates (vivianite) or mixed carbonates (Berner 1981; Aller et al. 1986; Rude and Aller 1989; Boughriet et al. 1997; Trolard et al. 1997).

TEMPORAL RESPONSE TO INDUCED ANOXIA

There was a dynamic interaction between the various Mn pools through time during anoxia in the Kærby Fed sediment (Figs. 3, 5, and 7). A large fraction, 26%, of the total Mn inventory was lost via diffusive Mn^{2+} transport into the overlying water during the 28-d anoxic period (Table 1). Aller (1994) found a similar significant loss of the Mn inventory in Long Island Sound sediments after periods of low O_2 in the bottom water. The primary source of Mn^{2+} in the present experiment appears to be Mn(IV) reduction, as the highest rate of inventory loss (20%) occurred during the first 14 d when Mn(IV) reduction near the surface was most rapid. The concurrent loss of near-surface carbonate bound Mn(II), which was caused by dissolution associated with pH and redox induced changes in equilibrium conditions (Friedl et al. 1997), potentially accounted for 20–30% of the Mn^{2+} flux during this period. The accumulation of porewater Mn^{2+} below the Mn(IV) layer during the first 14 d indicate net production and diffusion into deeper layers (down to 15 cm). The accumulation of porewater Mn^{2+} was quantitatively unimportant compared with fluxes and was 1–2 orders of magnitude lower than the total Mn(IV) loss. The dramatic decrease in diffusive efflux of Mn^{2+} after about 14 d occurred when reactive Mn(IV) and carbonate bound Mn(II) was exhausted. The residual efflux during the last 14 d reflects the gradual elimination of all remaining porewater Mn^{2+} . The increase in adsorbed Mn(II), although

of limited quantitative magnitude, was temporally and spatially correlated with both the exhaustion of Mn(IV) and the increased downward diffusion of dissolved Mn²⁺. It appears that some of the Mn²⁺ (30%) generated from Mn(IV) reduction was directly adsorbed to the sediment matrix. Canfield et al. (1993) found a similarly high Mn²⁺ adsorption to surfaces of mineral particles and metal oxides in the upper oxidized zone of Skagerrak sediment. The adsorption also primarily occurred in the upper few centimeters of the Kærby Fed sediment, and may be associated with the less reduced conditions and higher detritus content in this layer. Only limited desorption was associated with the subsequent decline in dissolved Mn²⁺ at the end of the experiment, leading to the assumption that adsorption is Mn²⁺ concentration dependent and rapid in oxidized sediment, but that desorption is hampered by subsequent low redox conditions.

Mn(IV) reduction is either a microbially mediated organotrophic respiration process or a spontaneous abiotic reoxidation process with reduced compounds such as Fe and S as electron donors. Data compiled by Thamdrup (2000) indicate that microbial Mn(IV) respiration is unimportant in sediments where the concentration is < 20 μmol cm⁻³ and Mn oxides reach < 2 cm below the sediment surface. It is likely that Mn(IV) primarily served as a sink of electrons from reduced Fe in the anoxic Kærby Fed sediment. The solid Fe dynamics was dependent on the termination of Mn(IV) reduction and the Fe(III) inventory appeared protected as long as sufficient reactive Mn(IV) was present (Figs. 5 and 6). Upward diffused or locally produced Fe²⁺ is oxidized by Mn(IV) at the same pace as Fe(III) is reduced with no apparent net change of both Fe(II) and Fe(III) (Lovley and Phillips 1988; Postma and Appelo 2000).

The development of Fe(III), Fe(II), and dissolved Fe²⁺ after the disappearance of reactive Mn(IV) demonstrates a clear succession (Figs. 3 and 6). Redox reactions first induced a reduction of Fe(III) either coupled to abiotic oxidation of reduced S or to microbial oxidation of organic carbon (Canfield 1989; Thamdrup et al. 1994a). It has been shown that microbially mediated carbon oxidation with Fe(III) as electron acceptor is more widespread than predicted in the past (Thamdrup 2000) and that it is more important than abiotic reduction in a range of sediment types (Canfield et al. 1993; Kostka et al. 2002). Most of the generated Fe²⁺ was instantly precipitated as various Fe(II) forms, e.g., non-S-Fe(II) with no immediate release of Fe²⁺ to the overlying water (Fig. 7). The absence of H₂S in the porewater until late in the experiment does not exclude active sulfate reduc-

tion and precipitation of Fe sulfides (Canfield et al. 1992). As redox continued to decrease, a slow dissolution of solid Fe(II) forms then drove a modest efflux of Fe²⁺ from day 10 to 18. When all reactive Fe(III) had disappeared and redox decreased even further, a rapid dissolution of the various Fe(II) species was responsible for a substantial efflux of Fe²⁺ from the sediment. The Fe²⁺ release ceased when all dissolvable and mobile Fe pools were exhausted. The cumulated release of Fe²⁺ at day 28 accounts for 23% of the initial Fe inventory (Table 1). Balzer (1982) found that a similar release of Fe²⁺ from anoxic Kiel Bight sediment was controlled by equilibria with solid Fe-phases (Fe oxides and amorphous Fe sulfide). It is obvious that a net dissolution of solid Fe(II) forms must have occurred in anoxic Kærby Fed sediment since the total loss of Fe(III) only accounted for 59% of the Fe²⁺ loss to the overlying water. The low recovery of total Fe in the budget (Table 1) at the end of incubation (80–90%) is probably caused by the uncertainty in quantification of the large Fe(II) fraction (within core SEM of up to 30%), which renders the budget calculations for this compound doubtful.

The absence of H₂S efflux to the water phase at any time indicates that sufficient reactive Fe forms were available to precipitate the front of upward diffusing H₂S. Even though the temporal development in porewater H₂S and Fe²⁺ efflux (Figs. 3 and 7) indicates that given sufficient time (probably only few days) H₂S eventually would have penetrated to the sediment surface and released to the overlying water. The zone of H₂S accumulation, which almost reached the surface during the last 14 d, coincided with complete absence of porewater Fe²⁺.

IMPLICATIONS

Although the overall metal concentration in Kærby Fed sediment is relatively low, the metal buffer zone preventing sulfide from reaching the sediment surface is effective for at least one month of complete anoxia in the overlying water. Few published data are available on the capacity of metals to prevent H₂S reaching the surface of coastal sediments. Organic-poor sandy sediment from the oligotrophic Fællesstrand lagoon is only capable of preventing H₂S release for 2–3 wk under complete anoxia (Kristiansen et al. 2002). In the fine-grained and relatively Fe-rich sediments of Aarhus Bay, the pool of reactive metals can prevent the escape of sulfide for a period of 6–12 wk (Fossing et al. 1992), whereas the organic-rich and relatively Fe-poor Nørrefjord on the island of Fyn can only withstand anoxia for 1–4 wk before sulfide is liberated to the overlying water (Hansen unpublished data).

The H₂S interception in anoxic Kærby sediment can only be ascribed to the Mn(VI) and Fe(III) pools during the first 18 d, whereas the large pools of solid S-Fe(II) and non-S-Fe(II) is responsible subsequently.

Although Kærby Fed sediment can prevent the release of H₂S for periods of time covered by *U. lactuca* mats, repeated incidences of anoxia with excessive efflux of dissolved metals may eventually deplete the metal inventories completely. Since depletion does not occur the stores are refurbished from external sources. Supplies from the overlying water must allow for a rapid build-up of surface Mn and Fe oxides when oxic conditions are reestablished between periods of anoxia. The external supply can be supported by a high input from nearby riverine sources, by redeposition of metal oxide-rich material eroded from adjacent areas, or by deposition of metal oxides formed in the water column (Aller 1994; Slomp et al. 1997).

ACKNOWLEDGMENTS

We thank H. Brandt for skilful technical assistance. This work was supported by Danish National Research Foundation grants no. 9901749 and 21020463.

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SOURCE OF UNPUBLISHED MATERIALS

HANSEN, M. W. Unpublished Data. Institute of Biology, Odense University, SDU, DK-5230 Odense M, Denmark.

Received for consideration, October 9, 2001

Revised, June 24, 2002

Accepted for publication, August 22, 2002