Cycling of iron and manganese in freshwater, estuarine and deep sea sediments
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4. Effect of macrofauna, sediment ventilation and particle reworking on sedimentary iron and manganese pools in a mesocosm experiment

Imola Ferro, Paul van Nugteren, Jack J. Middelburg, Peter M. J. Herman, Carlo H.R. Heip

4.1. Abstract

Benthic fauna exerts a major impact on biogeochemical processes. Bioturbation can be partitioned into a pore-water irrigation and a particle-mixing component, which in most studies are lumped in an overall effect. Depending on sediment conditions, governing processes and studied constituents, the importance of each component may differ, as both have specific effects (e.g. oxygen input by irrigation, mixing of oxidized and reduced particulate metals by particle mixing). Here we present results from mesocosm experiments, using a marine sediment, in which we investigate the importance of both components for the sedimentary iron and manganese cycle. Solid-phase and dissolved iron and manganese were studied in sediment cores with four different treatments: control, ventilation, particle mixing and bioturbation by the polychaete Nereis diversicolor. Results for iron and manganese were similar for control cores and sediments bioturbated by worms with low metal concentrations in the porewater. In the latter sediments were oxygenated by the macrofaunal activity, resulting in an efficient retainment of both metals in the sediment. The effects of particle mixing and ventilation were different for both metals. The effect of ventilation on manganese cycling is larger than the effect of particle mixing, resulting in a better retainment of manganese in the sediment due to extensive oxidation of Mn (II). Despite the lack of a complete macrocycle or an external metal oxide source, indicate metal oxide reduction continued, likely due to a microcycle involving mobile oxidized metal phases. Particle mixing is more important for iron cycling than ventilation, resulting in a smaller flux to the overlying water than the ventilation treatment. The differences in the effect of ventilation and mixing on iron and manganese can be attributed to the differences in aquatic chemistry of the metals and are consistent with recent research on rate limiting steps in the sedimentary cycling of iron and manganese.
4.2. Introduction

Organic carbon mineralization in sediments involves a number of electron acceptors including oxygen, nitrate, manganese- and iron oxides and sulphate. The presence of macrofauna and their structures is an important biogenic factor influencing organic matter degradation pathways (Kristensen 2000). Bioturbation can be split in two mechanistic components: (1) irrigation of the sediment and (2) sediment mixing, the latter resulting in mixing of both (aerobic and anaerobic) porewater and particles.

Irrigation of sediments by fauna activities or their structures involves the enhanced exchange of dissolved constituents between bottom water and pore-water. Irrigation itself can be divided in two components: (1) enhanced gas exchange (mainly O₂ and CO₂) between the sediment and the overlying water (aeration) and (2) enhanced exchange of dissolved components such as NH₄⁺,Mn (II) and Fe (II). Ingalls et al. 2000 reported increased transport of dissolved solutes in the presence of bioturbating fauna. This resulted in a faster removal of degradation products and a higher input of oxygen and nitrate from the bottom water. Especially in systems with aerobic bottom waters and mostly anoxic sediment, ventilation can result in significant mineralization coupled to iron- and manganese-oxide reduction and thereby prevent a shift from sub-oxic mineralization to sulfide reduction (Hines et al. 1997). Moreover a higher oxygen input may result in a faster and more complete mineralization (Aller 1994a, Dauwe et al. 2001, Kristensen 2000).

Sediment mixing involves displacement of porewater and particles. Sediment mixing results in homogenisation of sediment properties, downward transport of oxidized elements and degradable organic carbon into the anoxic zone, and upward transport of reduced components into the oxidized zone. The downward transport of degradable organic carbon maintains mineralization in the deeper sediment layers. Herman et al. 1999 showed that sediment mixing results in a deeper average depth of organic matter mineralization.

Organisms exert through bioturbation multiple effects on degradation pathways. Aller and Aller 1998, Herman et al. 1999 and Kristensen 2000, provided an overview of recent knowledge on the role of bioturbating fauna in sediment diagenesis and mineralization. A number of studies have addressed the effect of bioturbation on (anaerobic) mineralization (Aller 1990, Aller 1994a, Banta et al. 1999, Burdige 2001, Kristensen and Holmer 2001). Aller 1994b showed that the role of Mn as intermediate oxidant in mineralization is largely determined by particle mixing which transports MnO₂ and degradable organic matter into reduced zones and by the efficiency of Mn (II) oxidation at the sediment-water interface.
Iron and manganese are both solid phase oxidants resembling each other in their role in diagenesis and iron is likely to be affected by bioturbation in a similar way as manganese.

The effect of bioturbation on iron-oxide reduction has not yet been investigated in detail. Aller and Aller 1998 investigated the dependence of mineralization on diffusive exchange. Net mineralization rates were calculated based on porewater-overlying water gradients using sediment plugs of different thickness. They found a strong dependence of anaerobic mineralization on diffusive transport distances and concluded that apparent small changes in burrow geometry are likely to have a significant effect on reaction balances. Recently Roden and Urrutia 1999 reported that removal of adsorbed Fe (II) promotes iron oxide reduction by retarding inhibiting effect of Fe (II) sorption on iron oxides or bacterial cell surfaces. The ventilation activity of benthic fauna may promote ferrous iron removal because of (1) higher porewater replenishment and (2) enhanced oxidation of ferrous iron and subsequent precipitation of ferric iron oxides. Therefore irrigation may also promote iron-oxide reduction. Glud et al. 2000 concluded that the high iron-oxide reduction rates they measured in a high-arctic sound needed an intense bioturbation. However, the dependence on particle mixing or porewater irrigation was not investigated separately.

The importance of iron and manganese oxide reduction in organic matter mineralization is often dependent on the rate and efficiency of their oxidation-reduction cycles (Wijsman et al. 2001b). To complete a cycle dissolved and particulate reduced components have to be transferred to a re-oxidation zone and particulate oxidized mineralization components have to be mixed into the reduction zone. The two components of bioturbation together provide a mechanism for this, but it is unknown, which of the two components is more important for the completion of the manganese and the iron cycle.

In this study we aim to elucidate the role of particle mixing and irrigation on iron and manganese oxide reduction. Therefore we studied the effect of a macrofauna species, *Nereis diversicolor*, and compared it with artificially enhanced transport of porewater-dissolved gases (ventilation) and particle mixing (without mixing of aerobic and anaerobic layers). We compared sediment-water fluxes, porewater profiles and metal oxide speciation of sediment cores among these 3 treatments. Differences were expected to be reflected in porewater profiles, fluxes across the sediment-water interface and metal oxide distributions. Based on the few literature studies to date we anticipated enhanced iron and manganese reduction at the end of the experiment in the sediment cores with *Nereis diversicolor* because this worm mixes and irrigates sediments. In the mixed and ventilated sediment lower or no
reduction were expected due to the lack of a complete cycling or another source of metal oxides to sustain metal oxide reduction after the sedimentary metal oxide pool has been used (i.e. after the number of days necessary for complete turnover of the pool).

4.3. Material and Methods

4.3.1. Set-up mesocosm experiment

For the experiment 30 cm Plexiglas cores (id = 52 mm) were filled with ~ 15 cm sieved (1 mm mesh) sediment from Katsplaat, a tidal flat in the Oosterscheldt (a tidal inlet in the south-western part of the Netherlands). The sediment has a medium grain size of 93 µm, an organic carbon content of 0.36 wt.%, a carbonate content of 7.5 wt % and a sediment molar C/N ratio of 12.5. A 14 cm water column of Oosterscheldt seawater was put on top and cores were allowed to settle for 7 days at 20ºC in a darkened aerated seawater tank. Following acclimation cores were transferred to a continuous flow system. The whole system was maintained in a climate controlled room. Sediment and specimens of *Nereis diversicolor* were collected simultaneously.

*Nereis diversicolor* is a common macrofauna species in the estuaries in the North Sea area. The worm lives on shallow soft bottoms in U-shaped burrows. *Nereis diversicolor* is considered to be a suspension feeder. The worm performs active porewater pumping. Riisgard 1991 showed that the total population-pumping rate could be several (upto 10) times the water column per day (Odense Fjord, Denmark). By its activities and high porewater pumping rate the animal can have an important effect on diagenesis.

Cores were divided into six groups with different treatments each consisting of three replicates. One group had no sediment and was used to measure non-sediment related Fe (II) and Mn (II) production. The other five groups had a sediment column and were used for the following treatments: (1) t=0-group was sliced immediately at the beginning of the experiment, (2) control, (3) bioturbation (addition of 3 specimens of *Nereis diversicolor*, ~1500 ind m⁻²), (4) ventilation (2 artificial U-shaped burrows constructed of silicone tubing to 8 cm depth) and (5) mixing (stirring device 50 mm id placed ca. 5 cm below the sediment surface). For an elaborate description we refer to the paper of VanNugteren et al. 2002.

Flux measurements were performed at 1, 5, 10 and 16 days after start of the experiment by temporarily closing the circuit so that the continuous flow was stopped. In between incubations there was a continuous flow of aerated seawater. During incubations 4 ml samples of overlaying water were taken at 0, 30, 60, and
120 minutes. After collection samples were put in N₂ filled headspace vials and acidified with 20 % H₂SO₄ (20 µl ml sample⁻¹).

At the end of the experiment cores were sliced in appropriate intervals. Porewater was collected by centrifugation (20 min, 355 G) using tubes like Saager et al. 1990. Porewater samples were capped in headspace vials, acidified and stored until analysis.

4.3.2. Solid-phase extractions

The centrifuged sediment was sub-sampled for solid phase extractions. A number of extractions were used to characterise the pools of particulate iron and manganese oxides. Ascorbate and HCl extractions were performed in an anaerobic chamber (Coy Laboratory Products) filled with > 95 % N₂ and < 5 % H₂. All extractions were done in duplicate. We were aware that these represent pseudo-replicates, but due to sample size restrictions it was not possible to do it otherwise. The pool of amorphous Fe (III) oxides was extracted using ~0.3 g wet sediment and 5 ml of an anaerobic solution of 10 g sodium citrate, 10 g sodium bicarbonate and 4 g ascorbic acid in 200 ml demineralised water (Kostka and Luther 1994). Extraction lasted about 24 hrs and the samples were continuously shaken in the dark. After filtration (0.45 µm filter, cellulose / acetate) iron concentrations were analysed in the filtrate. The amorphous iron extracted with this method is considered the most reactive part of the total sediment iron pool.

The pool of dithionite extractable iron represents amorphous iron (III) oxides, crystalline iron (III) oxides and the pool of iron bound to acid volatile sulfides (FeS), i.e. the pool of chemically reactive iron oxides, and was based on Canfield 1988. Mn-oxides (crystalline oxides available for reduction) are extracted as well (Canfield 1988, Kostka et al. 1999b). Leachant (5 ml, 0.35 M acetic acid/0.2M Na-citrate solution 50 g l⁻¹ dithionite) was added to ca. 0.3 g wet sediment. After two hours shaking, samples were filtered over a 0.45 µm filter and the filtrate was acidified with 0.1 ml 6 N HCl ml filtrate⁻¹. The excess Fe₅ν and Mn₅ν (Table 2a,2b) were calculated by subtracting background concentrations of deep layer form the higher ones in the surface layers.

The HCl extractable pool (sensu Kostka and Luther 1994) was also measured. This involves the addition of 10 ml of a 0.5 M HCl solution to ca. 0.3 g of wet sediment. After 1 hour of incubation the sediment is filtered over 0.45 µm. Fe (II) and total FeHCl are measured in the filtrate with the ferrozine method (Stookey 1970) using HEPES or reducing HEPES buffer. HCl extraction allows determination of the reduction state of the sediment and adsorbed Fe (II). The difference between Fe (II) content before and after the experiment represents the amount of reduced iron
that is within the solid phase or has adsorbed to the sediment during the experiment.
The pool of total iron was measured on a freeze-dried split of the well-mixed sediment at the start of the experiment. The method used HCl/HNO₃ as destructant, a microwave for high temperature and a pressure digester (Nieuwenhuize et al. 1991).

4.3.3. Analyses & calculations

Except for the HCl-extraction solutes (Fe analysed using the ferrozine method (Stookey 1970), all Fe and Mn analyses were measured by Inductively Coupled Plasma – Optical Electron Spectrometry (ICP-OES, Perkin-Elmer Optima 330 DV, using either the axial or radial view method dependent on concentrations). Concentration changes of iron and manganese in the overlying water were used to calculate fluxes. In some of the cores the oxygen saturation in the overlying water decreased below 50% saturation during the incubations. As this affected iron concentrations in solution and induced more anoxic conditions in sediments, this resulted in extremely high flux values. Therefore, these iron data (t = 120 minutes) have not been used in flux calculations.

4.3.4. Statistical analysis

Average values are shown for all results; error bars represent the standard deviation of the replicates. Statistical significance has been evaluated using analysis of variance (ANOVA with an LSD post-hoc comparison) and has been performed with Statistica.

4.4. Results

4.4.1. Fluxes to the overlying water during incubations

Concentration changes in the overlying water during incubations are used to calculate fluxes of Fe and Mn out or into the sediment. Fluxes (Fig 1) are the net result of all biogeochemical processes related to Fe and Mn taking place in the sediment and the water column. Differences among treatments and changes during the experiment have been investigated. Fe fluxes decreased significantly during the experiment (p = 0.005, F = 5.3, n=48) and did not depend on treatment (p = 0.09, F = 2.4, n=48). Whereas Mn fluxes depend on the treatment (p = 0.02, F = 3.8, n=48).
This is caused by the fluxes in *Nereis* cores being significantly lower than in the control cores (p=0.005). Additionally, Fe fluxes of the *Nereis* treatments were lower than those in the ventilated treatment (p < 0.05) and Mn fluxes of in *Nereis* treatments were lower than fluxes of the control and the mixed sediments (p < 0.05). The most remarkable feature is the large uptake in *Nereis* sediments of Fe (II) and Mn (II) at 5 days. This indicates the presence of extremely low concentrations of both solutes in the porewater of the top layers at that time due to well oxygenated sediments.

Fig. 1a

**Fig. 1b**

**Fig.1** Fluxes of dissolved Fe (II) (a) and Mn (II) (b) from sediment cores to the overlying water (µmol m⁻² d⁻¹) measured in incubations at 1, 5, 10 and 16 days.
4.4.2. Porewater

Porewater concentration versus depth profiles of dissolved Fe (II) and Mn (II) are presented in Figure 2. Average values of the ventilation treatment are based on 2 replicates, as the third replicate showed indications of a sampling artefact (oxidation). These profiles reflect the final results of the processes going on in the cores during the experiment and profiles are the net result of all interactions within the sediment.

The overall effect of treatment, depth and their interaction was significant for the dissolved Fe (II) profiles ($p=0.03, F = 2.4; p < 0.001, F = 11.7; p <0.001, F = 2.4; n = 88$ respectively) (fig 2a). Profiles of control and *Nereis* were not significantly different from each other; both have low porewater iron concentrations and exhibit almost no changes with depth. However, these profiles were significantly ($p< 0.05$) lower than the $t=0$, ventilation and mixing profiles. These three treatments had classical profiles with subsurface maxima for dissolved Fe (II) concentrations. The ventilation and the mixing treatment differed significantly ($p< 0.01$) because the subsurface peak of the mixed profile was situated more to the surface and had higher values. Both treatments resembled the $t=0$ profile.

The manganese profiles only had an overall significant effect of treatment ($p < 0.001, F = 21.5, n = 88$) (Fig 2b). The *Nereis*, control and $t=0$ profiles of Mn (II) resembled each other and were significantly lower ($p< 0.05$) than those of the ventilation and mixing treatment.

4.4.3. Solid phase extractions

The data on the solid phase iron extractions are rather variable. This variability depends on the iron fraction and the factors playing a key role in the distribution/formation of that fraction.

Fedith (dithionite extractable iron) had an overall effect of depth ($p < 0.001, F = 6.7, n = 64$) (Fig 3a) mainly due to the high values in the top layers of the control, *Nereis* and ventilation cores. No effect of treatment was discerned for Fe dith profiles. Dithionite extractable Mn (Fig 3b) had a similar distribution and variance pattern as Fedith ($p = 0.018, F = 2.9, n = 64$).

Feasc (ascorbate extractable iron oxides) (Fig 4) had significant effects of depth ($p < 0.001, F = 63.27, n = 64$). This is the only profile with an effect of treatment ($p < 0.001, F = 39.7, n = 64$). This is caused by the ventilation profiles being on average slightly higher than the control ($p< 0.05$), *Nereis* and mixing profiles ($p<0.01$).
Fe (II) (HCl extractable Fe (II)) is an indicator of the reduction state of the sediment. No clear differences can be seen in this iron fraction. However values in the stirred (p = 0.015) and the ventilated cores (p = 0.045) are significantly lower than those in the control. Despite the fact that the mixing does not involve the aerobic top-layer, the mixing events affect the availability of oxidants, resulting in less reducing conditions and lower Fe (II) than in the control cores. Total FeHCl (total HCl extractable sedimentary iron) changed significantly with

Fig. 2a

Fig. 2b

Fig. 2. Porewater profiles of dissolved Fe (II) (a) and Mn (II) (b) (µmol l⁻¹) at the end of the experiment for control (squares) Nereis (triangles), ventilation (dots) and mixing (diamonds). Start profile at t=0 (asterix)
depth for *Nereis* and ventilation treatment (n= 16; p = 0.02, F = 5.0; p < 0.001, F = 13.2). The mixing treatments had significantly lower total FeHCl (p = 0.04) than the control cores (Fig. 6).

**Fig. 3a**

Fe-dith (µmol g⁻¹)

**Fig. 3b**

Mn-dith (µmol g⁻¹)

**Fig. 3:** Solid phase profiles (µmol g dry⁻¹) of dithionite extractable iron (a) and manganese (b) oxides for control (squares), *Nereis* (triangles), ventilation (dots) and stirring (diamonds).
Fig. 4. Sediment profiles for ascorbate extractable Fe-oxides (µmol g dry⁻¹): control (squares), *Nereis* (triangles), ventilation (dots) and mixing (diamonds)

Fig. 5. Adsorbed Fe (II) profiles (µmol g dry⁻¹): control (squares) *Nereis* (triangles), ventilation (dots) and mixing (diamonds)
4.5. Discussion

The construction of burrows by benthic fauna and their ventilation activities affects the ratio of oxic to anoxic sediment. Kristensen 2000 calculated that, by combining data from Davey 1994, Kristensen 1984, Hylleberg and Henriksen 1980 and Fenchel 1996, the ratio of oxic sediment volume associated with Nereid burrows relative to the oxic surface layer is between 0.9 and 3.3. The U-shaped silicone tubing in our ventilation treatment also increased the entry of oxygen and the ratio of tube surface to cores surface was 1.47, thus the tubing allowed for a significant increase of the oxygenated area. However, silicone tubing only allows exchange of gases, and no dissolved constituents have been exchanged. Whereas in sediments active porewater pumping provides refreshment of the burrow water with oxic bottom water. This results not only in an enhanced gas-exchange but also enhances supply of electron acceptors such as nitrate and sulphate and removal of reduced porewater products. Reduced metals are then transported into the oxic zone more readily. Davey and Watson 1995 have shown that the degree of transport enhancement is directly related to burrow wall surface area and thus to the increase in sediment-water contact zone. As Fe (II) oxidation and subsequent formation of iron oxide precipitates is essential to complete the sedimentary iron cycle the effect of irrigation in nature might be longer lasting than the effect of
ventilation observed in our cores because the treatment lacks a solute transport component.
Mixing was introduced by a stirring device placed ca. 5 cm below the sediment surface, i.e. in the anaerobic sediments (Van Nugteren et al. 2002). Although this treatment mainly involves particle mixing some porewater movement will occur as well. The thin oxic surface layer (about 2 mm) of the sediment was not mixed. However, in bioturbated sediments mixing includes the oxic layer. Therefore sediment mixing causes additional oxygen input and a higher incorporation of settled material (i.e. degradable organic matter and allochthonous metal oxides). The mixing of aerobic and anaerobic layers also enables adsorbed Fe (II) to be oxidized and recycled. This re-oxidation of Fe (II) may occur directly with oxygen or by re-oxidation with Mn-oxides, the latter will end when all Mn-oxides are reduced. Because the aerobic zone in our mixing treatment is not being mixed, the re-oxidation of Fe (II) most likely depends on reaction with Mn-oxides. When Mn-oxides are depleted iron recycling will come to an end and the barrier to retain reduced iron in the sediment will then disappear. The low fluxes in the mixing and _Nereis_ treatment indicate that at least for the duration of the experiment large escape of dissolved Fe (II) to the overlying water is prevented.
Studies on the effect of bioturbation on sediment properties have used a large number of animals, for example the polychaete _Heteromastus filiformis_, the bivalves, _Macoma balthica_ and _Tellina texana_ (Aller and Yingst 1985), the amphipod _Corophium volutator_ (Pelegri and Blackburn 1994), a heart urchin _Brisopsis lyrifera_ Widdicombe and Austen 1999). Bioturbation studies have not been restricted to macrofauna, the effects of microfauna and meiofauna have been studied as well (Fenchel 1996, Aller and Aller 1992). _Nereis diversicolor_ has been used in a number of studies (Davey 1994, Banta et al. 1999), e.g. to study the impact of benthic macrofauna on degradation of macroalgal detritus (Kristensen et al. 1992). Kristensen and Hansen 1999 reported that an important part of the irrigation effect of _Nereis_ pumping activity in sandy sediments is based on the solute fluxes across the burrow wall. Banta et al. 1999 attributed the effect of macrofauna on the balance between aerobic and anaerobic microbial metabolism to the oxidising effect of irrigation. A clear bioturbation activity and the documented effects on sediment biogeochemistry in sediments justify the use of _Nereis diversicolor_ to investigate the effect of bioturbation on sediment biogeochemistry.

4.5.1. Effect on total mineralization
In the companion paper the effects of the treatments on overall mineralization rates, carbon dynamics and their biogeochemical consequences have been
presented and discussed. We provide a short summary of these observations before discussing the effects of the treatments on iron and manganese.

Total inorganic carbon profiles of the treatments showed different patterns. At the start of the experiment $\Sigma$CO$_2$ profiles were classically shaped. Concentrations were low in the top-layer ($\sim$ 4 mM) and increased with depth ($\sim$ 10 mM). In the control cores, $\Sigma$CO$_2$ build up to 29 mM in the deepest layer during the experiment. The irrigation treatment resulted in a low $\Sigma$CO$_2$ concentration in the top 4 cm (3.5 - 7.5 mM) and a high concentration (up to 17.5 mM) deeper in the profile. Mixing treatment had a similar pattern as ventilation, but accumulation of $\Sigma$CO$_2$ in the deeper layers was slightly higher (22.2 mM). In the Nereis cores only low $\Sigma$CO$_2$ concentrations were observed in the top 6 cm (3.5 - 4.5 mM) but in the deepest layer $\Sigma$CO$_2$ increased to 9.5 mM. Mineralization rates, as calculated from the measured fluxes and changes in pore water inventories $\Sigma$CO$_2$, are given in table 1. Highest production rates were seen in the Nereis treatment, followed by ventilation, mixing and the control. Van Nugteren et al. 2002 concluded that improved transport of dissolved gases is more important with respect to mineralization enhancement than pure physical mixing of organic and mineral particles.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Mineralization rate ($\mu$mol cm$^{-2}$ d$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>9.4</td>
</tr>
<tr>
<td>Nereis</td>
<td>21.2</td>
</tr>
<tr>
<td>Ventilation</td>
<td>14.9</td>
</tr>
<tr>
<td>Mixing</td>
<td>10.7</td>
</tr>
</tbody>
</table>

4.5.2. Biogeochemical interactions

All results together provide an insight in the biogeochemical differences between the treatments.

Shape and concentration levels of porewater profiles of dissolved Fe (II) and dissolved Mn (II) contain information on the ‘net’ process and vertical distribution of iron- and manganese-oxide reduction and available sources of reducible metal-oxides. All iron and manganese related reactions are included in these profiles. Profiles with a clear subsurface maximum in Fe (II) or Mn (II) indicate a metal-oxide reduction zone (Thomas and Bendell-Young 1999). Reduced iron or manganese can diffuse out of the reduction zone. Downward diffusion of reduced
iron results in a reaction with sulphide and consequently acid volatile sulphide or pyrite (FeS₂) formation (Murase and Kimura 1997, Pyzik and Sommer 1981, Jorgensen 1982, King 1990). Upward diffusing reduced iron or manganese can be re-oxidized, chemically or microbial, with oxygen (Nealson 1978, Santschi et al. 1990, Canfield 1989) or, in the case of Fe (II) (Postma 1985, Postma and Appelo 2000), with Mn-oxides forming a (sub) surface peak of newly formed iron oxides (Aller 1990, Sundby and Silverberg 1985). Low porewater concentrations imply low reduction rates or fast Fe (II) / Mn (II) removal by one of the processes described above.

The fluxes out of the sediment to the overlying water reflect net metal-oxide reduction and the ineffectiveness of the sediment processes to retain all reduced metals within the profile, either by re-oxidation or by reaction with other constituents such as products of sulphate reduction. Epping et al. 1998 studied iron and manganese oxidation in sediment covered by microalgae. During benthic oxygenic photosynthesis there is sufficient oxygen to oxidise reduced components. Thus there is precipitation of Fe and Mn oxides and a low flux of reduced metals to the overlying water. Thamdrup et al. 1994b indicated that the balance between oxidation of Mn (II) in the oxidized zone and escape to the overlying water depends both on oxygen penetration depth (i.e. area of oxygenated sediment) and the intensity of Mn-oxide reduction.

The porewater concentrations of dissolved Fe (II) in the control cores decreased from 196 µmol l⁻¹ to 30 µmol l⁻¹ in the subsurface maximum and from 54 µmol l⁻¹ to 33 µmol l⁻¹ in the deepest layer with lowest concentrations (Fig. 2a) indicating a lack of net metal oxide reduction. The cores supported no flux of Fe (II) to the overlying water and the flux of Mn (II) is rather large (Fig. 1a). The low porewater concentrations of iron and manganese, the low mineralization rates and the black colour of the sediment indicate that sulfate reduction is the dominant anaerobic mineralization process in these cores, and bacterial metal oxide reduction has decreased. Due to the inefficiency of processes causing retention of manganese almost all manganese reduced in the control sediments could escape to the overlying water. Whereas Fe (II) reacts with products of sulfate reduction forming iron sulphide (AVS) and pyrite (FeS₂). These solid-phase sinks are not recycled so that no metal cycling occurred. As a consequence the sediment became depleted in reactive iron- and manganese oxides and bacterial metal oxide reduction diminished.

Literature data indicate that bioturbation stimulates benthic metabolism and that aerobic mineralization usually increases at the expense of anaerobic mineralization (Kristensen 2000; Banta et al. 1999, Herman et al. 1999). Consistently, Nereis cores
had highest mineralization rates (Table 1). The low porewater concentrations of dissolved Fe (II) and Mn (II) (Fig. 2) and negligible fluxes of dissolved Fe (II) and Mn (II) (Fig. 1) all indicate a shift to more aerobic mineralization in the *Nereis* treatment. The decrease in dissolved Mn (II) in the porewater as a result of bioturbation was also observed by Watson and Frickers 1990 in their experiment of 14 days with the burrowing polychaete *Nereis (Hediste) diversicolor* (1400 individuals m⁻²). Dissolved Mn (II) decreased with ~0.6 µmol Mn l⁻¹ d⁻¹ in the Mn-oxide reduction layer in their cores (0-5 cm depth), whereas we observed a decrease of ~ 0.25 µmol Mn l⁻¹ d⁻¹ (1-5 cm depth). In contrast to our results the decrease in their cores was accompanied by a flux of manganese to the water column. This difference can be attributed to bioturbation intensity and initial sediment conditions. In our *Nereis* treatment the iron-oxide reduction zone has moved into the sediment relative to the other treatments (Fig. 2a). The small dissolved Fe (II) maximum in the 6 through 8 cm layer of the *Nereis* sediment likely reflects the active zone of iron oxide reduction. However, the Mn-oxide reduction zone that would be expected above the Fe-oxide reduction zone was not found. This could be due to intensive particle mixing in these cores and the relatively large interval (1 or 2 cm) of the slices. The deepening of iron-oxide reduction zone is consistent with the model of Herman et al. 1999 that predicts a deeper average depth of mineralization and a less reduced sediment as a result of particle mixing accompanied with irrigation. Unfortunately our sediment cores were not long enough to reveal changes in deeper, more anaerobic layers.

The ventilation cores represent the effect of increased oxygen input and removal of dissolved carbon dioxide without concurrent mixing of sediment. The enhanced oxygen input results in an enlargement of the oxic and sub-oxic area (Aller 1983), which in turn supports a larger area with metal-oxide reduction and re-oxidation. This may account for the high reduced metal concentrations in the porewater of the ventilation cores when compared with the control and the *Nereis* treatment. The effects of an increased oxygenated surface are also reflected in the Feₚₐₚ profile (Fig. 4). These changes are consistent with documented effects of burrows on ammonium and total organic carbon cycling (Aller and Aller 1992, Kristensen and Hansen 1999, Van Nugteren et al. 2002). The mineralization rate in the ventilation treatment is higher than in the control (Table 1), indicating that the overall metabolism has been stimulated (Aller and Aller 1998, Kristensen 2000, Dauwe et al. 2001).

Porewater Fe (II) concentrations in the ventilation treatment are high (Fig. 2) likely due to the larger sub-oxic sediment volume. Dissolved metal concentrations are high and Fe (II) and Mn (II) escape to the overlying water mainly during the initial
period (Fig. 1). Although some reduced metal can be re-oxidized around the tubes, apparently this is not sufficient to retain metals in the sediment. Eventually, this results in a net decrease of available oxides in the sediments and consequently a decrease in metal-oxide reduction. In theory, despite of the additional oxygen, iron (or manganese) oxide reduction will end in due time, as no cycling occurs because of the lack of a particle mixing component. Moreover, in natural sediments porewater flushing in sediments results in the loss of degradation products like dissolved Mn (II) and Fe (II). This may result in less efficient iron and manganese cycling if significant amounts of iron and manganese are lost without replenishment from the overlying water or settling particles.

The high dissolved Fe (II) concentrations in the porewater of the mixing cores are indicative of iron oxide reduction and an active iron cycle. Apparently sediment mixing resulted in a shift towards the optimal conditions to maintain the iron cycle. Reduced iron (in dissolved and particulate form) is mixed upwards where it is re-oxidized with manganese oxides or oxygen. The formed iron-oxide minerals will subsequently be transported into the iron-oxide reduction zone. Iron is well retained in the mixing sediment since dissolved Fe (II) effluxes are very small (only little higher than those of the bioturbated sediments). A zone with a high concentration of reactive oxides can be expected in such a profile due to the re-oxidation of reduced metals and the subsequent precipitation in oxygenated surface layers (Burdige 1993, Slomp et al. 1997). Porewater profiles of dissolved Mn (II) and a high flux of dissolved Mn (II) indicate Mn-oxide reduction in the very near surface layer and support the idea of ferrous iron oxidation coupled to manganese oxide reduction. This re-oxidation of iron allows efficient retention of iron within the sediment. The efflux of dissolved Mn (II) is relatively large because the Mn-oxide reduction zone is close to the surface and the diffusion distance is too short for the slow Mn oxidation kinetics to completely re-oxidize Mn (II) (Sundby and Silverberg 1985).

The differential effects of ventilation and particle mixing on iron and manganese cycling are best illustrated by comparing the ventilation and mixing treatment. Particle mixing results in a redistribution of reduced particulate and adsorbed metals into the upper layers which otherwise would not have happened. This stimulated iron and manganese oxidation and reduction without a major change in the area of oxic to anoxic sediment with the consequence that more manganese could escape. The higher ammonium accumulation in the porewater of the mixed sediment (Van Nugteren et al. 2002) also indicate that these sediments are less oxic than the ventilation and Nereis treated sediments. In the ventilation treatments oxygen is transported into the sediment resulting in a longer time for re-oxidation.
of the reduced metals before they reach the sediment surface. Van der Zee 2002, described the escape of reduced manganese to the water column when manganese reduction occurs near the sediment surface for Iberian margin sediments. In these sediments the rate limiting steps in the manganese cycle were slow oxidation kinetics and particle mixing whereas for the iron cycle only particle mixing was rate limiting. Our experimental observations support their field data in the importance of particle mixing for iron and manganese cycling and the importance of irrigation for Mn-oxidation.

4.5.3. Turnover times

To obtain insight in the metal cycling efficiency and dynamics it is instructive to calculate turnover times. These are calculated by dividing the pool of Fe_{diss} (here calculated by the excess of reactive iron-oxides compared to the background values) by the dissolved Fe (II) production, which is calculated from measured fluxes and porewater inventory changes. It should be mentioned that the metal cycling efficiency, i.e. the number of cycling times before burial, is more relevant than the turnover time because it gives the potential amount of organic matter that can be mineralised by one metal molecule (Canfield et al. 1993b, Wijsman et al. 2001b). Unfortunately we can not calculate this number because the natural processes of bioturbation and sedimentation are missing in most of the cores (except of bioturbation in the *Nereis* treatment). It should also be noted that turnover times as presented in Table 2a & 2b are maximum values because metal oxide reduction rates can be underestimated due to re-oxidation of reduced Fe and Mn and other side reactions. A long turnover time indicates a slow or incomplete cycling of the metals, whilst a short turnover time indicates either a high metal oxide reduction rate (i.e. a large flux or a large increase in porewater concentrations) or a small metal oxide pool. Due to low fluxes, turnover times of Fe and Mn calculated for the *Nereis* cores were longest, also in these cores flux direction is opposite (i.e. into the sediment) from the other fluxes (in Table 2a and b indicated by italic numbers).

The turnover times of Fe (< 10 days, Table 2a) are somewhat shorter than those reported for other sediments. Thamdrup and Canfield 1996 found Fe turnover times of 70 days in sediments from the slope of Chile. In the Skagerrak Canfield et al. 1993b calculated Fe and Mn turnover times of 70-250 days. Their turnover times are based on the dissimilatory iron-oxide reduction rates (i.e microbial iron oxide reduction coupled to carbon oxidation) only. Turnover times based on the total iron-oxide reduction (i.e. including the iron reduction coupled to sulfide oxidation) are faster, e.g. 46 to 61 days in the Slope of Chile. Our estimates
represent total iron-oxide reduction, because we have not differentiated the metal oxide reduction pathways. The fast turnover time in the control treatment resembles those of Van der Nat and Middelburg 1998. They reported a turnover time of 4 days for iron in a vegetated tidal freshwater marsh (without macrofauna). The pools of reactive iron oxides (dithionite extractable iron) in the different treatments (~ 430 µmol cm^{-2}) are similar to the values of Skagerrak, 350-400 µmol cm^{-2} (Canfield et al. 1993b) but higher than those of the Slope of Chile, 39-77 µmol cm^{-2} (Thamdrup and Canfield 1996). This is also the case for dissolved Fe (II) production rates (our cores, except the *Nereis* treatment: 0.9-1.1 µmol cm^{-2} d^{-1}; Skagerrak: 4.4-5.7 µmol cm^{-2} d^{-1}; Slope of Chile: 0.14-0.27 µmol cm^{-2} d^{-1}).

Table 2a. Fe-oxide reduction rates (µmol cm^{-2}d^{-1}), excess dithionite extractable Fe oxide (µmol cm^{-2}), pool size of ascorbate and dithionite extractable iron (µmol cm^{-2}), turnover times (days) and total importance iron plus manganese oxide reduction in organic carbon mineralization (%).

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Fe (II) production (µmol cm^{-2}d^{-1})</th>
<th>Excess Fe (µmol cm^{-2})</th>
<th>Fe asc pool (µmol cm^{-2})</th>
<th>Fe dith pool (µmol cm^{-2})</th>
<th>Fe turnover time (days)</th>
<th>Fe &amp; Mn in mineralization (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0.92</td>
<td>5.61</td>
<td>195</td>
<td>433</td>
<td>6.10</td>
<td>0.6</td>
</tr>
<tr>
<td><em>Nereis</em></td>
<td>-2.61</td>
<td>22.78</td>
<td>183</td>
<td>429</td>
<td>8.75</td>
<td>0</td>
</tr>
<tr>
<td>Ventilation</td>
<td>2.93</td>
<td>11.26</td>
<td>206</td>
<td>430</td>
<td>3.83</td>
<td>8.1</td>
</tr>
<tr>
<td>Mixing</td>
<td>1.11</td>
<td>2.06</td>
<td>187</td>
<td>434</td>
<td>1.85</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Table 2b. Mn-oxide reduction rates (µmol cm^{-2}d^{-1}), excess dithionite extractable Mn oxide (µmol cm^{-2}), pool size of ascorbate and dithionite extractable manganese (µmol cm^{-2}), turnover times (days) and total importance manganese oxide reduction in organic carbon mineralization (%).

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Mn (II) production (µmol cm^{-2}d^{-1})</th>
<th>Excess Mn (µmol cm^{-2})</th>
<th>Mn asc pool (µmol cm^{-2})</th>
<th>Mn dith pool (µmol cm^{-2})</th>
<th>Mn turnover time (days)</th>
<th>Mn in total mineralization (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0.15</td>
<td>0.33</td>
<td>2.0</td>
<td>18</td>
<td>2.23</td>
<td>0.1</td>
</tr>
<tr>
<td><em>Nereis</em></td>
<td>-0.02</td>
<td>0.91</td>
<td>1.3</td>
<td>19</td>
<td>42.5</td>
<td>0</td>
</tr>
<tr>
<td>Ventilation</td>
<td>0.04</td>
<td>0.26</td>
<td>1.5</td>
<td>18</td>
<td>6.35</td>
<td>0.2</td>
</tr>
<tr>
<td>Mixing</td>
<td>0.09</td>
<td>0.12</td>
<td>1.3</td>
<td>18</td>
<td>1.30</td>
<td>0.4</td>
</tr>
</tbody>
</table>
Mn turnover times (1.3 – 42.5 days, Table 2b) agree with those found in Long Island Sound, 0.37-344 days (Aller 1994b and the Skagerrak, 250 days Canfield et al. 1993b). In deep-sea sediments from Panama basin turnover times at high particle mixing were 365 days, low particle mixing resulted much longer turnover time, 1241 days (Aller 1990). The excess Mn$_{dith}$ in our cores, 0.12-0.91 µmol cm$^{-2}$ (Table 2b) is lower than values of excess manganese in Long Island Sound and Panama basin, 5 -10 µmol cm$^{-2}$ and 173 µmol cm$^{-2}$ respectively. The pool of dithionite extractable manganese (~ 18 µmol cm$^{-2}$) is much smaller than in the Skagerrak, 900 µmol cm$^{-2}$, (Canfield et al. 1993b). Dissolved Mn (II) production rates (0.04 – 0.4 µmol cm$^{-2}$ d$^{-1}$) were much higher than in Panama Basin, 0.002 µmol cm$^{-2}$ d$^{-1}$, and lower than rates found in Long Island Sound, 13.3-29.0 µmol cm$^{-2}$ d$^{-1}$ and Skagerrak (3.64 µmol cm$^{-2}$ d$^{-1}$). The relatively small size of excess Mn$_{dith}$ and high dissolved Mn (II) production underly the fast manganese turnover observed in our experiment.

4.5.4. Mineralization pathways

The contribution of metal oxide reduction to carbon oxidation is variable among sediments. In most sediments the contribution of iron oxide reduction to the organic carbon mineralization is much higher than for manganese oxide reduction. The production of dissolved Mn (II) is often completely attributed to chemical reduction with Fe (II) (Postma 1985, Canfield et al. 1993b, Kostka et al. 1999b). Total iron oxide and manganese oxide reduction rates can be converted to carbon respiration rates via the stoichiometry of the dissimilatory reduction process (Froelich et al. 1978). Together with mineralization rates, based on total inorganic carbon during incubation, the relative importance of the metal-oxide reduction processes for the mineralization have been calculated (Tables 2a & 2b). In control cores Fe and Mn together accounted for 0.6 % of mineralization. Calculations for ventilation and mixing treatments were 8% and 3 % respectively. In Nereis cores no net metal-oxide reduction was observed indicating that the overall effect of bioturbating fauna could not be described by either the ventilation or mixing alone and that their mutual effect was not additive. In treatments with detectable metal-oxide reduction the contribution of Mn-oxide reduction was very small, 0.1-0.4 %. The contribution of iron oxide reduction in the ventilation treatment approached but remain lower than those found for the Slope of Chile, 12-29 % (Thamdrup and Canfield 1996). Rates of metal oxide reduction in the Skagerrak (site S4 and S6) are much higher, 21-78 %, with a maximum contribution of Mn-oxide reduction of 5-14% (Canfield et al. 1993b). In Long Island Sound manganese-oxide reduction accounts for 3-4 % of mineralization (Aller 1980).
4.5.5. Porewater profiles

The porewater profiles contain clear indications for metal-oxide reduction. At the start of the experiment the profile indicate a lack of manganese oxide reduction and the presence of iron oxide reduction at 2-3 cm depth (t=0, fig. 2a and b). Because of the fast turnover rates, the presence of metal-oxide reduction at the end of the experiment reflects the presence of metal-oxide sources. In the control treatment metal-oxide reduction has diminished because of the lack of an oxide source and porewater concentrations of Fe (II) and Mn (II) are low throughout the profile. The porewater profiles of the Nereis treatments showed a small increase of Fe (II) at 6-8 cm depth. In these treatments the iron oxide availability is ensured by the particle mixing and irrigating activity of the worms. In contrast Mn concentrations were low in the whole profile, apparently the irrigation activity of Nereis is not sufficient for manganese to be re-oxidized efficiently and to complete the cycle (see paragraph on difference between iron and manganese).

Despite the lack of particle mixing the porewater profiles of iron and manganese in the ventilated sediments show clear indications of iron- and manganese oxide reduction. This implies the presence of a mechanism, either biotic or abiotic, to resource the reducible metal oxides in the reducing layer without particle mixing. Recently Sobolev and Roden 2001 reported on the suboxic deposition of ferric iron in opposing gradients of Fe (II) and O₂. They suggest that some type of Fe (II) oxidising bacteria produce mobile forms of Fe (III) as the initial product. These compounds which are formed at the oxic-anoxic interface are subject to diffusion, destabilise and hydrolyse and before they precipitate as Fe (III) oxides. The Fe (III) oxides can subsequently be used in iron oxide reduction, thereby providing a rapid and small scale coupling between oxidation and reduction. Furthermore, they suggested that the process was able to compete with abiotic iron oxide formation. Results of the ventilated sediment cores are consistent with the presence of such a microcycle. Due to the enlarged oxic-anoxic interface the process can cover a large surface and result in an significant role for iron oxide reduction despite the lack of a particle mixing component as required in the macro cycle with non-mobile oxidized metal oxides. The profiles of Mn could be explained by a similar process. However, the existence of a manganese micro-cycle has not yet been investigated.

4.5.6. Iron and manganese

Porewater profiles of iron and manganese differ among and within treatments, indicating the differential behaviour of these two metals. Known differences between iron and manganese include (1) manganese oxide reduction has a higher
energy gain than iron oxide reduction (Froelich et al. 1978) generally resulting in Mn-oxide reduction occurring before and thus above iron-oxide reduction, (2) Fe (II) can be re-oxidized in a micro cycle (Sobolev and Roden 2001), thereby decreasing the importance of bioturbation components for complete cycling (see above) (3) Fe (II) can be re-oxidized with Mn-oxides (Postma 1985, Burdige et al. 1992) (4) oxidation kinetics of Fe (II) are faster than that of Mn (II) (Stumm and Morgan 1981), (5) Fe (II) can react with hydrogen sulfide or disulphide with the result of sulfide mineral formation (Jorgensen 1977, Pyzik and Sommer 1981, Moeslund et al. 1994), while Mn (II) can react with a carbonate surface or precipitate in the form of Mn, Ca carbonate (Middelburg et al. 1987). This differential behaviour of Mn and Fe has consequences for their recycling efficiency and their role in organic carbon mineralization.

While Mn in our experiments mainly escapes recycling by efflux to the overlying water, iron escapes recycling by a flux to the overlying water and reaction with sulphides to form solid phase iron sulphides. Therefore the sulfidic conditions in the control cores, had a larger effect on iron recycling than on manganese recycling. Enhanced irrigation, in our experiment represented as enhanced ventilation, resulted in an additional oxygen input and an increased area of oxygenated surface. The effect on the biogeochemical processes depends on the specific conditions. Oxidation kinetics for iron is much faster than for manganese (Stumm and Morgan 1981). Thus addition of oxygen, even small amounts, affects iron on a very short time scale. Furthermore, a short period of enhanced oxygen penetration or a small oxygenated layer is sufficient to retain significantly more iron in a sediment. For Mn these conditions have to last longer and have to be more extensive (e.g. a larger aerobic layer). Irrigation may result in (1) a larger metal oxide pool (2) a smaller flux out of the sediment and (3) an increase in the number of times these metals are recycled. In our experiments the effect of ventilation is not straightforward. The Fe asc concentrations indeed are significantly higher in the ventilation treatment than in the others, but for Mn-oxide such a difference is not observed, though the ventilation period was long and there was a steady supply of oxygen. Iron effluxes in the ventilated cores are not different from those in the other treatments. Although not significant, there seems to be a trend that Mn-fluxes are lower due to ventilation (Fig. 1b). A porewater peak of Mn (II) just below the sediment interface might reflect microbial Mn-reduction or chemical manganese reduction coupled to oxidation of reduced iron. This should be reflected in an increase of iron oxides at the depth of the dissolved Mn (II) peak and a decrease in Mn dith. There is some indication for this (Fig 3a, 3b) but this is not very clear because of the coarse
resolution of our data and the large differences between relative changes in Mn-oxide concentrations and Fe-oxide pools. The enhanced oxygen supply increases the porewater concentrations of Mn (II) and Fe (II) about 3 and 2 times, respectively. Apparently, the effect of a larger sub-oxic area is relatively more important for Mn than for Fe. The limited increase of dissolved Fe (II) could however be due to a faster re-oxidation near the site of liberation. Altogether the effect of oxygen on manganese appears to be larger than that on iron.

In the mixing treatment re-oxidation of Fe (II) with Mn-oxides and the mixing of the particles are essential for maintaining the iron cycling. Manganese oxide reduction coupled to Fe (II) oxidation affects the relative importance of Mn-reduction in organic matter mineralization, because less Mn-oxides will be available for Mn-oxide based respiration. In the mixing treatment the Mn-oxide reduction layer is very close to the sediment surface with the results that most Mn (II) diffuses to the overlying water causing depletion of Mn in the sediment. This in turn results in a decreasing role, directly and indirectly, in the organic carbon oxidation. As long as Mn-oxides are present to re-oxidize reduced iron the mixing events stimulate the iron-oxide reduction more than the ventilation treatment. Furthermore, iron oxide reduction rate is increased 1.6 times relative to the ventilation treatment.

The study of Sundby and Silverberg 1985, showed that the cycling rate of Mn in the Gulf of St. Lawrence was tightly coupled to Mn (II) production rates and depended mostly on particle mixing. In these sediments maxima of dissolved Mn (II) were at 4-10 cm depth. This is much deeper than in our cores and allows a better retention of Mn in the sediment. Thus Mn-oxide reduction rates in the mixing cores could have been stimulated if the reduction layer would have been deeper in the sediment. Aller 1994b concluded that Mn can be important as intermediate electron acceptor during periods of high bioturbation with well oxygenated overlying waters and moderate organic carbon fluxes. Some diagenetic modelling studies have explored the importance of mineralization pathways as a function of organic matter load and provided an insight on the effect of the organic carbon load on the metal cycling (Soetaert et al. 1996, Wijsman et al. 2002). With increased organic matter loading the iron oxide reduction increases at the expense of manganese oxide reduction. In Aller 1990, Banta et al. 1999, Kristensen 1985 and our experiments it was shown that animal activity decreases the importance of anaerobic mineralization. Parallel increases of faunal biomass, bioturbation, and estuarine productivity allow for a longer lasting period with a high importance of the metal-oxide reduction pathways in organic matter mineralization. The resulting environmental conditions are more favourable for
benthic fauna than those resulting from sulfate reduction, with the consequence that there is positive feedback between animals and sediment biogeochemistry.

4.6. Conclusions

The effect of bioturbation on iron and manganese cycling depends on particle mixing and sediment irrigation. Results show that both components are necessary to complete the cycle and maintain the sub-oxic mineralization pathways using metal-oxides. Particle mixing, in the experiment mimicked by a mixing device, is important for redistribution of (re) oxidized metal-oxides. Irrigation, here imitated by enhanced sediment ventilation (i.e. enhanced exchange of porewater dissolved gases), is essential for the input of dissolved oxidants. However, this aspect is more important for Mn than for Fe because Fe has a higher affinity for oxygen and can also re-oxidize with Mn-oxides, while, because of the slow oxidation kinetics, a longer oxygen-Mn (II) contact is needed for sufficient retainment in the sediment. Therefore the efficiency of Fe-cycling is determined primarily by particle mixing. Both particle mixing and irrigation determine Mn-cycling efficiency. Our results indicate that the combined effect of ventilation and particle mixing is not simply additive.