Redox oscillation and benthic nitrogen mineralization within burrowed sediments: An experimental simulation at low frequency

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ABSTRACT

Possible effects of sediment ventilation by benthic organisms on the nitrogen cycle were investigated using an experimental setup that mimicked stable or relatively low frequency oscillating redox conditions potentially found in bioturbated deposits. Three different conditions inside burrowed sediments were simulated using 2 mm thick sediment layers: 1) continuously oxic sediment exposed to oxygenated overlying bottom water (e.g., burrow walls, surface sediment), 2) continuously anoxic sediment out of reach from either O_2 or NO_3^- diffusion and 3) the lining/boundary of burrow structures or sediment pockets (e.g., excavated during feeding) subject to intermittent irrigation and redox fluctuations over several day timescales. Results demonstrated that intermittent redox fluctuations allowed sustained denitrification and episodic nitrification, whereas significant denitrification and both nitrification and denitrification were absent after ~5–10 days from continuously oxidized and anoxic zones respectively. Intermittent redox oscillations enhance metabolic diversity, magnify loss of dissolved inorganic N to solution, and permit sustained coupling between ammonification, nitrification, and denitrification despite lack of a stable stratified oxic-anoxic redox structure. Even relatively low frequency redox oscillations induce greater N loss compared to sediment that is continuously exposed to oxic and anoxic conditions.

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1. Introduction

Bioturbation (sensu Kristensen et al., 2012) plays a major role in the early diagenesis of sedimentary organic matter (OM) (Gilbert et al., 1996; Mayer et al., 1996; Aller and Aller, 1998; Sun et al., 1999; Reise, 2002). Particle reworking by benthos directly affects the distribution and fate of particulate organic substrates and adsorbed OM (Boudreau et al., 1998; Gérino et al., 1998; Widdows et al., 1998; Smallwood et al., 1999; Gilbert et al., 2001). Bioirrigation of sediments due to burrow or feeding-pocket ventilation promotes solute exchange across the sediment-water interface, enhances the removal of metabolites from pore water and supplies respiratory reactants such as O_2 and SO_4^{2-} (Jørgensen and Revsbech, 1985; Forster et al., 1999; Timmermann et al., 2006; Behrens et al., 2007). As an example, bioirrigation has been shown to increase both O_2 and NO_3^- penetration into deposits (Aller, 1982; Kristensen et al., 1991; Kristensen, 2000). With a few exceptions (e.g. Altmann et al., 2004; Jordan et al., 2009), bioirrigation generally stimulates sedimentary denitrification (Sayama and Kurihara, 1983; Kristensen and Blackburn, 1987; Gilbert et al., 1995, 1998; Rysgaard et al., 1995; Bartoli et al., 2000; Webb and Eyre, 2004). Stimulation results from coupled nitrification-denitrification enhanced by biogenic structure and/or to denitrification fuelled by an increased supply of nitrite and nitrate from the overlying water or from sedimentary nitrification (Aller et al., 1983; Pelegri et al., 1994; Pelegri and Blackburn, 1995; Tuominen et al., 1999; Karlson et al., 2005). Bioirrigation of pore water also promotes the transport of ammonium and other possible inhibiting metabolites from the sediment-pore water system (Nedwell and Walker, 1995; Kristensen and Hansen, 1999; Stief et al., 2013). In addition, ventilation and particle reworking have been found to strongly affect bacterial distributions and activity (Reichardt et al., 1991; Goñi-Urriza et al., 1999).

Thus, sediments subjected to the activities of benthic animals have high spatial and temporal heterogeneity of biogeochemical properties, extending across micro- to macro-scales (Gutiérrez and Jones, 2006; Polerecky et al., 2006; Pischedda et al., 2008). Indeed, ventilation can result in varying solute transport and redox conditions within the different sectors of single large burrows depending on the location and activity patterns of the inhabitants (e.g., *Callianassa*; irrigation frequency range $10\times$ to ~$0\times$ d^{-1}; Forster, 1991). A radial geometry can be defined around individual cylindrical burrows or burrow sections to differentiate distinct biogeochemical zones as a function of oxygen penetration (Aller, 1988, 2001). The diagenetic reaction balances and rates related to this radial geometry have been demonstrated to be

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dependent on the spacing between burrows or sections of burrows (Aller and Aller, 1998; Gilbert et al., 2003; Kristensen and Kostka, 2005). Ventilation is also variable with time, and is an intermittent rather than a continuous process. Burrow ventilating species are known to periodically inject overlying water into their burrows (e.g., Wetzel et al., 1995; Matisoff and Wang, 1998; Stief and de Beer, 2006). However, the relative frequency between the ventilation period and other activities (including resting period) is highly variable from one species to another (e.g., Forster and Graf, 1995; Kristensen and Kostka, 2005; Volkenborn et al., 2012). Moreover, for the same species, the periodicity and patterns of ventilation (continuous or periodic) can depend on environmental parameters such as water temperature and food availability (Gérino, 1989; Frenzel, 1990).

Continuous measurements of redox potential in sediment deposits have demonstrated dynamic redox conditions with oscillation frequency timescales of <1 h to >1 day immediately adjacent to natural burrows due to the diffusion of oxygen from the lumina of burrows, or from cavities such as feeding pockets, into the adjacent sediment (Forster and Graf, 1992; Volkenborn et al., 2012). Episodic exposure of anoxic sediment to oxygenated conditions during feeding, burrow construction, or locomotion can also vary over a wide range of timescales from <0.1 days to >1500 days, with typical resting periods (~anoxic) of ~1–100 days for multiple infaunal species (e.g., Myers, 1977; Wheatcroft et al., 1990; Marinelli, 1992). Such redox fluctuations may contribute to making burrow walls and feeding cavities highly reactive microbial sites compared to the surrounding sediments (Henriksen et al., 1983; Aller and Aller, 1986; Jumars et al., 1990; Kristensen and Kostka, 2005).

Previous work on the effects of redox oscillation on rates and dominant pathways during OM remineralization have demonstrated, for example, that Chlorophyll-*a* does not completely degrade under continuously anoxic conditions (Sun et al., 1993), and that periodic re-exposure of sediment to oxygen results in an intermediate or more complete (and sometimes more rapid) decomposition compared with stable oxic or anoxic conditions (Aller, 1994; Hulthe et al., 1998; Sun et al., 1999; Grossi et al., 2003; Caradec et al., 2004). This suggests that redox oscillation and mixing of particles by fauna across redox zonations likely result in an overall stimulated metabolic activity.

In the present study, sediment was incubated together with overlying sea water under diffusively open conditions (sediment plugs; e.g., Aller and Mackin, 1989; Gilbert et al., 2003; Caradec et al., 2004) to further investigate how redox conditions affect rates and pathways of sedimentary nitrogen cycling. In addition to monitoring the evolution of solutes in the pore water and overlying water, aerobic (nitrification: oxidation of NH_4^+ to NO_3^-) and anaerobic (denitrification: reduction of NO_3^-/NO_2^- to N_2 and dissimilatory nitrate reduction to ammonium: reduction of NO_3^-/NO_2^- to NH_4^+) nitrogen transforming activities were directly measured. The experimental setup, and especially 2-mm thick sediment layers, was designed to mimic stable or relatively low frequency (multi-day) oscillating redox conditions corresponding to three different conditions inside or at the surface of burrowed muddy sediments: 1) oxic sediment continuously exposed to oxygenated overlying bottom water, 2) anoxic sediment out of reach from O_2 or NO_3^- diffusion from the overlying water or from ventilated biogenic structures, and 3) regions of biogenic structures subject to intermittent ventilation and redox fluctuations (Fig. 1). In this latter case, the fluctuation timescales chosen were several days and thus roughly comparable to relatively remote zones of either stable burrow structures (e.g., *Callianassa*; Forster, 1991) or to many feeding-pockets or temporary structures periodically formed and ventilated by mobile infauna (e.g., deposit feeding bivalves, hemichordates, polychaetes; Wheatcroft et al., 1990). The experimental focus was on the effects of unsteady redox conditions over specific, representative time-scales of several days.
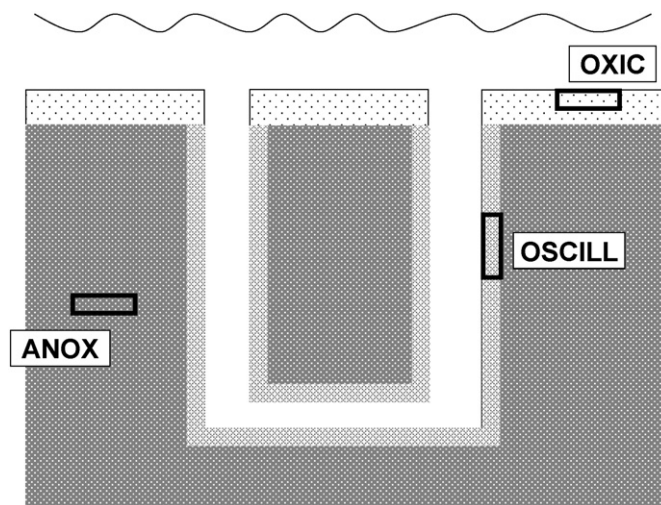

Fig. 1. Schematic representation of the three different parts of a burrowed sediment (with associated environmental conditions) that were mimicked during the experimentation. OXIC: continuously oxygenated surface layer or zones of closely spaced burrow structures, ANOX: continuously anoxic deep layer out of diffusive reach from O_2 or NO_3^-; OSCILL: wall layer of an inhabited burrow subjected to intermittent irrigation over multiple day timescales, or equivalently, the wall of a recently excavated cavity.

2. Materials and methods

2.1. Experimental setup

Surface (0–2 cm) muddy sediment and seawater were collected at the SOFI Station in the Gulf of Lion (Mediterranean Sea; 43°04N, 5°08E; 170 m depth) in February 2000. This sediment was composed of 34% clay, 46% silt and 20% sand (0–10 cm), had a mean porosity of 0.54 in the two first centimetres (Denis et al., 2001) and was inhabited by the polychaetes *Hyalinoecia bilineata* and *Lumbrineris latreilli*, the molluscs *Abra longicallus* and *Mendicula ferruginosa* and the crustaceans *Eriopisa elongata* and *Natatolana borealis* as major species (Georges Stora, pers. comm.). Sediment was sieved through a 0.25-mm mesh, homogenized and augmented with phytoplankton cells (*Nannochloropsis salina*) cultured in f/2 medium. The source sediment organic carbon and total nitrogen contents were originally 0.35% and 0% respectively. Organic C was increased to 1.58% following the addition of phytoplankton cells. Unfortunately, N analyses of amended sediment were compromised by a combination of instrument malfunction and sample size limitation but initial values are estimated as ~0.3% based on reported N/C ratios in N-replete *Nannochloropsis* cultures (Flynn et al., 1993).

After collection and manipulation, the surface sediment was incubated under diffusively open conditions in 2 mm thick plugs made of PVC plastic rings fixed on individual circular PVC sheets (Aller and Mackin, 1989; Hulth et al., 1999; Gilbert et al., 2003). Three diameters of plugs were utilized: 3.3 cm (small plugs) for metabolic rates and micro-distributions of oxygen in the pore water, 4.8 cm (medium plugs) for solute concentrations in the pore water, and 6.8 cm (large plugs) for solid phase lipid analyses (Caradec et al., 2004).

All plugs were filled with the mixture of sediment and phytoplankton, and then equally distributed in 3 sets of 3 polycarbonate containers containing 14 L of 0.2-μm filtered seawater (salinity 38.1). Because of destructive sampling, plug areas in containers averaged 299 cm² at the start of the experiment and 49 cm² at the end. Each container was placed in an individual glove bag and kept in the dark. In one set of containers (termed OXIC), the overlying water was continuously purged with water-saturated air. In another set (termed ANOX), anoxic conditions were maintained by continuous N_2/CO_2 bubbling in the overlying water. The 2.3% CO_2 in N_2 allowed the maintenance of overlying water pH at 8.09 ± 0.04 (mean $\pm$ SD; $n = 6$) during the experiment, as measured every 5 days with a WTW 320 portable pH/mV meter (NIST scale).