

Coupled anoxic nitrification/manganese reduction in marine sediments

STEFAN HULTH,^{1,*} ROBERT C. ALLER,² and FRANCK GILBERT³

¹Department of Analytical and Marine Chemistry, Göteborg University, S-412 96 Göteborg, Sweden

²Marine Sciences Research Center, State University of New York at Stony Brook, Stony Brook New York 11794-5000, USA

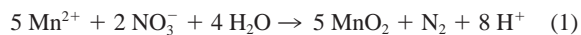
³Laboratoire d'Océanographie et de Biogéochimie (COM)-Campus de Luminy-Case 901, F-13228 Marseille Cedex 9, France

Abstract—Pore water and solid phase distributions of oxygen, manganese, and nitrogen from hemipelagic and shelf sediments sometimes indicate a close coupling between the manganese and nitrogen redox cycles. Reaction coupling must be sustained in part by biological reworking of Mn-oxide-rich surface sediments into underlying anoxic zones. Surface sediment from Long Island Sound (USA) was used in laboratory experiments to simulate such intermittent natural mixing processes and subsequent reaction evolution. Mixed sediment was incubated anoxically under either diffusively open (plugs) or closed conditions (jars). In closed anoxic incubations, pore water NO_3^- increased regularly to a maximum (up to $17 \mu\text{M}$) after one to several days, and was subsequently depleted. Mn^{2+} was produced simultaneously with NO_3^- . N_2O was also clearly produced and subsequently reduced, with a formation-depletion pattern consistent with coupled nitrification-denitrification in the anoxic sediment. Manipulative additions of Mn-oxides ($5\text{--}10 \mu\text{mol g}^{-1}$ net) demonstrated that net anoxic NO_3^- production correlated directly with initial Mn-oxide content. During initial net NO_3^- production there was no evidence for SO_4^{2-} reduction. A direct correlation was also observed between anoxic nitrification rates and estimated sulfate reduction rates; the larger nitrification rates, the larger the eventual net sulfate reduction rates. Diffusively-open incubations using sediment plugs of four different thicknesses (2, 5, 10 and 20 mm) exposed to anoxic overlying water, also showed net production of pore water NO_3^- ($\sim 15\text{--}20 \mu\text{M}$) despite the absence of NO_3^- in the overlying water for at least five days. In general, higher nitrate concentrations were maintained in the open relative to the closed incubations, due most likely to lower concentrations of dissolved reductants for NO_3^- in the open system. These experiments imply simultaneous coupling between the benthic nitrogen, manganese, and sulfur redox cycles, involving anoxic nitrification and sulfide oxidation to SO_4^{2-} . Anoxic nitrate production during Mn reduction indicates that nitrification and denitrification can occur *simultaneously* in subsurface sediments, without vertical stratification. The existence of anoxic nitrification implies new reaction pathways capable of increasing coupled sedimentary nitrification-denitrification, particularly in bioturbated or physically mixed deposits. *Ltd*

1. INTRODUCTION

Benthic nitrification-denitrification represents a significant component of the marine nitrogen cycle, particularly in organic rich shelf and hemipelagic sediments underlying oxygenated waters (Christensen, et al., 1987; Seitzinger, 1988; Reimers, et al., 1992; Seitzinger and Giblin, 1996). Nitrification and denitrification reactions in sediments are often conceptualized as occurring in a largely stratified reaction sequence characterized by an upper oxic layer, dominated by aerobic nitrification, and an underlying suboxic or anoxic region into which NO_3^- is transported and reduced during C_{org} remineralization (Froelich, et al., 1979; Jahnke, et al., 1982; Billen, 1982; Christensen and Rowe, 1984). Burrows, tubes, and fecal structures formed by benthic fauna superimpose various microenvironmental patterns of radially or spherically distributed aerobic nitrification-anaerobic denitrification patterns onto this overall stratified reaction sequence (Jahnke, 1985; Kristensen, 1988; Aller, 1988; Brandes and Devol, 1995). In some sedimentary deposits, however, the average distributions of O_2 and NO_3^- are apparently not consistent with nitrification exclusively in oxic regions, or with reduction of NO_3^- by C_{org} alone (Sørensen et al., 1987; Bender, et al., 1989; Aller, 1990; Murray et al., 1995;

Luther, et al., 1997; Aller, et al., 1998). In particular, circumstantial evidence has mounted that within organic and Mn-rich regions of continental margin sediments, the N and Mn cycles may be closely coupled through reactions such as:



Evidence for the oxidation of Mn^{2+} by NO_3^- comes from the apparent oxidation of Mn^{2+} in surficial sediments where O_2 is absent, that is O_2 and Mn^{2+} distributions do not overlap, and where the only additional energetically favorable oxidants available in sufficient quantity, are NO_3^- and particulate MnO_2 . Depending on the assumed form of MnO_2 , reaction (1) is not thermodynamically favorable except in zones of relatively high NO_3^- and pH (Table 1). NO_3^- maxima well below the surficial oxic zone may sometimes result from biogenic irrigation and oxic microzones, but anoxic nitrification during MnO_2 reduction, such as defined by reaction (2), is also clearly energetically possible under typical sedimentary conditions (Table 1). Because Mn-oxide enriched surficial sediment is rapidly mixed into subsurface anoxic zones during normal biogenic and physical reworking, an anaerobic, lithotrophic nitrification pathway could be a significant mode of biologically mediated N cycling.

In the present study, we experimentally simulated the natural

* Author to whom correspondence should be addressed.

Table 1. Change in standard free energy of the reaction R (ΔG_R ; kJ mol⁻¹) at conditions often found in marine sediments. Organic material is for simplicity represented as carbohydrate, CH₂O.

	N OXIDATION	ΔG_R pH=7	ΔG_R pH=8
Nitrification	$2 O_2 + NH_4^+ \Rightarrow 2 H^+ + NO_3^- + H_2O$	-341	-353
Oxidation N ₂ generation	$3/2 MnO_2 + NH_4^+ + 2 H^+ \Rightarrow$ $3/2 Mn^{2+} + 1/2 N_2 + 3 H_2O$	-224	-212
Anoxic nitrification	$4 MnO_2 + NH_4^+ + 6 H^+ \Rightarrow$ $4 Mn^{2+} + NO_3^- + 5 H_2O$	-175	-141
	N REDUCTION		
Denitrification	$5/4 CH_2O + NO_3^- + H^+ \Rightarrow$ $5/4 CO_2 + 1/2 N_2 + 7/4 H_2O$	-596	-590
Anoxic sulfide oxidation I	$5/8 FeS + 4 MnO_2 + NH_4^+ + 7 H^+ \Rightarrow$ $1/2 N_2 + 4 Mn^{2+} + 5/8 SO_4^{2-} + 5/8 Fe^{2+} + 11/2 H_2O$	-590	-550
NH ₄ ⁺ oxidation	$5/3 NH_4^+ + NO_3^- \Rightarrow 4/3 N_2 + 3 H_2O + 2/3 H^+$	-421	-426
Anoxic sulfide oxidation II	$NO_3^- + 5/8 FeS + H^+ \Rightarrow$ $1/2 N_2 + 5/8 SO_4^{2-} + 5/8 Fe^{2+} + 1/2 H_2O$	-419	-413
Fe ²⁺ oxidation	$NO_3^- + 5 Fe^{2+} + 12 H_2O \Rightarrow$ $5 Fe(OH)_3 + 1/2 N_2 + 9 H^+$	-319	-370
Anoxic Mn ²⁺ oxidation	$5/2 Mn^{2+} + NO_3^- + 2 H_2O \Rightarrow$ $5/2 MnO_2 + 1/2 N_2 + 4 H^+$	-48.9	-71.4
	ADDITIONAL Mn REDUCTION		
Mn reduction	$1/2 CH_2O + 3/2 CO_2 + 1/2 H_2O + MnO_2 \Rightarrow$ $Mn^{2+} + 2 HCO_3^-$	-190	-190
S ⁰ oxidation	$4/3 H^+ + MnO_2 + 1/3 S^0 \Rightarrow$ $Mn^{2+} + 1/3 SO_4^{2-} + 2/3 H_2O$	-157	-147
Anoxic sulfide oxidation III	$2 H^+ + MnO_2 + 1/4 FeS \Rightarrow$ $Mn^{2+} + 1/4 SO_4^{2-} + 1/4 Fe^{2+} + H_2O$	-148	-137
Anoxic sulfide oxidation IV	$3 H^+ + MnO_2 + HS^- \Rightarrow Mn^{2+} + S^0 + 2 H_2O$	-136	-119
	C OXIDATION		
Oxic respiration	$CH_2O + O_2 \Rightarrow CO_2 + H_2O$	-521	-521
Sulfate reduction	$CH_2O + 1/2 SO_4^{2-} \Rightarrow H_2S + HCO_3^-$	-122	-122
Fe reduction	$CH_2O + 7 CO_2 + 4 Fe(OH)_3 \Rightarrow$ $4 Fe^{2+} + 8 HCO_3^- + 3 H_2O$	-107	-107

Conditions used to calculate ΔG_R : [O₂] = 150 μM; [CO₂] = 50 μM; [HCO₃⁻] = 2 000 μM; pN₂ = 0.781 atm; [NO₃⁻] = 5 μM; [NH₄⁺] = 25 μM; [Mn²⁺] = 100 μM; [Fe²⁺] = 5 μM; [SO₄²⁻] = 24 mM; [H₂S] = 25 μM; [HS⁻] = 5 μM. Activity coefficients were assumed to be 1.

Values on the standard free energy of formation, ΔG_f° , were taken from Berner (1980) and Stumm and Morgan (1996).

reworking of surficial Mn-oxides into underlying anoxic sediments and evaluated the possible occurrence of anaerobic, lithotrophic nitrification during subsequent Mn reduction. We show that NO₃⁻ can be produced during Mn-oxide reduction, and that the rate of anoxic nitrification is directly proportional to the quantity of Mn-oxide available. It is clear that the juxtaposition of Mn-oxides, NO₃⁻, NH₄⁺, C_{org}, and Fe-sulfides that results from bioturbation and physical mixing processes in organic-rich deposits, creates the potential for complex coupling between the Mn, N, C, and S redox cycles in surficial sediments.

2. MATERIAL AND METHODS

The general experimental approach was to physically mix the upper ~2 cm of sediment obtained from an organic-rich mud deposit in central Long Island Sound, and to either enclose the mixed material in sealed anoxic containers (closed incubation series), or expose defined thicknesses of sediment for a set period to an anoxic overlying water reservoir (open incubation series). Sediment and pore water were then sampled serially or at a discrete time subsequent to mixing in order to document net reaction patterns. Dissolved O₂ penetrates only a few millimeters into the sediment and the surface-most material (0–1 cm) is typically enriched in Mn-oxides by normal diagenetic cycling at the sampling site used (Aller, 1994). Mixing thus served to rapidly introduce Mn-oxides into underlying anoxic sediment. The naturally present Mn-oxides were augmented in one experimental series by addition of variable amounts of laboratory synthesized MnO₂.

2.1. Study Site and Sediment Sampling

Surface sediment was sampled at the PULSE study site in central Long Island Sound, USA (41 10.03N, 72 57.43W) during June, September, and November 1997. A number of studies have been carried out in the general location of the site, and biological, geochemical, and physical sedimentary properties are relatively well-characterized (Station NWC; Station P, PULSE site; e.g., Benninger, et al., 1979; Aller, 1994; Gerino, et al., 1998). Water depth averages ~15 m, sediments contain ~2% organic carbon, ~2% CaCO₃, and have an average porosity of ~0.8 (0–1 cm). Salinity is relatively constant between 24 and 25, and temperature varies sinusoidally between 2 and 22°C annually. The bottom was sampled with a Smith-MacIntire grab, obvious macrofauna and shell debris picked out, and the top ~2 cm of sediment removed. Sediment was sieved through a 0.45 mm Nylon mesh and homogenized. No water was added during sieving and homogenizing. Sediment collected in June was homogenized under N₂, initial handling of sediment in September and November was done under air.

2.2. Closed Incubations

A portion of the sieved and homogenized sediment was removed separately and placed in 20 ml (June and September) or 50 ml (November) polypropylene centrifuge tubes (jars). The completely filled jars were sealed, put in plastic bags, and incubated at room temperature in a bucket of anoxic mud obtained from the collection site (Fig. 1). Subsequent to the manual removal of air, the bags were placed with the upper edges at least 5 cm into the mud to ensure completely anoxic

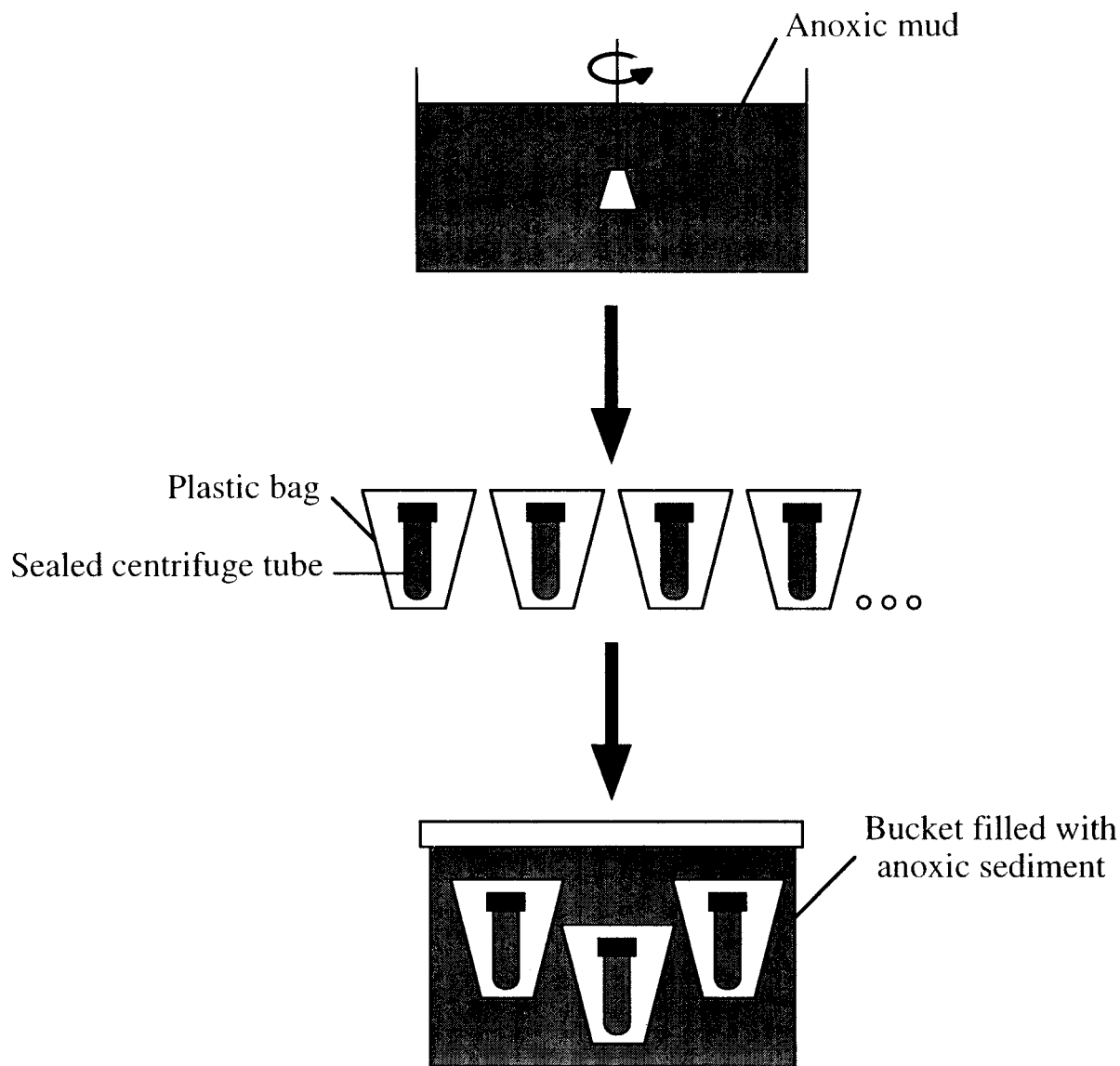


Fig. 1. Schematic illustration of the experimental set-up used to study net reaction rates within sediments under diffusively closed conditions (closed anoxic incubation). To ensure completely anoxic conditions the jars were placed with their upper edges at least 5 cm into the mud. Reaction rates were inferred from the production rates of solutes to the pore water with time of incubation.

conditions (surficial O_2 penetration $\sim 1\text{--}2$ mm, Fe-monosulfides present). Temperatures were $20.7\text{--}21.6^\circ\text{C}$ (June), $20\text{--}22.1^\circ\text{C}$ (Sept.), and $21.2\text{--}22.1^\circ\text{C}$ (Nov.). This type of incubation is referred to as “closed anoxic incubation” (e.g., Martens and Berner, 1974).

During the November incubation experiment, Mn-oxide was added to two separate sediment portions before enclosure. The MnO_2 used was formed from the oxidation of Mn^{2+} by MnO_4^- under basic conditions, equilibrated with sea water, and aged ~ 12 years at 4°C (Balistrieri and Murray, 1982; Aller and Rude, 1988). The precipitate has been inferred as the mineral phase vernadite (δMnO_2) based on the average oxidation state of the solid ($O:Mn = 1.94 \pm 0.02$), and its X-ray diffraction pattern (Burns and Burns, 1979; Balistrieri and Murray, 1982). In this case, the sieved and homogenized natural sediment was split into three portions, corresponding to three different treatments. No extra MnO_2 was added to the first sediment portion (A), while an estimated amount of ~ 13 and $\sim 33 \mu\text{mol g}^{-1}$ dry sediment (assuming molecular weight of MnO_2) of the synthesized MnO_2 was added to the second (B) and third (C) portion, respectively. All three

portions were homogenized by hand using plastic spoons before packing the sediment into jars.

During each incubation series, 1–3 tubes were removed every 1–3 days, centrifuged (12 minutes, 3800 rpm), filtered ($0.4 \mu\text{m}$) and the obtained pore water analyzed for total carbonate (ΣCO_2 or C_T), alkalinity (A_T), DIN (NO_3^- , NO_2^- , and NH_4^+), Mn^{2+} and pH. The centrifuged sediment was frozen for later analyses of manganese.

2.3. Diffusively Open Incubations

Portions of the surface sediment from the June sampling were also used for anoxic incubations under diffusively *open* conditions. The sieved and homogenized sediment was placed in polycarbonate tube-sections sealed at the base (plugs), and the sediment surface was smoothed using a stainless steel spatula. Plugs had variable thickness of 2, 5, 10 and 20 mm. The sediment-filled plugs were placed in a polycarbonate reservoir containing filtered ($0.2 \mu\text{m}$), anoxic overlying water from the sampling location (salinity of 24). The anoxic overlying

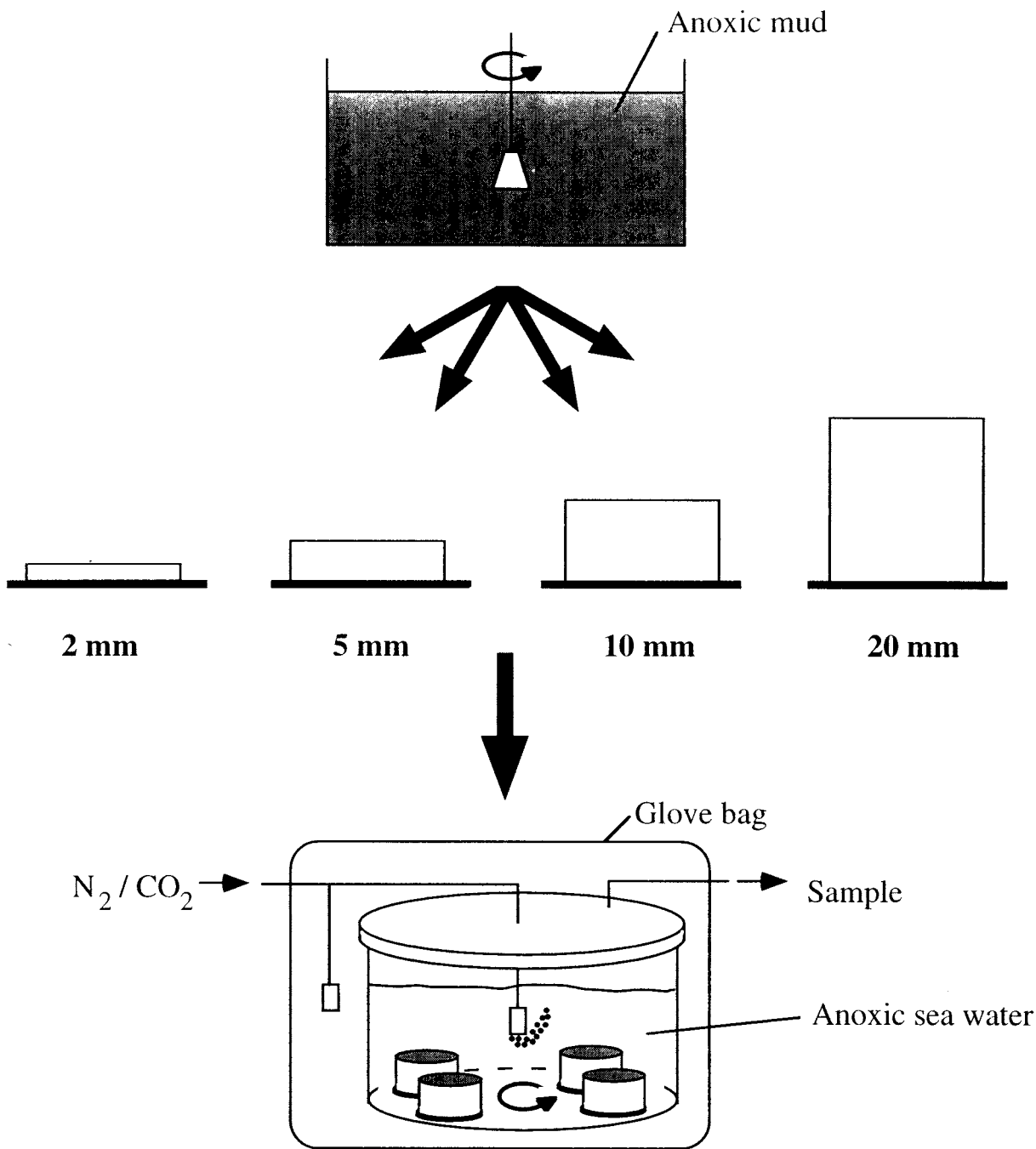


Fig. 2. Typical experimental set-up illustrating the open plug incubation technique. Anoxic sediment was incubated in plugs (52 mm diameter; 2, 5, 10 and 20 mm thickness) under diffusively open conditions, where exchange was possible between the sediment and overlying water. The reservoir (15.4 L of overlying water) was kept in a glove bag and to ensure anoxic conditions, the glove bag and the overlying water were constantly purged with a mixture of oxygen free N_2 and CO_2 gas.

water reservoir was in a glove bag, and was constantly purged before (over night) and during the experiment with a mixture of N_2 and CO_2 gas scrubbed of O_2 using an Alltech O_2 trap and an O_2 indicating assembly (Fig. 2). Previous experiments have demonstrated that O_2 is maintained below detection in this set-up. The incubation was performed in the dark at a temperature of 19.4–21.7°C. This type of incubation is referred to as “diffusively open” because exchange of solutes is possible between sediment and overlying water (e.g., Aller and Mackin; 1989). The water reservoir was mixed by a centrally

located Teflon-coated magnetic stirring bar. Before use, the polycarbonate reservoirs, plug assemblies, and stirring bars were soaked in 4% HCl for 10 days or more. After soaking they were thoroughly rinsed in double distilled water (DDW) and soaked in DDW for at least 7 days.

Overlying water (~20 ml) was sampled periodically during the open plug incubations for ΣCO_2 , DIN (NO_3^- , NO_2^- , and NH_4^+) and Mn^{2+} using a polypropylene syringe and Tygon tubing extension. Prior to use, the assembly was washed in 4% HCl, thoroughly rinsed with DDW and then with sample. Overlying water was filtered through

in-line polycarbonate filters (0.40 μm pore size) directly into acid cleaned polypropylene vials.

After 12 days, plugs were sampled for pore water and solid phase composition. Plugs were individually removed from the water reservoir using stainless steel forceps, sediment quickly transferred to a polypropylene syringe (prewashed in 4% HCl and rinsed with DDW and overlying water from the container) using a stainless steel spatula. The front of the syringe contained a small amount ($\sim 2\text{ cm}^2$) of folded nylon screen to prevent sediment extrusion. The syringe was placed into a press which applied pressure by moving the plunger forward, and pore water passed through an in-line mounted 0.4 μm polycarbonate filter directly into an attached receiving polypropylene syringe without air contact (Aller, et al., 1998). The filter had been rinsed with overlying water from the incubation reservoir. Sediment from which the pore water was separated was frozen for later analyses of manganese in the solid phase.

Additional plugs were incubated for the determinations of pore water distributions of pH by direct insertion into sediment of a mini-combination electrode (Ag-AgCl) mounted on a micro-manipulator.

2.4. Analytical Methods

Sediment plug processing and pore water separation were complete within a few minutes ($<5\text{ min}$) after removal from the overlying water reservoir.

Samples for ΣCO_2 were analyzed immediately by FIA conductivity (Hall and Aller, 1992). DIN samples were frozen. Concentrations of NO_2^- and NO_3^- were determined using standard colorimetric methods (Strickland and Parsons, 1972) applied to a flow injection system (FIA). NH_4^+ was determined using flow injection conductivity (Hall and Aller, 1992). Measurements of pH were standardized on the Hansson pH scale (Hansson, 1973). Alkalinity was determined by potentiometric titration and Gran evaluation according to the principles outlined by Haraldsson et al. (1997), with a precision (1 mL sample volume) better than 0.7% RSD. 50–100 μl of concentrated HCl was added to the Mn^{2+} samples, producing a pH of 1–2, before storage in a refrigerator. Dissolved manganese was determined using a Shimadzu flame AAS. Sulfate in the pore water from the closed anoxic incubations was determined gravimetrically with BaCl_2 . Reactive solid phase Mn was estimated by leaching a small portion of the sediment for 15 hours using hydroxylamine/acetic acid (Chester and Huges, 1967), and measuring manganese in the leachate.

Porosity (ϕ), was calculated from the weight of water loss after drying 5 mL of sediment at 70°C for at least 24 hours (until constant weight) at the beginning of each incubation series.

Net reaction rates in the closed incubations were calculated over specific time intervals from least squares linear fits to concentration versus time plots. Corrections for reversible adsorption were made for NH_4^+ , assuming a linear adsorption coefficient $K = \phi K^* \rho_s (1 - \phi)$, where $\rho_s = 2.6\text{ g cm}^{-3}$, and $K^* = 0.77$ (K^* previously measured, Aller and Aller, 1998).

Net production or consumption rates of pore water solutes (R) in plugs were calculated assuming the steady state relation (Aller and Mackin, 1989):

$$R = 3^* D_s^* (C_{ss} - C_T) / L^2 \quad (3)$$

where D_s is the whole molecular diffusion coefficient ($D_s \sim \phi^2 D_0$ (Ullman and Aller, 1982); D_0 is the free solution diffusion coefficient at the appropriate temperature and salinity, estimated from Li and Gregory, 1974), C_{ss} is the average steady state concentration in a plug of thickness L , and C_T is the overlying water solute concentration at the end of the experiment.

3. RESULTS AND DISCUSSION

3.1. Closed Jar Incubations—Unamended

The closed incubations demonstrated time-dependent patterns and rates of organic matter degradation typical of surface sediment in central Long Island Sound (Fig. 3; Table 2). Net remineralization rates, as evidenced by the initial linear pro-

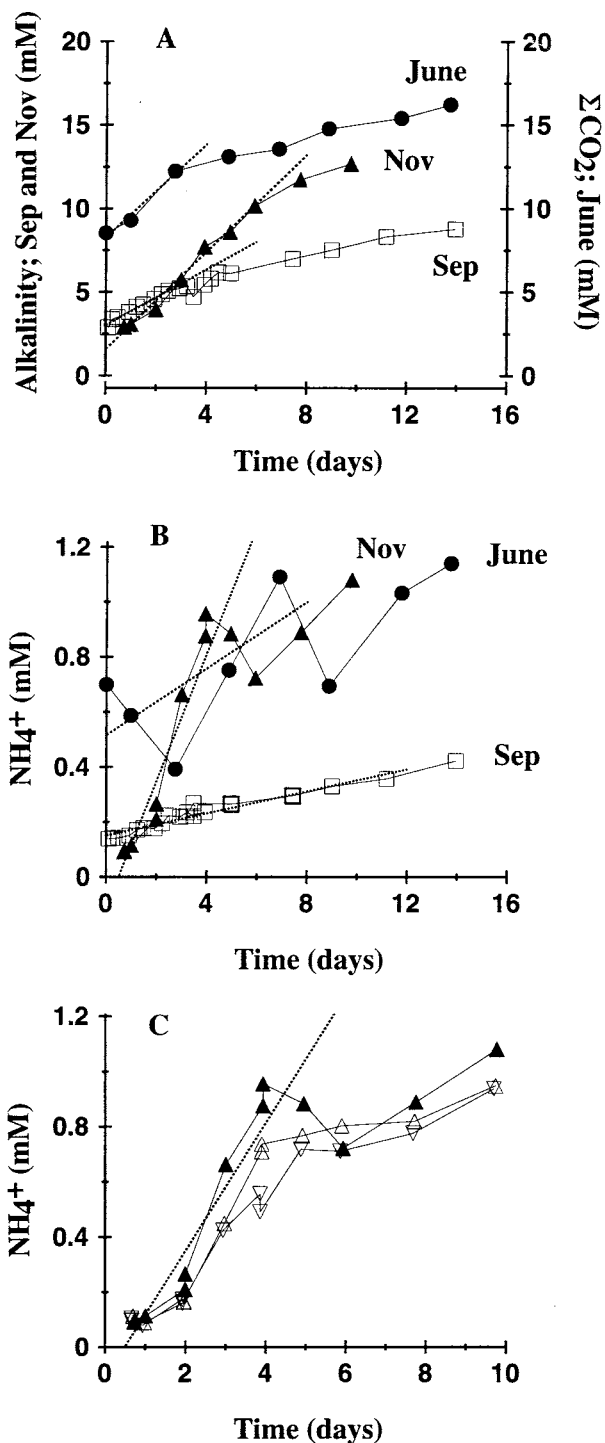


Fig. 3. Organic matter mineralization during the June (filled circles), September (open squares), and November (filled triangles) closed jar incubations. A. Mobilization of total carbonate (ΣCO_2 or C_T) and alkalinity (A_T) to the pore water during the June, September, and November incubations. B. Production of ammonium during the un-amended and, C. amended November incubation. In the amended incubation, no MnO_2 was added to the control (A; \blacktriangle), while an amount of 13 and 33 $\mu\text{mol of MnO}_2\text{ g}^{-1}$ dry sediment was added to the (B; \triangle) and (C; ∇) incubation series, respectively. The dashed lines represent the initial production used to calculate net rates of solute mobilization.

Table 2. Calculated net rates of solute mobilization to the pore water during the closed jar and open plug incubations.

Incubation	Mn ²⁺ ; pw	Mn ²⁺ ; sp	K _{Mn}	NH ₄ ⁺	ΣCO ₂	A _τ	Nitr.	Denitr.	SO ₄ ²⁻	φ	
Closed	June	7.86	31.0	3.9	76	1390	–	11	–6.5	–175	0.77
	Sep.	24.3	252	10	52	–	828	4.0	–0.61	–	0.71
	Nov.; A	157	317	2.0	187	–	1450	0.44	–0.32	–147	0.76
	Nov.; B	152	216	1.4	171	–	1440	1.0	–1.1	–211	0.76
	Nov.; C	150	244	1.6	167	–	1400	2.3	–0.64	–243	0.76
Open	L	Mn ²⁺ ; pw	Mn ²⁺ sp	K _{Mn}	NH ₄ ⁺	ΣCO ₂	A _T	ΣNO ₃ ⁻	NO ₂ ⁻	SO ₄ ²⁻	φ
	2	n.d.	384	–	623	n.d.	–	1090	68.2	–	0.77
	5	42.0	363	–	108	1300	–	195	10.9	–	0.77
	10	88.9	348	–	154	404	–	47.9	1.60	–	0.77
	20	71.9	230	–	94.5	489	–	8.97	0.439	–	0.77

All rates are in $\mu\text{M d}^{-1}$. Net rates of nitrification (nitr.) were calculated from the initial mobilization of ΣNO_3^- to the pore water. The phase of nitrate disappearance was used to estimate net denitrification rates (denitr.). Production rates of Mn^{2+} were estimated both from net pore water concentration changes (pw), and from loss of solid phase reactive MnO_2 (sp). The absorption coefficient, K_{Mn} , was calculated as the (Mn^{2+} ; sp/ Mn^{2+} ; pw) ratio. Also given are the actual plug thickness (L, mm) used during the open plug incubations, and the porosity (ϕ). A, B and C refer to the different additions of Mn-oxides to the sediment prior to starting the November incubation (0, 13 and 33 $\mu\text{mol g}^{-1}$ dry sediment).

duction rates of ΣCO_2 , alkalinity (A_T), and NH_4^+ were similar during the June and November incubations, but somewhat lower during the September incubation (Fig. 3; Table 2). These measured production rates would support, for example, a

steady state flux of ΣCO_2 from the top 2 cm of ~ 21 , 12, and 22 $\text{mmol m}^{-2} \text{d}^{-1}$ (June, Sep., Nov.), values comparable to those observed in previous remineralization measurements in the sediment collection area (e.g., Aller, 1980; Westrich and

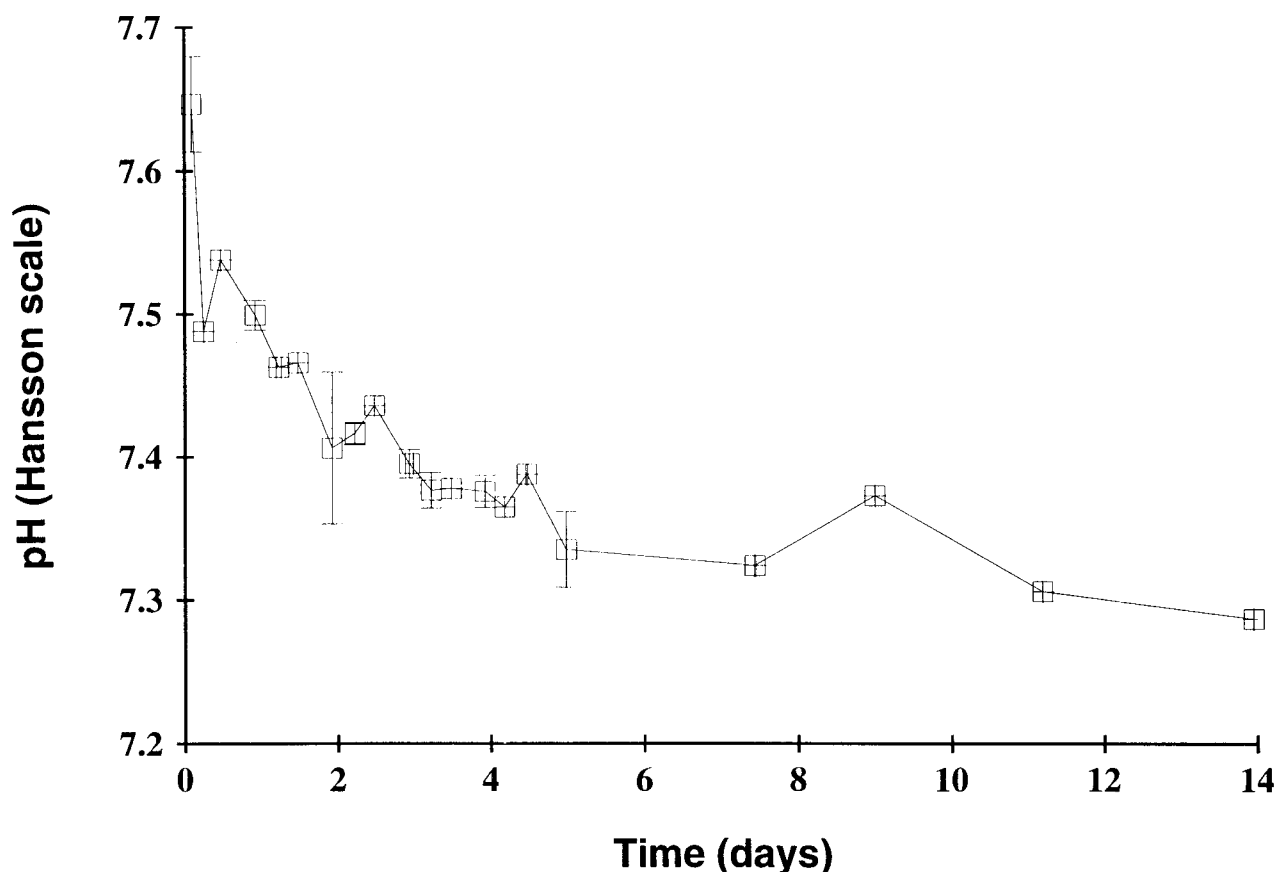


Fig. 4. The evolution of pH in the pore water during the September incubation is shown as a representative example on the behavior of pore water pH during the closed jar incubations. One to three replicate sediment samples were incubated. Average and standard deviation of these replicates are indicated. The samples were standardized using the Hansson pH scale (Hansson, 1973).

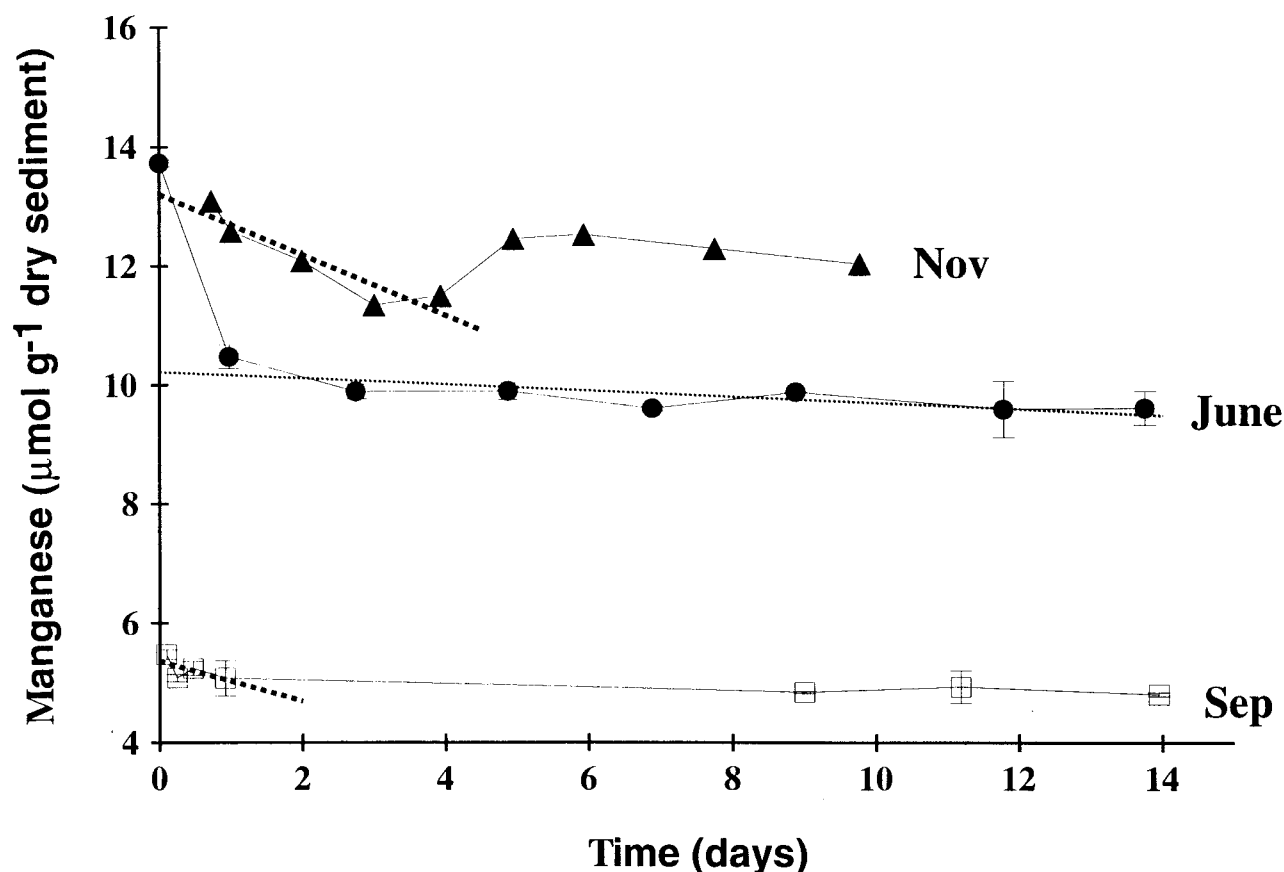


Fig. 5. Manganese in the solid phase of the sediment during the June (filled circles), September (open squares), and November (filled triangles) closed jar incubations. The dashed lines represent the initial consumption of reactive MnO_2 used to calculate production rates of Mn^{2+} to the pore water. Indicated are the average and standard deviations of one to three replicate sediment samples.

Berner, 1984; Sun, et al., 1991). ΣCO_2 and NH_4^+ net production rates were more or less constant during an initial period of four to six days, then decreased, most likely reflecting the depletion of labile organic matter, and/or in the case of CO_2 , precipitation of solid phase carbonates (e.g., Ca, Mn-carbonates). During the build-up of decomposition products, pore water pH decreased exponentially from initial values near seawater, to about 7.3 (Fig. 4).

Elevated Mn^{2+} concentrations, coupled with decreasing reactive solid phase Mn, are evidence of net Mn reduction during C_{org} remineralization within the incubation series (Fig. 5, 6). Both the quantities of reactive Mn and the overall concentration of dissolved Mn^{2+} differed in the various unamended incubations. Initial reactive Mn was highest in the June and November samples ($\sim 14 \mu\text{mol g}^{-1}$) and lowest in September ($\sim 6 \mu\text{mol g}^{-1}$). Likewise, maximum pore water Mn^{2+} concentrations were 700–800 μM during the June and November incubations, but reached only $\sim 260 \mu\text{M}$ in the September samples (Fig. 6). The observations of the lowest net remineralization rates, as measured by ΣCO_2 and NH_4^+ release, and the lowest reactive Mn in the September incubation series, are consistent with partial loss of the surface most sediment layer or homogenization of a surface interval >2 cm during sample collection.

Nevertheless, the primary characteristics of all incubation series are relatively rapid remineralization and substantial Mn-oxide reduction. The differences in the estimates of Mn^{2+} production rates based on pore water net concentration changes and those calculated from loss of solid phase reactive Mn (Table 2), imply reversible adsorption coefficients in the range of K_{Mn} 2–10 (simple ratio estimates), similar to those reported from other sediments (Canfield, et al., 1993).

Although the closed incubations were anoxic, there was clear evidence of a pattern of progressive net NO_3^- formation over a period of 2 to 4 days (Fig. 7A). Based on the measured remineralization rates of $\sim 1 \text{ mM } \Sigma\text{CO}_2 \text{ d}^{-1}$ (Table 2), any O_2 occluded initially in the pore water could not have persisted for more than a few hours after enclosure (Table 2). The excess NO_3^- produced during the first few days of incubation was subsequently depleted, but it was lost at a sufficiently slow rate given the intensity of ΣCO_2 remineralization, that continued production of NO_3^- must have occurred during the entire period of incubation. Similarly, NO_2^- was also obviously produced and depleted in a net sense, but again, concentrations were sustained at a readily detectable level throughout the incubations. Maximum NO_2^- concentrations occurred after NO_3^- maxima, indicating a coupling between the two constituents con-

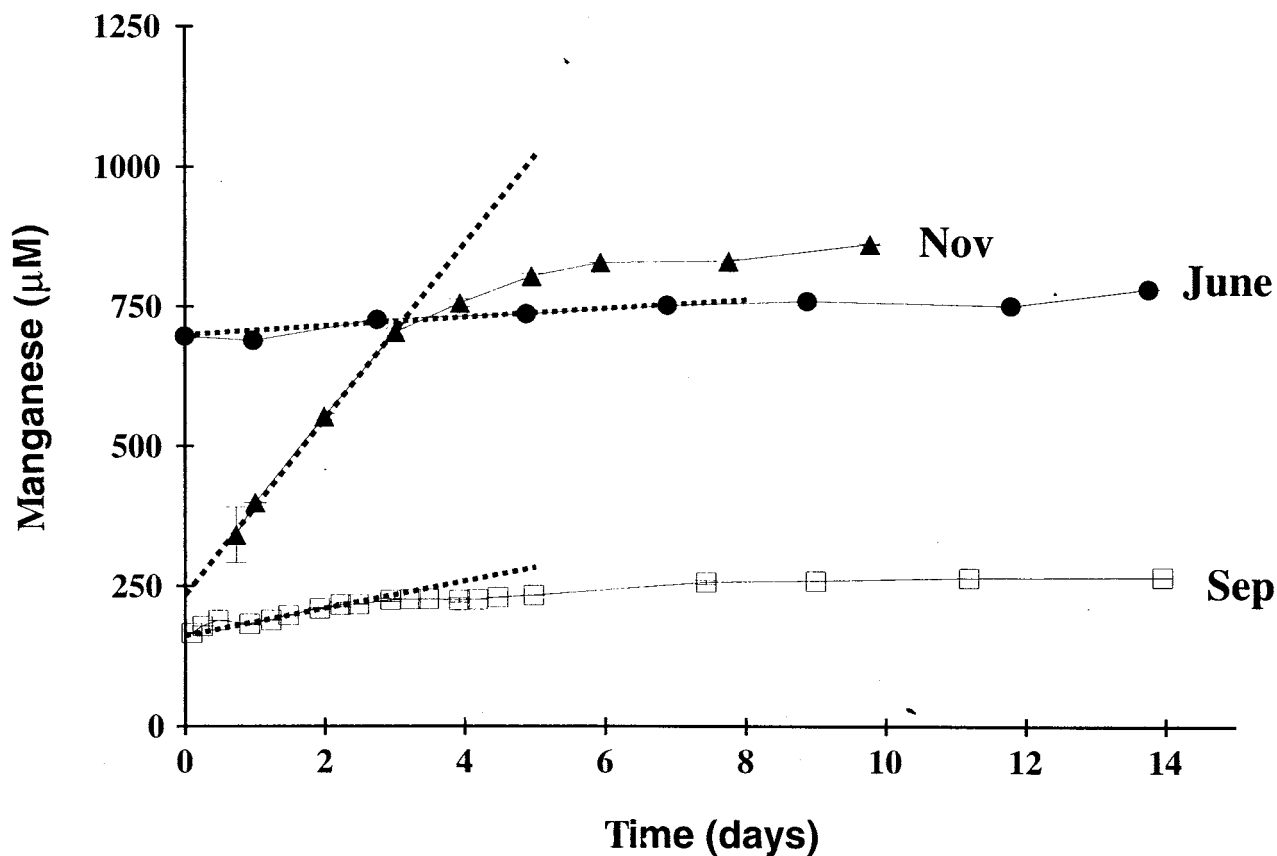


Fig. 6. Pore water concentrations of manganese during the June (filled circles), September (open squares), and November (filled triangles) closed jar incubations. The dashed lines illustrate the initial net pore water concentration changes used to calculate mobilization rates of Mn^{2+} .

sistent with denitrification. Most importantly, these time-dependent concentration patterns directly and categorically demonstrate the production of pore water NO_3^- and NO_2^- for extended periods in the absence of detectable O_2 or any conceivable source of dissolved O_2 .

Although NO_3^- and NO_2^- were produced in all incubations, the net rates of production and the maximum NO_3^- or NO_2^- concentrations attained, differed substantially between the various incubation series (e.g., maxima: 0.7–17 $\mu\text{M NO}_3^-$, Fig. 7; rates: 0.4–11 $\mu\text{M NO}_3^- \text{ d}^{-1}$, Table 2). The anoxic nitrate production rate measured during the June incubation was the largest found in this investigation. The initial increase in this case corresponded to a net nitrification rate of $\sim 11 \mu\text{M d}^{-1}$, or a steady state flux of $\sim 170 \mu\text{mol m}^{-2} \text{ d}^{-1}$, assuming the rate applied over a 2 cm depth interval. Such a rate is similar to, or higher than, net nitrification rates reported from other coastal marine sediments open to O_2 diffusion (Szweringi, 1981; Enoksson and Samuelsson, 1987). The only known sedimentary constituents present under the incubation conditions with sufficient oxidation potential and abundances capable of sustaining such nitrification rates are Mn-oxides. It is clear that Mn reduction occurred simultaneously with net NO_3^- production and at rates generally sufficient to account for the observed NO_3^- production rates assuming stoichiometric relations such as reaction (2) (Tables 1, 2).

3.2. Stimulation of Anoxic NO_3^- Formation by Addition of MnO_2

Addition of Mn-oxide to sediment in the November closed incubation series stimulated the anoxic formation of NO_3^- and increased the rate of NO_3^- formation in direct proportion to the quantity of Mn-oxide added (Figs. 8, 9). The additions of ~ 13 and $\sim 33 \mu\text{mol of MnO}_2 \text{ g}^{-1}$ dry sediment stimulated NO_3^- production rates 2 to 5X compared to unamended controls. The calculated anoxic nitrification rates for the different treatments were 0.4, 1, and 2.3 $\mu\text{M d}^{-1}$, respectively (Table 2). In the present cases, the added Mn increased the extractable, reactive Mn by ~ 15 –50% above the initial starting values in the unamended sediment, but the quantity extracted was well within the range found in diagenetically enriched surface sediments from Long Island Sound (e.g., Aller, 1994). Only $\sim 20\%$ of the total added MnO_2 was extracted by the hydroxylamine / acetic acid leach, presumably because the aged oxides were relatively well crystallized (Fig. 9B). The percent recovery, however, was constant.

Further support for substantial metal-oxide reduction came from the excess alkalinity production relative to net SO_4^{2-} reduction observed in the incubations. Calculated rates correspond to C : S production / consumption ratios (A_T / SO_4^{2-}) of ~ 9.9 for the incubation without additional MnO_2 (A), ~ 6.8 for the (B) incubation, and ~ 5.8 for the incubation with the largest

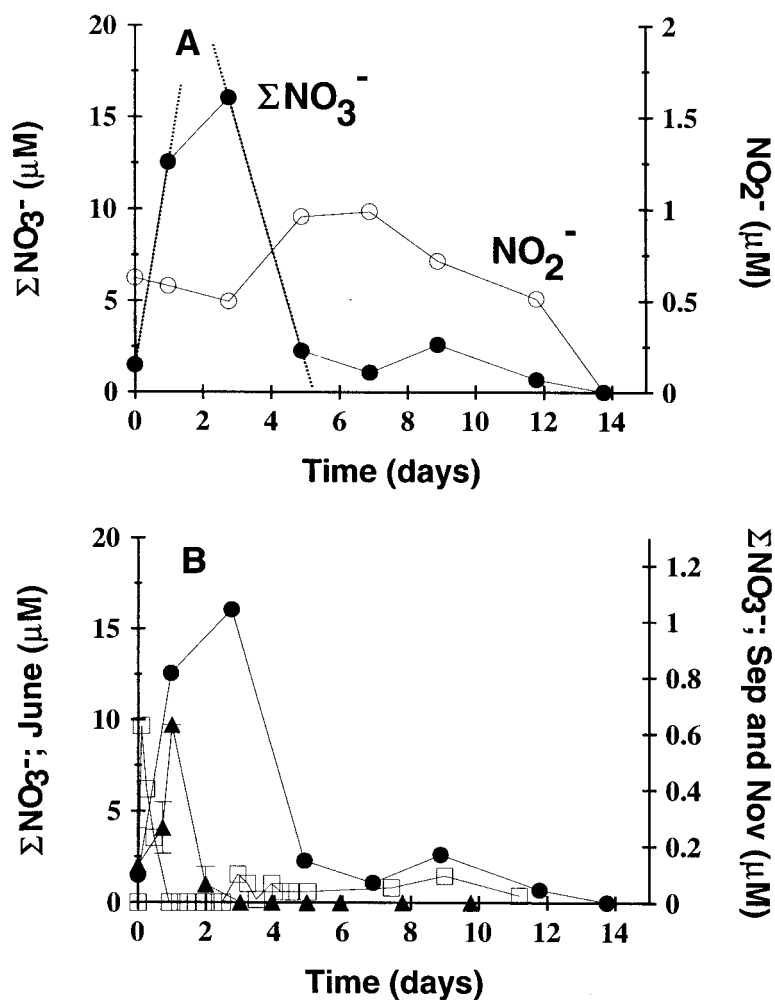


Fig. 7. A. Nitrate (filled circles) and nitrite (open circles) concentrations in the pore water during the June closed jar incubation. Nitrate and nitrite were found to be mobilized to the pore water despite anoxic conditions. The initial mobilization of nitrate corresponds to an anoxic nitrification rate of $11 \mu\text{mol dm}^{-3} \text{d}^{-1}$. The dashed lines indicate the initial generation and removal of nitrate, used to calculate the nitrification and denitrification rates. B. During the September (open squares) and November (filled triangles) closed incubations, nitrate was again found to be mobilized to the pore water. Pore water nitrate from the June incubation is shown for comparison (filled circles).

amount of MnO_2 added to the sediment (C) (Fig. 10; Table 2). These ratios are significantly larger than that expected from the reaction of net sulfate reduction alone ($\text{C} : \text{S} \sim 2$), and are consistent with alkalinity production during Mn reduction. When comparing net rates of A_T or ΣCO_2 production with net rates of sulfate and manganese reduction, there appears to be additional alkalinity generated beyond that accountable by Mn^{2+} remaining in solution (Table 2). This indicates either Fe reduction (not measured) or ion exchange of Mn^{2+} with major elements such as Ca^{2+} , Mg^{2+} , Na^+ , or K^+ (not measured).

Increased metal reduction in November incubations (B) and (C) were also indicated by pore water pH, where after 8–10 days of incubation, the pH was increased by approximately 0.05 pH units in the (B) and (C) incubations compared to the control (A) (Fig. 11). The increased pH with additions of MnO_2 is consistent with stimulated Mn-reduction (Emerson, et al., 1982). In each incubation series, there was an initial phase of obvious net Mn^{2+} production. The net Mn^{2+} build-up stabi-

lized either as reactants were depleted or consumption processes, such as precipitation of Mn-carbonates, began to dominate (Fig. 12). The initial rates of net Mn^{2+} -production, as estimated from pore water concentrations, were found to be more or less constant for the different treatments at $150\text{--}160 \mu\text{M d}^{-1}$ (Table 2). However, there was a relatively lower net alkalinity attained with increasing additions of Mn-oxides, indicative of Mn-carbonate precipitation (Fig. 10A). After 8–10 days of incubation, alkalinity was found to be 6–7% higher in (A) compared to (B) and (C).

3.3. Effect of Diffusive Exchange

The diffusively open plug incubations also demonstrated clear evidence of NO_3^- production in sediment under anoxic conditions, but with some important contrasts compared to the closed incubations (Figs. 7, 8, 13). The initial overlying water NO_3^- concentrations were completely depleted after ~ 1 week,

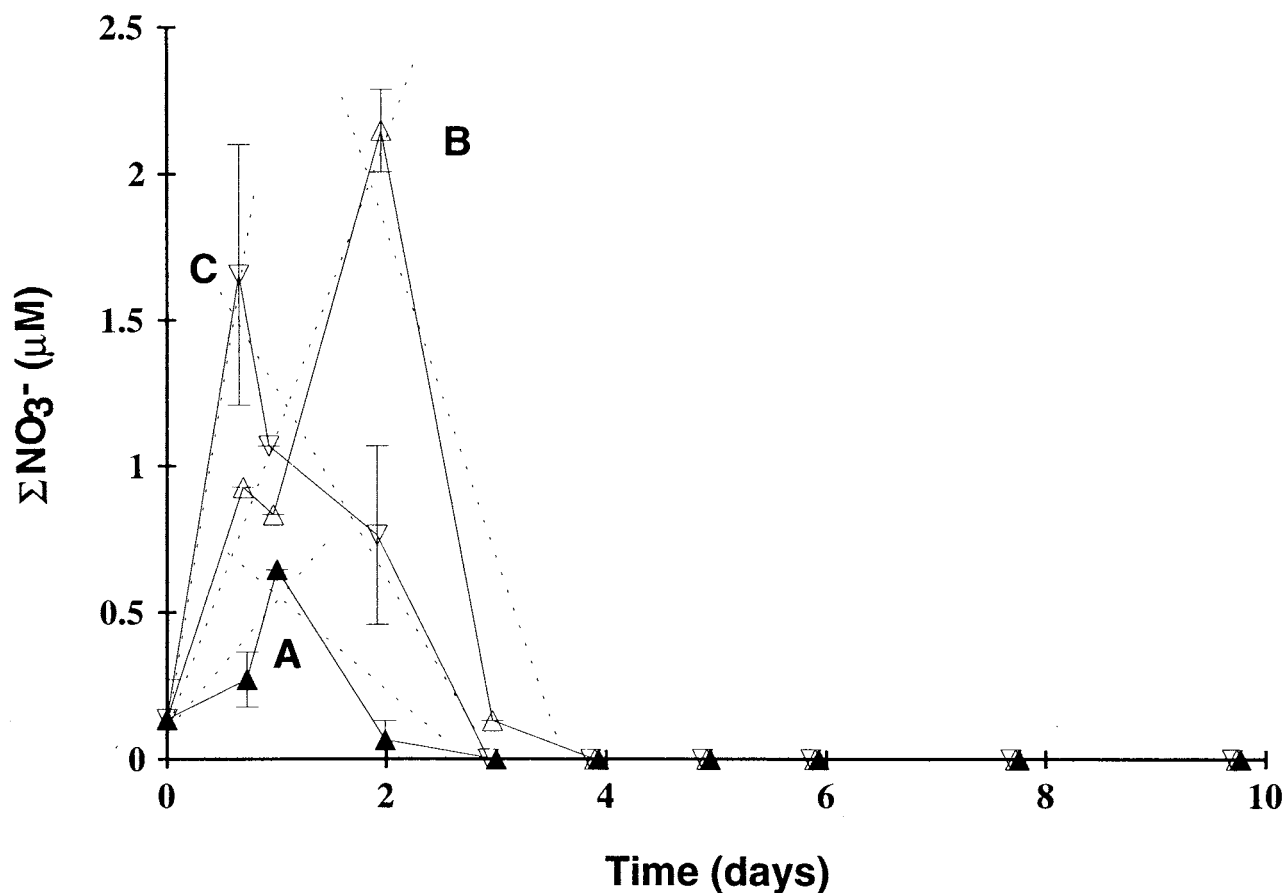


Fig. 8. Nitrate concentrations in the pore water during the November closed jar incubation. Net mobilization of nitrate to the pore water was related to the amount of solid manganese that was added to the sediment prior to the experiment. The additions of 13 (B) and 33 (C) $\mu\text{mol MnO}_2 \text{ g}^{-1}$ dry sediment were reflected both in the absolute nitrate concentrations as well as the mobilization/reduction patterns in the pore water. No Mn-oxide was added to the sediment used in the (A) series. Indicated are the concentration changes used to estimate nitrification and denitrification rates from the mobilization and removal of nitrate.

while NH_4^+ increased progressively with time, indicative of net denitrification and the absence of O_2 in the overlying water as well as a net flux of NH_4^+ from the sediment plugs (Fig. 14). Nitrate concentrations of 14–20 μM were found in the pore water of all the plugs incubated under anoxic conditions, despite the fact that no NO_3^- had been detected in the overlying water for more than five days prior to sediment sampling (Fig. 13), and there was no hint of oxidized sediment in the plugs (i.e., Fe-oxides). The calculated anoxic production rates of NO_3^- for the different plug thicknesses of 2, 5, 10 and 20 mm (based on equation 3) were 1090, 195, 48 and 9 $\mu\text{M d}^{-1}$, respectively (Table 2). Net production of NO_2^- and NH_4^+ were also evident in the plugs, with average formation rates also varying inversely with plug thickness as for NO_3^- (Fig. 15; Table 2).

Pore water and solid phase distributions of manganese suggested that Mn-oxide reduction was occurring in all plugs at the time the experiment was terminated and the pore water extracted (Fig. 16). Rates of Mn-reduction, as evidenced by the production rates of Mn^{2+} to the pore water (equation 3) at the time of experiment termination, were (2 mm not detectable),

42, 89, and 72 $\mu\text{M d}^{-1}$ (Table 2). The lack of a calculable production rate from the pore water data for the 2 mm plug reflects a relatively high overlying water Mn^{2+} concentration that resulted from the Mn^{2+} flux out of all plugs (i.e., small concentration difference in equation 3). The contents of reactive MnO_2 in the sediment were clearly sufficient to support Mn reduction and anoxic nitrate formation in all plugs over the incubation period (Fig. 13, Table 2). Note the solid phase based estimates of reaction rates tend to integrate over a longer period of net reaction than do the pore water based estimates, the latter reflecting conditions close to the time of plug sampling.

The inverse relations of solute production rates with sediment plug thickness are typically found for a variety of diagenetically reactive constituents under diffusively open conditions, and reflect a combination of changes in both absolute and relative reaction rate (Aller and Aller, 1998). For example, the lowered build-up of reactive solutes in diffusively open sediment often results in less intense back-reactions such as authigenic mineral precipitation (e.g., MnCO_3), and thus a greater net release of produced solutes into the contacting water reservoir (e.g., Mn^{2+} , HCO_3^-). In addition, there is evidence for an

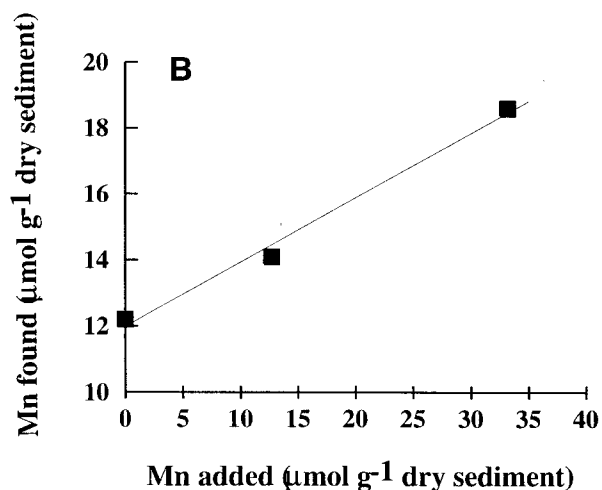
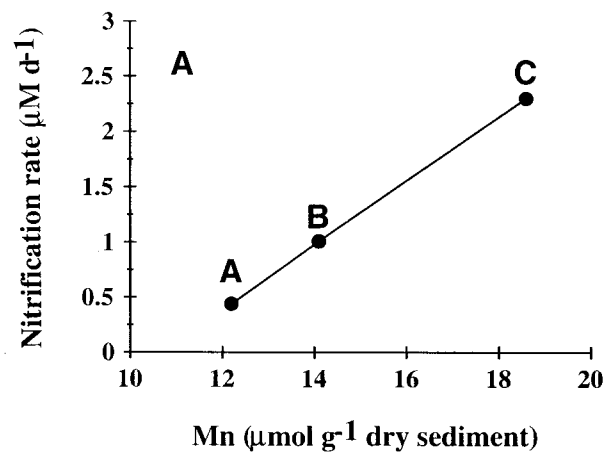


Fig. 9. A. There was a direct linear relation between measured concentrations of manganese in the solid phase of the sediment and net anoxic nitrification rates, as evidenced by the initial mobilization of nitrate to the pore water. The additions of Mn-oxides stimulated net nitrate production rates 2.3 (B) and 5.2 (C) times compared to the control series (A). B. The relation between the amount of manganese that was added before starting the incubations, and that extracted by the hydroxylamine/acetic acid leach, indicated that only about 20% of the added MnO_2 was extracted.

absolute stimulation of anaerobic microbial activity under conditions of progressively greater solute exchange (Aller and Aller, 1998).

The primary conclusion from both types of incubation treatments is that NO_3^- and NO_2^- can be produced in the absence of O_2 , and that N oxidation takes place simultaneously with Mn-oxide reduction. These results are consistent with net reactions such as reaction (2), but how is it that high nitrate concentrations could be maintained for a more extended period and at a greater concentration in the open anoxic, but not in the closed anoxic incubations (Fig. 7, 8 and 13)? Both treatments used exactly the same sediment, the only difference being the solute transport regime. We think the major differences in the incubations result primarily from changes in the rates of concentration-dependent reactions and multiple competitive reactions, rather than the occurrence of different reactions per se. The

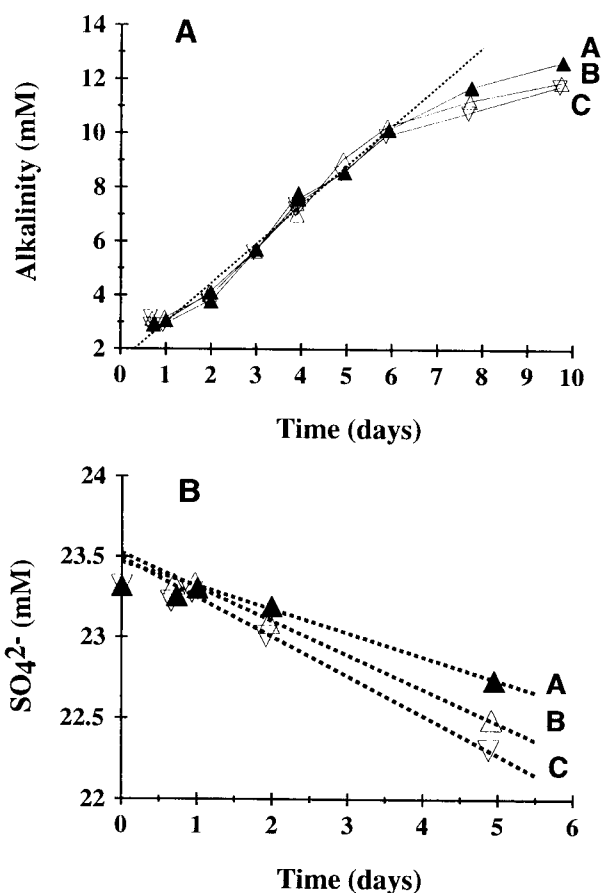


Fig. 10. A. Generation of alkalinity to the pore water during the November closed jar incubation. There was a relatively decreasing net alkalinity production attained with increasing additions of MnO_2 , indicating possible Mn-carbonate precipitation. B. Evolution of sulfate in the pore water during the first five days of the November closed jar incubation. Lack of net sulfate reduction during the initial stage of the incubation suggests the occurrence of net anoxic sulfate production simultaneously as anoxic nitrification. No MnO_2 was added to the control (A), while 13 and 33 $\mu\text{mol g}^{-1}$ dry sediment were added to the (B) and (C) incubation series, respectively.

concentrations of reduced solutes in the closed incubations are higher than in the open plugs. Mn-oxides likely competitively react with reduced C, HS^- , DOC, DON, and NH_4^+ . Higher concentrations of reduced reactants, for example DOC (e.g., Stone and Morgan, 1984), may either competitively suppress NH_4^+ oxidation or use up oxidant (MnO_2) more rapidly than in a diffusively open case where a portion of reduced solutes escape into overlying water. In a similar way, NO_3^- , once anoxically produced, is also exposed to higher concentrations of potential reductants (e.g., DOC, DON, NH_4^+ , HS^-). Thus, local consumption rates for NO_3^- in the closed system are likely higher than in the open one. When sediment is otherwise equivalent, and the diffusively open system is not so thin that eventual concentration build-ups vanish, a higher concentration of NO_3^- should be sustained in the diffusively open case (higher production, lower consumption reactions). It is also possible that the open system results in diffusive loss of a dissolved

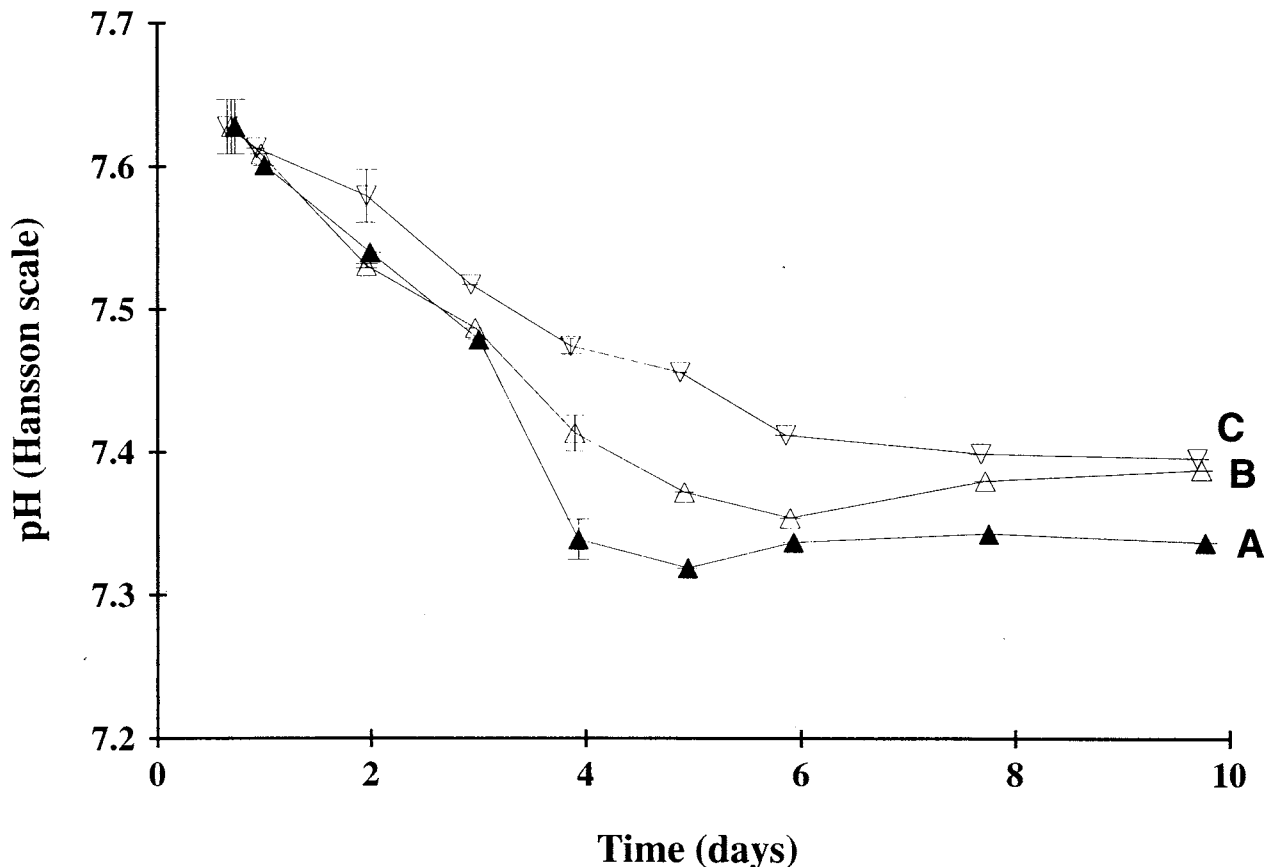


Fig. 11. The evolution of pH in the pore water during the November closed jar incubation. After 8–10 days of incubation, the pH was increased by approximately 0.05 pH units in the (B) and (C) incubations compared to the control (A). This relative pH increase with increasing additions of Mn-oxides is consistent with increasing acid consumption following Mn-reduction. Indicated are average and standard deviation of one to three replicate sediment samples.

inhibitor of anoxic nitrification, thereby increasing production rates.

Because of pH gradients in the diffusively open plugs (Fig. 17), it is possible that oxidation of Mn^{2+} by NO_3^- (reaction 1) could occur more favorably in surficial regions of the sediment sections or in the overlying water reservoir (pH-dependent ΔG_R , Table 2). Under such circumstances, or in the case of an oxic surface layer in the presence of oxygenated overlying water, an internal redox cycle could be set up in the sediment whereby production of a dissolved oxidized Mn (possibly chelated Mn^{3+} ; Luther et al., 1994; Kostka et al., 1995) in a surface zone could diffusively supply oxidant to an underlying anoxic region.

3.4. Anaerobic, Lithotrophic Nitrification and Denitrification

We interpret the experimental results to indicate that anoxic nitrification occurs in sediments and, because of the favorable energetics, that the overall reaction is likely to be microbially mediated through a process of anaerobic, lithotrophic nitrification associated with Mn-oxide reduction (reaction 2). The depletion of NO_3^- and NO_2^- subsequent to their formation is

additional evidence that denitrification is closely coupled to lithotrophic nitrification. The abundance of potential reductants of NO_3^- in anoxic sediments implies that denitrification may not be strictly coupled to C oxidation as is often depicted. In particular, NH_4^+ , Fe^{2+} , HS^- (S^0 , FeS , FeS_2), and C_{org} are known reductants utilized by bacteria during denitrification (Bender, et al., 1989; Straub, et al., 1996; Luther, et al., 1997). The very rapid denitrification that would occur in subsurface sediments subsequent to anoxic nitrification is a likely reason why anoxic nitrification as a net reaction is not always evident in pore water profiles.

One consequence of a lithotrophic based nitrification cycle is that a greater proportion of benthic O_2 uptake could be directed to the N cycle indirectly through Mn-oxidation/reduction. Particle bioturbation and physical mixing processes would then play a dominant role in controlling solid phase oxidant transport into underlying sediments and promoting coupled lithotrophic nitrification-denitrification. The occurrence of a subsurface internal nitrification-denitrification cycle with small net production of NO_3^- would complicate interpretation of N_2 production rates from NO_3^- profiles (underestimates), and might cause discrepancies between various types of estimates

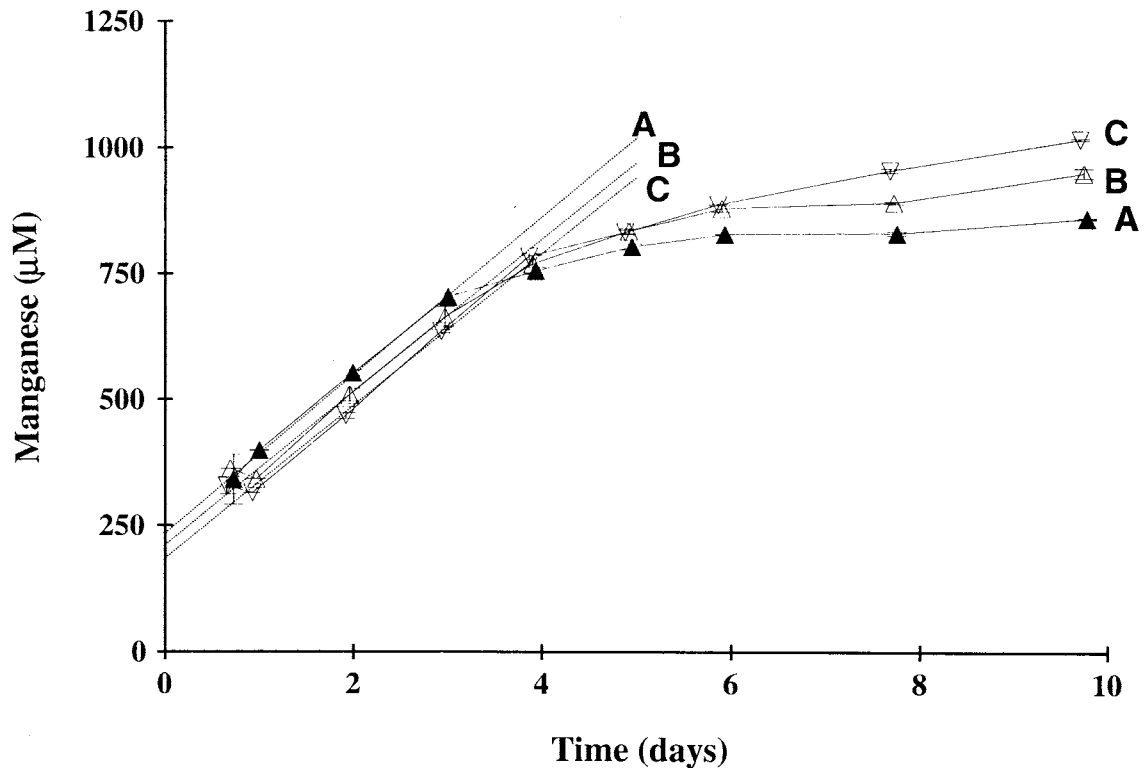


Fig. 12. Manganese in the pore water during the November closed jar incubation. Following the initial phase of Mn^{2+} production, net Mn^{2+} build-up slowed down as reactants became limiting and consumption reactions were initiated (e.g. the formation of Mn-carbonates). Dashed lines represent initial mobilizations used to estimate net Mn^{2+} production rates.

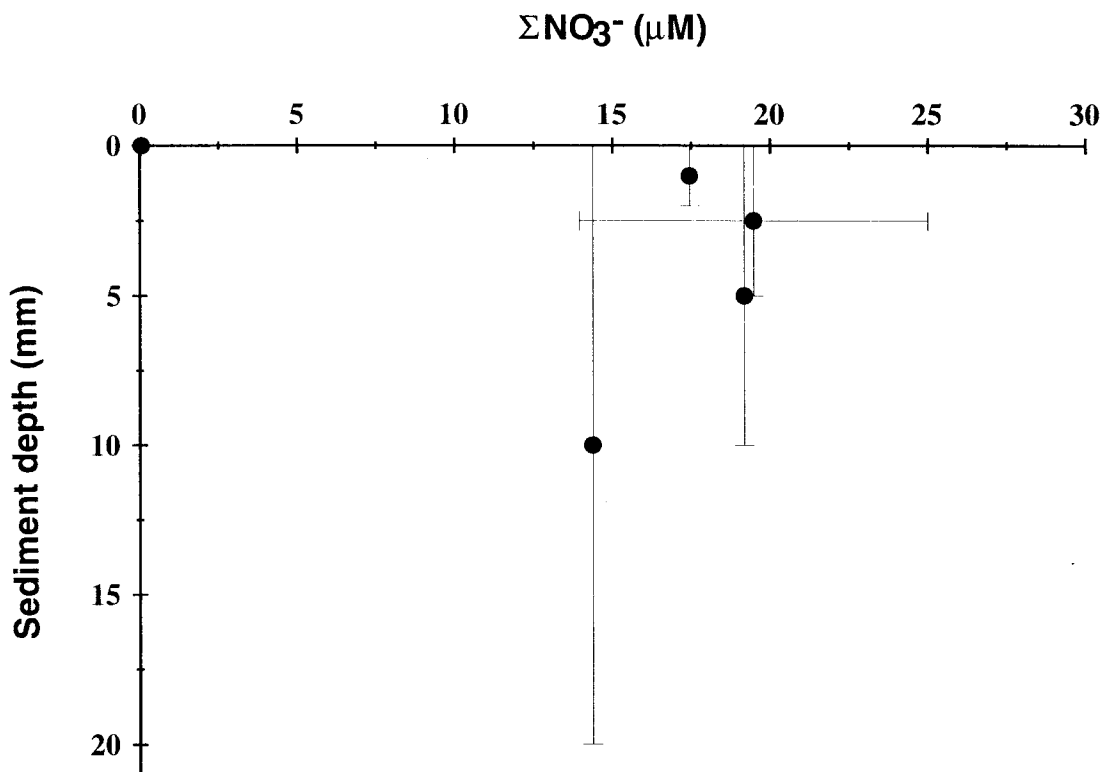


Fig. 13. Nitrate was found to be produced anoxically in all plugs, despite that no nitrate had been detected in the overlying water for more than five days. Calculated anoxic nitrification rates were 1090, 195, 47.9 and 8.97 $\mu\text{mol dm}^{-3} \text{d}^{-1}$ for the 2, 5, 10 and 20 mm plugs, respectively.

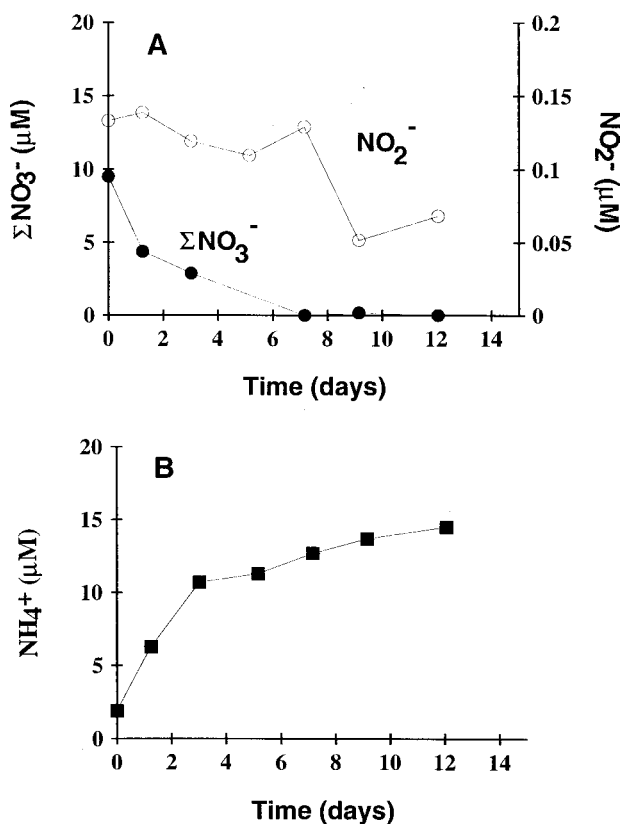


Fig. 14. A. The evolution of nitrate (filled circles) and nitrite (open circles) in the overlying water during the open plug incubations. The depletion of nitrate after a week, in conjunction with low and decreasing concentrations of nitrite, support the assumptions of anoxic conditions at the termination of the experiments. B. Ammonium concentrations in the overlying water increased progressively with time of incubation, although mobilization rates decreased when the labile organic material in the plugs was depleted.

of denitrification (e.g., Devol, 1991). Most likely, these types of reactions are of importance in nearshore sediments where anoxic sediments are more or less constantly mixed with Mn-oxides from the oxidized surface layers, and in organic-rich, hemipelagic sediments close to hydrothermal vent sites. Luther et al. (1997) suggested that the direct formation of N_2 through the oxidation of organic-N and ammonium by Mn-oxides (Table 1) was probably the most important process for N_2 formation in Mn-rich sediments. However, it is clear from the present results that lithotrophic nitrification may be an intermediate step in eventual denitrification, and that the relative importance of the myriad possible pathways remains to be demonstrated in the field.

The documentation of an apparent lithotrophic nitrification pathway emphasizes the potential complex redox reaction web that can occur in physically and biologically mixed surface sediments. Previous experiments have shown that the reworking of Mn-oxides into anoxic sediments can be coupled to the biogenic oxidation of labile sulfides (HS^- , FeS) to S^0 and SO_4^{2-} (Burdige and Nealson, 1986; Aller and Rude, 1988; King, 1988). Overall reactions such as (4), (abiogenic; Burdige and Nealson, 1986) and (5), (biogenic, Aller and Rude, 1988; King, 1988) were proposed.

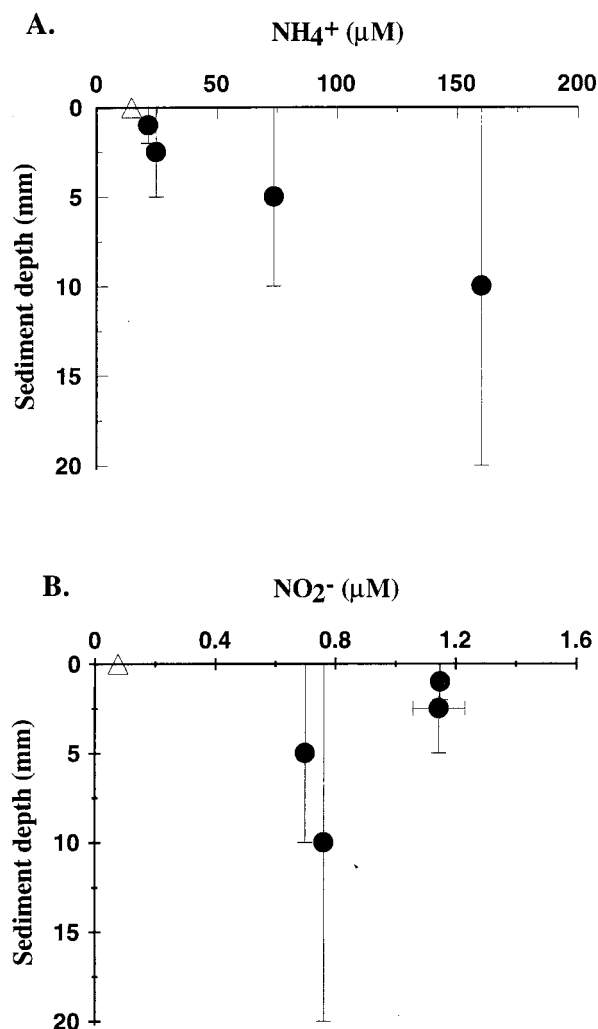
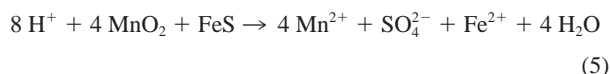
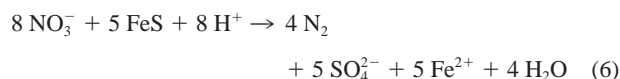


Fig. 15. A. NH_4^+ in pore water of anoxic plug series demonstrated net production in all cases, and the differences between overlying and pore water concentrations implied increasing net production with decreasing plug thickness (Table 2). B. Nitrite was also found to be produced during the anoxic incubation. Measured pore water concentrations (0.7 – $1.2 \mu\text{M}$) were significantly higher than the concentration obtained in the overlying water. This implied flux of nitrite from the sediment to the overlying water could, however, not be detected as increased concentrations of nitrite in the overlying water with time of incubation. Most likely, this observation reflected consumption of nitrite during denitrification.



The apparent occurrence of lithotrophic nitrification suggests that additional coupled reactions, such as a combination of reactions (2) and (5), are likely to occur in parallel (6) or in series (7), resulting in overall sedimentary redox reactions such as:



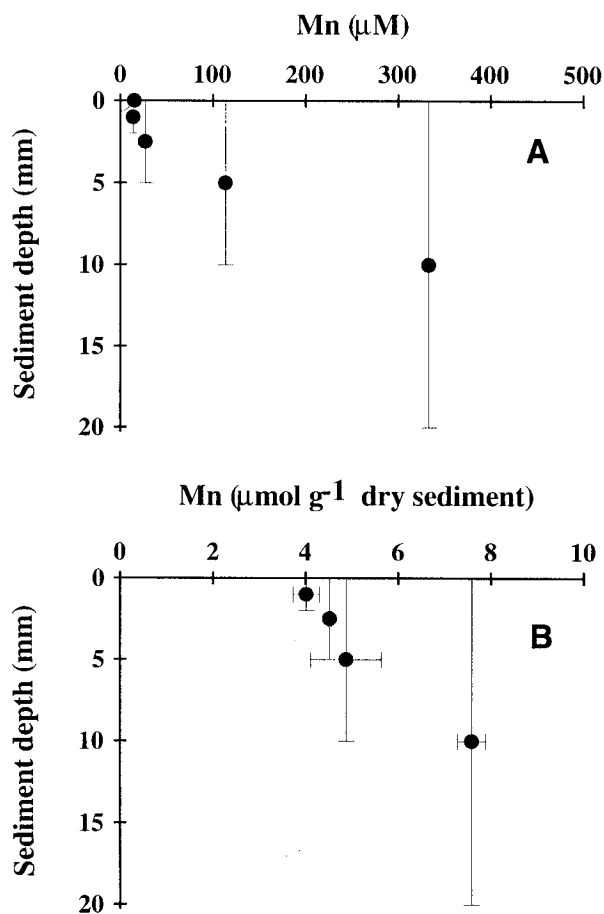
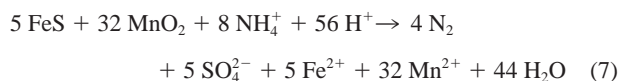


Fig. 16. A. Pore water concentrations of manganese in the 2, 5, 10 and 20 mm plugs after terminating the open plug experiment. The concentration gradients between the overlying water and the pore water indicated a diffusive transport of manganese from the plugs towards the overlying water. This gradient increased with increasing plug thickness and the calculated manganese production rates for the plugs were n.d., 42, 89, and 72 $\mu\text{mol dm}^{-3} \text{d}^{-1}$, respectively. B. Concentrations of manganese in the solid phase of the sediment. The pore water and solid phase distributions of manganese indicated that manganese reduction was occurring in the sediment. Clearly, the contents of reactive MnO_2 in the sediment were sufficient to support Mn reduction and anoxic nitrification in all plugs over the incubation period. Net production rates of Mn^{2+} , estimated from loss of reactive Mn-oxide, were 384, 363, 348 and 230 $\mu\text{mol dm}^{-3} \text{d}^{-1}$ for the 2, 5, 10 and 20 mm plugs, respectively. Indicated are average together with maximum and minimum concentrations of duplicate sediment samples.



By utilizing the nitrate formed during anoxic nitrification, bacteria such as *Thiobacillus denitrificans* could generate sulfate anoxically in a consortium with lithotrophic nitrifiers (e.g., Baalsrud and Baalsrud, 1954). These reactions are sufficiently energetic to support chemoautotrophic C fixation (ΔG_R 's in Table 1). We note that the lack of net SO_4^{2-} depletion and the hint of net SO_4^{2-} production during the initial stages of our incubation experiments (e.g. Nov.) suggest the occurrence of

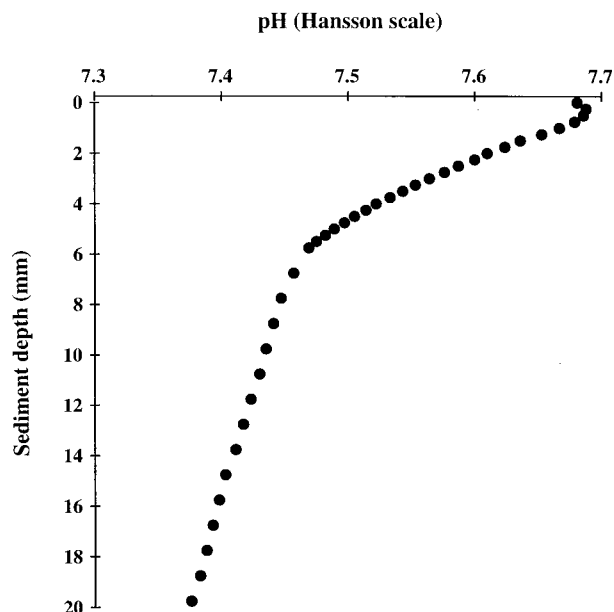


Fig. 17. One possible explanation why nitrate could be maintained for a more extended period and at greater concentrations in the open anoxic, but not in the closed anoxic incubations, may be due to elevated pH gradients close to the sediment-water interface in the diffusively open plugs. The pH dependent reaction of anoxic Mn^{2+} oxidation ($5 \text{Mn}^{2+} + 2 \text{NO}_3^- + 4 \text{H}_2\text{O} \Rightarrow 5 \text{MnO}_2 + \text{N}_2 + 8 \text{H}^+$) may occur more favorable in surficial regions of the sediment or in the overlying water reservoir, where the pH is higher. An internal cycle could thus be sustained where a dissolved oxidant (chelated Mn^{3+} ?) in the surface zone could be supplied to the underlying anoxic region with lower pH.

such sulfide oxidation reactions simultaneously with net NO_3^- production (Fig. 10). In summary, a significant consequence of biogenic and physical reworking of Mn-oxides into underlying anoxic sediment is likely to be the serial redox reaction coupling of O_2 , Mn, N, Fe, S, and C by opportunistic microbial consortia (Fig. 18).

Although we have emphasized redox interactions between the major oxidants, there may be additional effects on heterotrophic processes that result from nonsteady-steady introduction of Mn-oxide into anoxic sediments. Initially, the presence of Mn-oxide and produced NO_3^- seemed to inhibit reduction of pore water sulfate, due either to competitive utilization of higher energy oxidants (Lovley and Phillips, 1986), or the coupled redox reactions outlined previously. Following the initial period of no net sulfate reduction, the rates of sulfate reduction that eventually occurred in the Mn-oxide amended incubations (Nov) were modestly stimulated in direct proportion with the quantity of Mn-oxide added (Fig. 10B, Table 2). Assuming the proportional increases are real, such stimulation could result from 1) degradation of microbial biomass generated during the initial pulse introduction of the energetically favorable Mn-oxide; (2) degradation of partially oxidized degradation products formed during the period of enhanced Mn-reduction; and (3) removal and immobilization of inhibitory metabolites by adsorptive uptake onto the relatively fresh oxide surfaces.

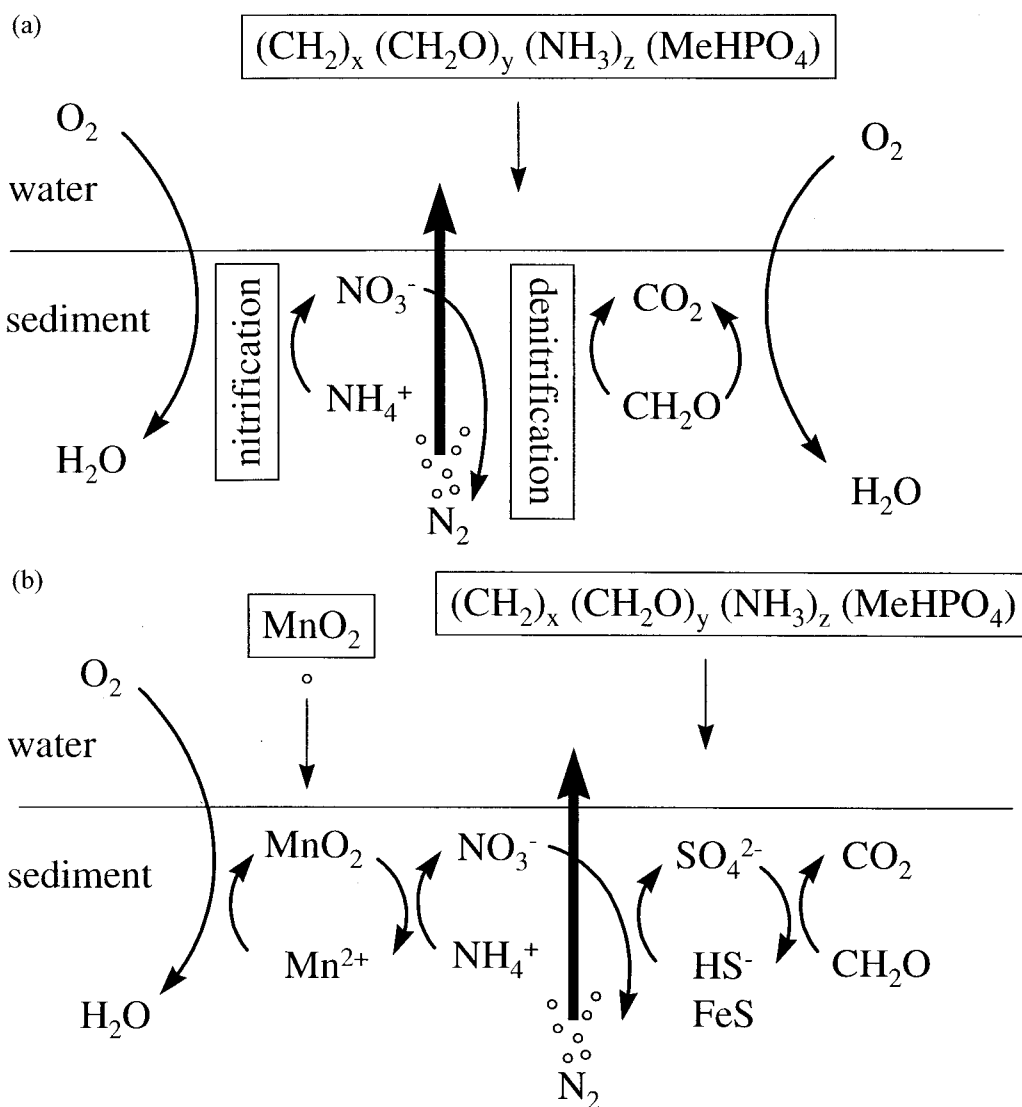


Fig. 18. A. Schematic representation of the traditionally accepted sedimentary nitrification-denitrification cycle, with nitrification directly coupled to oxygen reduction and denitrification to the oxidation of organic matter. B. Alternative anoxic cycles of nitrification-denitrification can be achieved through anoxic nitrification (anaerobic lithotrophic nitrification) during Mn cycling, together with denitrification coupled in series or parallel to organic matter oxidation through any of several possible diagenetically produced reductants (e.g., HS^- , Fe^{2+} , or NH_4^+).

4. CONCLUSIONS

Introduction of Mn-oxides from oxidized surface sediment into underlying anoxic regions during biogenic or physical mixing results in anoxic nitrification and net production of NO_3^- and NO_2^- .

Anoxic nitrification rates are proportional to the quantity of Mn-oxide available in the solid phase.

Anoxic nitrification occurs simultaneously with Mn-oxide reduction, implying the likely microbial coupling of the two reactions through an anaerobic pathway of lithotrophic nitrification.

Because of the multiple possible reduction reactions for NO_3^- under anoxic conditions (C_{org} , DOC, NH_4^+ , Fe^{2+} , HS^- (S^0 , FeS, FeS_2)), higher net NO_3^- production is observed in

diffusively open versus closed systems having greater metabolite concentrations.

The juxtaposition of pulsed inputs of Mn-oxides with reduced constituents in anoxic deposits makes likely the close coupling of the O_2 , Mn, N, S, and C cycles in a complex redox web rather than a simple succession in surface sediments.

Such redox coupling are likely to be of greatest importance in nearshore sediments with active biological and physical reworking, and in regions near hydrothermal vents where oxidized metals frequently contact reduced solutes and organic-rich deposits.

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