

## High sensitivity of ammonia and nitrite oxidation rates to nanomolar oxygen concentrations

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To date it remains unclear as to whether ammonia and nitrite oxidation can co-occur alongside and hence supply substrates for fixed N loss via either denitrification or anammox under nanomolar oxygen (O<sub>2</sub>) concentrations. Both culture and field based studies have been restricted to O<sub>2</sub> concentrations greater than 0.25 μM. With O<sub>2</sub> concentrations regularly observed to be less than 10 nM in the core of oxygen minimum zones (OMZ) it is essential to assess the oxygen sensitivity of these processes at these levels.

Sampling was undertaken across the oxycline in the seasonal OMZ off Concepcion, Chile to determine rates of ammonia / nitrite oxidation from short-term incubations at manipulated O<sub>2</sub> levels between 5 nM and 20 μM. Rates of both ammonia and nitrite oxidation were detectable to the limit of our O<sub>2</sub> measurements and demonstrated a strong dependence on nanomolar concentrations of O<sub>2</sub>. Michaelis-Menten kinetics fitted to this data produced half saturation constants (K<sub>m</sub>) of 330 and 780 nM O<sub>2</sub> for ammonia and nitrite oxidation respectively. These values were consistent across multiple depths sampled in this study and are shown to be applicable across OMZ systems. These K<sub>m</sub> values must be included in future modelling studies, in order to more realistically assess the impacts of ocean deoxygenation on nitrogen cycling.

## Titration curves, column experiments, and reactive transport models

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Surface reactions related to e.g. transport and retardation processes in groundwater systems are correlated with geochemical conditions that vary in time and space. For long-term safety analysis of radioactive waste repositories it is of great interest to better understand and to realistically assess these geochemically driven surface and transport reactions, since they might strongly impact radiation exposure.

To get an advanced insight into these processes column experiments are conducted and subsequently modeled with the geochemical speciation code PhreeqC, Version 2.18 (coupled with UCODE\_2005). In order to set-up realistic reactive transport models so-called surface complexation parameters (SCP) such as surface site density, specific surface area, and protolysis constants need to be derived from titration experiments of relevant mineral phases.

Two different titration techniques are conducted for muscovite and orthoclase: continuous and batch titration. Derived results are compared offering an insight into pH-influencing reactions that contribute to surface reactions but also to cation exchange and mineral dissolution.

In column experiments different solids are applied: natural sediments from the Gorleben site, Germany and pure mineral phases (orthoclase, muscovite, quartz). Parameters such as pH, ligands, ionic strength, and cation concentrations are varied in each experiment to reflect realistic environmental conditions. Moreover, transient pH conditions are applied in selected columns.

Both types of experiments (titration, column experiments) including each geochemical variation provide data to model reactive transport processes of hazardous pollutants more realistically in groundwater-flow driven environments with PhreeqC. Calculations will be conducted and first results offered for discussion.

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