



## **A triplet $^{15}\text{N}$ tracer experiment to evaluate the reaction pathways of N gases in soil during the processes nitrification and denitrification**

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NO is widely accepted to be an obligatory intermediate of  $\text{N}_2\text{O}$  formation in the denitrification pathway. However, in studies with native soils could not confirm NO as an  $\text{N}_2\text{O}$  precursor, and field experiments mainly revealed nitrification as the source of NO. Therefore the hypothesis was constructed, that the limited diffusion of NO in soil is the reason for this contradiction. To test this diffusion limitation hypothesis we using a black earth soil and conducted through-flow ( $\text{He}/\text{O}_2$  atmosphere)  $^{15}\text{N}$  tracer experiments in an experiment set up free of diffusion limitation. The three relevant inorganic N pools ammonium, nitrite, and nitrate in the soil were  $^{15}\text{N}$  labelled in separate experiments based on the kinetic isotope method (triplet experiment). During the incubation the partial pressure of  $\text{O}_2$  was decreased in four steps from 20% to about 0%.

Net NO emission increased up from 0.9 to 3.7  $\mu\text{g N kg}^{-1} \text{ h}^{-1}$  with decreasing  $\text{O}_2$  partial pressure. Compared to NO only small amounts of  $\text{N}_2\text{O}$  (0.1 to 0.4  $\mu\text{g N kg}^{-1} \text{ h}^{-1}$ ) were measured. Our results demonstrate that nitrite plays a key role in nitrification as well as denitrification and is at almost 100% the direct precursor for NO formed by both processes in the soil investigated. The contribution of nitrification of ammonium to the total nitrite production was approx. 88% under aerobic soil conditions and quickly decreased to zero with declining  $\text{O}_2$  partial pressure. Emitted  $\text{N}_2\text{O}$  originated only under strict anaerobic conditions (0-0.2%  $\text{O}_2$ ) to 100% from NO, providing evidence that NO is a free intermediate of  $\text{N}_2\text{O}$  formation by denitrification. To the best of our knowledge this is the first time that NO has been detected in a native soil as a free intermediate product of  $\text{N}_2\text{O}$  formation at denitrification. These experimental results were processed to a publication and submitted to Soil Biology and Biogeochemistry (Russow et al. 2009; Role of nitrite and nitric oxide in the processes of nitrification and denitrification in soil: results from  $^{15}\text{N}$  tracer experiments, submitted). For the presentation the measurements were analysed with the SimKIM model and the results demonstrate that nitrite is present in at least two separate endogenous pools.

In the future, the influence of the division of pools into process-related sub-pool on the calculation of gross rates by pool dilution technique must be investigated and this division should be consider in numerical models for analysing tracer experiments. The obtained results clearly verify the “diffusion limitation” hypothesis explaining the unsuccessful detection of denitrification as a source for NO in previous field and incubation experiments with bulk or undisturbed soils. These demonstrate the important control of soil structure (including bulk density) on emission of the different N gas species and a focus on the virtual field conditions (e.g. the soil structure, and  $\text{O}_2$  availability) is urgently required.