Investigations on the kinetics of denitrification in arable soils

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In a model describing the denitrification process in soils by a concept of competitive inhibition (Benckiser and Syring, 1992), oxygen and nitrate together with the intermediate products of the denitrification sequence are acting as competing acceptors for the electrons produced by the mineralization of soil organic matter. In a simplified form, the model can be stated as:

$$
\begin{aligned}
\frac{de(t)}{dt} &= P_e - e(t)\,(4\,k_{O2}\,O_2(t) + 2\,k_{NO3}\,NO_3^-(t) + 2\,k_{NO2}\,NO_2^-(t) + 2\,k_{N2O}\,N_2O(t)) \\[4pt]
\frac{dO_2(t)}{dt} &= -k_{O2}\,O_2(t)\,e(t) \\[4pt]
\frac{dNO_3^-(t)}{dt} &= -k_{NO3}\,NO_3^-(t)\,e(t) \\[4pt]
\frac{dNO_2^-(t)}{dt} &= -k_{NO2}\,NO_2^-(t)\,e(t) + k_{NO3}\,NO_3^-(t)\,e(t) \\[4pt]
\frac{dN_2O(t)}{dt} &= -k_{N2O}\,N_2O(t)\,e(t) + \tfrac{1}{2}\,k_{NO2}\,NO_2^-(t)\,e(t)
\end{aligned}
\tag{1}
$$

Here $e(t)$ denotes the electron activity, while P_e is the production rate of electrons from the mineralization of organic matter, while $O_2(t)$, $NO_3^-(t)$, $NO_2^-(t)$ and $N_2O(t)$ are the respective activities of the molecules. Here concentration is used as a proxy for activity. The k. are rate constants, where an important parameter is the ratio of the rate constants for oxygen k_{O2} and nitrate k_{NO3} reduction. If we consider the electron activity $e(t)$ and the concentration of the intermediate product NO_2^- as constant and set the rate constant for N_2O consumption k_{N2O} to zero (acetylene block), we can derive an Michaelis–Menten type equation for the rate of N_2O production

$$
\frac{dN_2O(t)}{dt} = \frac{\dfrac{k_{O2}}{k_{NO3}}}{\dfrac{k_{O2}}{k_{NO3}}\,O_2(t) + NO_3^-(t)} \cdot \frac{P_e}{8}\,NO_3^-(t),
\tag{2}
$$

where the maximum production rate of N_2O is controlled by the electron availability while the apparent K_m-value is given by $\dfrac{k_{O2}}{k_{NO3}}\,O_2(t) = k_a\,O_2(t)$.

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A series of experiments was set up to estimate the value of k_m in soils which had received a long-term treatment with varying amounts of organic and mineral N-fertilizers. Soil slurries (10 g soil/100 ml H_2O) were prepared from field moist soil, that had been passed through a 2 mm sieve. To avoid a strong limitation of denitrification by nitrate, potassium nitrate was added to give a concentration of 50 mg N/l solution. The soil slurry was incubated in a gas-tight 250 ml vessels equipped with a rotating magnet and placed on a magnetic stirrer at 20 C. Oxygen concentrations of 0.1 % to atmospheric were obtained by flushing the vessels with pure nitrogen and adding the calculated quantities of oxygen with a gas-tight syringe. The acetylene blocking of N_2O reduction was performed by injecting 2 ml acetylene per vessel. During the 72 h incubation period, gas samples ware taken at 24 h intervals and analyzed for N_2O, O_2 and CO_2 by gas chromatography.

The production rate of N_2O as function of oxygen concentration behaved as expected from Eq. 2 except in soils with a very low denitrification activity, where high variability of N_2O production between replications was observed. The CO_2 production rate remained constant over the incubation time, indicating the absence of severe changes in the microbial population density and its metabolic activity although no bacteriostatics were applied. The rate of electron production P_e was estimated from the CO_2 production of the samples kept at atmospheric oxygen concentration, assuming a bulk composition of CH_2O for the soil organic matter. The ratio of the oxygen and nitrate reduction rate constants k_m was estimated by fitting Eq. 2 to the measured values of N_2O production and O_2 concentrations.

Further experiments will address the problem of estimating the rate constant for N_2O reduction k_{N2O} to allow the calculation of the ratio of N_2O to N_2 production. This will require an estimation of the complete set of modell parameters and the use of isotopic tracers.

Reference:

Benckiser, G. and Syring, K.M. (1992):
Denitrifikation in Agrarstandorten - Bedeutung, Quantifizierung und Modellierung
BioEngineering 8, p. 46-52