

## NOTE

## Nitrogen gas flux from sediments: insights from simulation modelling

T. Henry Blackburn\*

Department of Microbial Ecology, Department of Biological Sciences, Aarhus University, DK-8000 Aarhus C, Denmark

**ABSTRACT:** Direct measurements of dinitrogen efflux from continental shelf sediments indicated that denitrification (mean  $3.2 \text{ mmol N m}^{-2} \text{ d}^{-1}$ ) was very important in nitrogen cycling. Most dinitrogen came from sediment-nitrate. All ammonium produced in these sediments was probably nitrified and then denitrified. In a closed incubation, the linear production of dinitrogen, as oxygen decreased, was unexpected as was the low ratio of oxygen consumption to denitrification (3.6:1). Simulation modelling suggests the following explanation: Most carbon is oxidised anoxically, but nitrogen (ammonium) diffuses to the oxygen zone relatively deep in the sediment, where high rates of coupled nitrification-denitrification result. As oxygen decreases, the zones of nitrification and denitrification move upward. The nitrate initially present in the enclosed overlying water decreases, but due to the decreasing diffusional path to the zone of denitrification, its rate of denitrification remains constant. The concentration of nitrate from sediment nitrification increases in the overlying water, but due to the decreasing rates of sediment nitrification, its rate of denitrification is also constant.

**KEY WORDS:** Nitrification · Denitrification · Model · Diffusion · Nitrate · Ammonium

To construct a model which simulates a particular sediment, a variety of factors must be known: quantity of degradable organic matter, its C/N ratio, its distribution in the sediment and the extent to which the reduced products of anoxic respiration are free to diffuse (Blackburn & Blackburn 1993a, b, c, Blackburn et al. 1994). In addition, the rate constants for the oxidation of carbon by  $\text{O}_2$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , and for the oxidation of  $\text{NH}_4^+$  and  $\text{SH}^-$  must be known. The values of the variables, outlined in the legend to Fig. 1, gave quite a close representation of the data for a continental shelf sediment (Devol 1991). Dinitrogen was produced at a linear rate (Fig. 1A). The total denitrification rate of  $\sim 3.7 \text{ mmol N m}^{-2} \text{ d}^{-1}$  was similar to that reported (mean  $3.2 \text{ mmol N m}^{-2} \text{ d}^{-1}$ ). In the simulation (Fig. 1B),

there was a slight increase in  $\text{NO}_3^-$  concentration, compared to the actual slight decrease (mean  $1.3 \text{ mmol m}^{-2} \text{ d}^{-1}$ ). Fine tuning of the nitrification and denitrification rates would correct this difference. During the time of  $\text{N}_2$  linear production (2 d), there was a fall in oxygen concentration from 200 to 20  $\mu\text{M}$ . The initial rate of oxygen uptake was  $11.9 \text{ mmol m}^{-2} \text{ d}^{-1}$ , very close to the reported value ( $11.4 \text{ mmol m}^{-2} \text{ d}^{-1}$ ). As  $\text{O}_2$  decreased, accumulation of  $\text{NH}_4^+$  increased, due to the sediment becoming less oxidised (Fig. 1C). The model predicted a time-dependent decrease in the rate of nitrification from  $\sim 4.5 \text{ mmol N m}^{-2} \text{ d}^{-1}$ , but denitrification ( $D_s$ ) of sediment- $\text{NO}_3^-$  ( $\text{NO}_3s$ ) was relatively constant at  $\sim 3 \text{ mmol N m}^{-2} \text{ d}^{-1}$  (Fig. 1D). Denitrification ( $D_w$ ) of  $\text{NO}_3^-$  originally in the water ( $\text{NO}_3w$ ), was also relatively constant at  $\sim 1 \text{ mmol N m}^{-2} \text{ d}^{-1}$ , even though  $\text{NO}_3w$  decreased from 30 to  $<10 \mu\text{M}$ .

The movement of the zone of denitrification closer to the sediment surface, as the depth of  $\text{O}_2$  penetration decreased with time (Fig. 2), can explain the apparent contradictions. The linear efflux of  $\text{N}_2s$  ( $\text{N}_2$  from  $\text{NO}_3s$ ) was due to the  $\text{NO}_3s$  which accumulated in the water. The diffusional path for this  $D_s$ , back through the nitrification zone to the zone of denitrification, decreased with incubation time. This counteracted the decreased rate of nitrification and resulted in an almost constant, but slightly increasing, rate of  $D_s$ . Similarly, the decreased diffusional path for  $\text{NO}_3w$  to the zone of denitrification counteracted the decreased concentration of  $\text{NO}_3w$  and resulted in an almost constant rate for  $D_w$ .

It was suggested that most of the  $\text{NH}_4^+$  produced in the sediment ( $\sim 2.5 \text{ mmol N m}^{-2} \text{ d}^{-1}$ ) (Christensen et al. 1987) would be nitrified and then denitrified (Devol 1991). This was unlikely, as nitrification initially exceeded  $D_s$  (Fig. 1D), and  $\text{NO}_3s$  escaped to the overlying water. It is only in the situation where this  $\text{NO}_3s$  is trapped in water overlying the sediment surface that  $D_s$

\*E-mail: henry@pop.bio.aau.dk

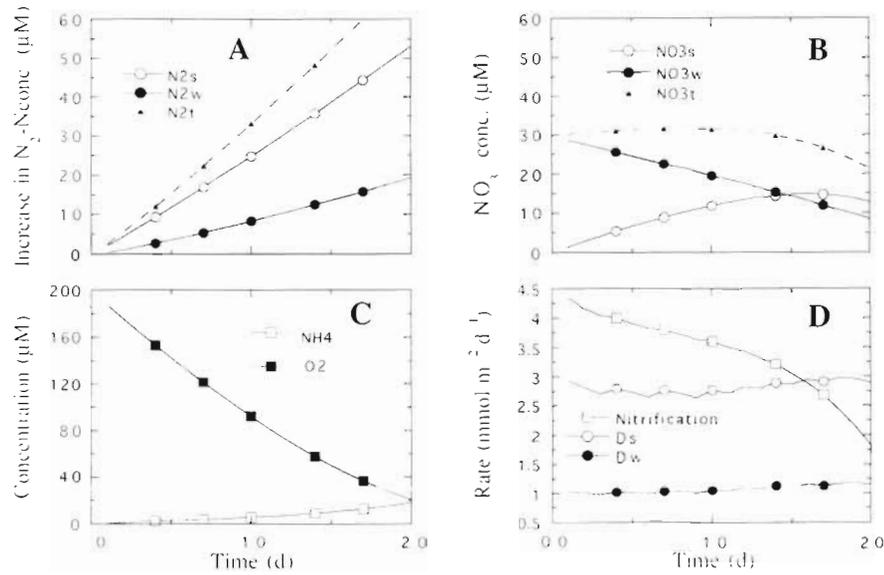


Fig. 1. Predicted time-dependent changes in the concentrations in the enclosed overlying water of dinitrogen ( $N_2s$ ) derived from sediment-nitrate ( $NO_3s$ ), in dinitrogen ( $N_2w$ ) derived from nitrate initially in the overlying water ( $NO_3w$ ), in total dinitrogen ( $N_2t$ ) derived from total nitrate ( $NO_3t$ ), in ammonium ( $NH_4$ ), and in oxygen ( $O_2$ ). Also shown are changes in the integrated rates of sediment nitrification, and denitrification of  $NO_3s$  ( $D_s$ ) and of  $NO_3w$  ( $D_w$ ). Predictions were derived from a reaction-diffusion model in Cellmatic (Blackburn & Blackburn 1993a). In the present model, the upper 1 cm of sediment was represented by 14 cells of 0.2 mm and 6 cells of 1.0 mm, overlaid by water (1 cell of 10 cm and 2 cells of 0.2 mm). Half the dissolved organic carbon ( $22.5 \text{ mmol m}^{-2} \text{ d}^{-1}$ ) was oxidised below 1 cm, and half was distributed evenly in the upper 1 cm stratum. Ammonium ( $4.5 \text{ mmol m}^{-2} \text{ d}^{-1}$ ) was produced at 1/10 the rate of carbon oxidation. Reduced products of anoxic respiration, e.g. iron sulphides, were not allowed to diffuse. The first order rate constants for nitrification and denitrification were 200 and  $500 \text{ d}^{-1}$ , respectively. Otherwise, constants were as previously reported (Blackburn & Blackburn 1993a). At time zero, the sediment core with 10 cm of overlying water was sealed

can equal nitrification. Simulations in which  $NO_3s$  was not allowed to accumulate in the increasingly  $O_2$ -deficient overlying water indicated that there was a very rapid fall in  $D_s$ , in parallel with the fall in nitrification.

The non-diffusion of sulphide was a very important factor. When sulphide was allowed to diffuse, it reacted with  $O_2$ , reducing  $O_2$  penetration and raising the zone of nitrification closer to the sediment surface. This reduced the rate of nitrification, but increased the proportion of  $NO_3s$  escaping to the overlying water (data not shown). This has been discussed elsewhere (Blackburn & Blackburn 1993b) and also results in observed low rates of  $O_2$  uptake (Canfield et al. 1993). In this simulation, although the rate of  $O_2$  uptake was  $11.9 \text{ mmol m}^{-2} \text{ d}^{-1}$ , the rate of carbon oxidation was close to  $45 \text{ mmol m}^{-2} \text{ d}^{-1}$ . Therefore, it is dangerous to equate  $O_2$  uptake with carbon oxidation, and it is likely that in the continental shelf sediments, most carbon oxidation is not  $O_2$ -dependent. This could account for the high ratio of denitrification/ $O_2$  uptake, in the original data (1:3.6) and in the simulation (1:3.2).

The irregularities in the sediment-based rates of nitrification and denitrification (Fig. 1D) may be due to the fact that these rates are influenced by multiple factors:  $O_2$  concentration, substrate concentration and

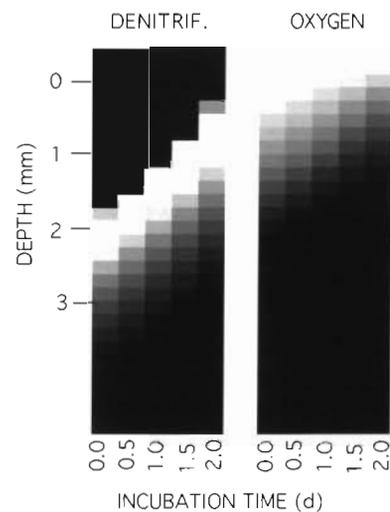


Fig. 2. Predicted time-dependent changes in the vertical distributions of sediment denitrifying activity and in pore water oxygen concentrations. Model parameters are described in Fig. 1. Light areas indicate high activity or concentration

varying diffusional path lengths. Therefore, it is not surprising that some unevenness is observed. These irregularities in the rates are not reflected in concentration changes in the overlying water, probably due to the larger volume of this overlying water, which dampens the oscillations.

In conclusion, the tight coupling between nitrification and denitrification can be attributed to the deep location of the zone of nitrification. The linear production of dinitrogen, despite oxygen depletion, can be explained by the accumulation of sediment-derived nitrate in the enclosed overlying water and to the movement of the zone of denitrification closer to the sediment surface.

This paper describes the novel employment of simulation analysis to explain apparent anomalies in experimental data. The confirmation that the data are consistent suggests that the high values for denitrification (Devol 1991) are reliable. This has important implications for global nitrogen budgets.

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