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Quantification of Ammonium Oxidation to Dinitrogen Coupled to Manganese Oxide Reduction in Marine Sediment

Bo Thamdrup (bot@biology.sdu.dk)[1] & **Tage Dalsgaard** (tda@dmu.dk)[2]

[1] Odense University, Institute of Biology, Campusvej 55, 5230 Odense M, Denmark
[2] Danish National Enviromental Research Institute, Vejlsøvej 25, 8600 Silkeborg, Denmark

Manganese-reducing bacteria convey the oxidation of organic carbon to CO_2 in anaerobic sediments holding manganese oxide. Manganese oxide is a also potential oxidant of ammonium in such sediments, and it has recently been suggested that ammonium is converted to dinitrogen with manganese oxide as the oxidant either by a direct oxidation (Luther et al., 1997), or by oxidation to nitrate followed by de-nitrification (Hulth et al., 1999), possibly by microbial catalysis. Anaerobic dinitrogen formation from ammonium has not been quantified in sediments, but could represent an important sink for nitrogen in aquatic ecosystems, with implications for the regulation of primary productivity. We studied the products of nitrogen mineralisation in manganese oxide-rich sediment from the Norwegian Trough, Skagerrak. Bacterial manganese reduction completely dominated anaerobic carbon oxidation to 10 cm depth at this site, and ammonium accumulated during anoxic incubations at rates that scaled with carbon oxidation rates at a normal C:N ratio, indicating no substantial anaerobic oxidation of ammonium relative to its production. Anoxic incubations with added N-15 ammonium showed no sustained accumulation of N-15 in dinitrogen, which constrained the rate of ammonium oxidation to dinitrogen to less than 2% of the ammonium accumulation rate. Added N-15 nitrate was rapidly reduced to dinitrogen indicating that denitrifying bacteria competed successfully with manganese reducers. Nitrate produced from N-15 ammonium would thus be reduced to and detected as dinitrogen. Because no N-15 labelled N2 was detected, ammonium oxidation to nitrate could also be excluded as a significant process. Thus, ammonium was the end product of nitrogen mineralisation in the anoxic manganese oxide-rich sediment. In contrast, N-15 accumulated as dinitrogen during oxic incubations with N-15 added as either nitrate or ammonium. Ammonium oxidation was not inhibited by allylthiourea (ATU), an inhibitor of aerobic nitrification. The lacking inhibition of nitrate reduction by oxygen and of ammonium oxidation by ATU suggested that the transformations did not involve normal nitrification and de-nitrification. We are currently investigating the mechanisms behind these nitrogen conversions.

Hulth S, Aller RC & Gilbert F, *Geochim. Cosmochim. Acta*, **63**, 49-66, (1999).

Luther GW III, Sundby B, Lewis BL & Brendel PJ, *Geochim. Cosmochim. Acta*, **61**, 4043-4052, (1997).