



## Estimating N<sub>2</sub> fluxes from denitrification using isotopologue signatures of N<sub>2</sub>O

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There is few information on N<sub>2</sub> fluxes from denitrification in the field, because this process is difficult to measure in situ. Isotopologue signatures of N<sub>2</sub>O such as  $\delta^{18}\text{O}$ , average  $\delta^{15}\text{N}$  ( $\delta^{15}\text{N}_{\text{bulk}}$ ) and  $^{15}\text{N}$  site preference (SP = difference in  $\delta^{15}\text{N}$  between the central and peripheral N positions of the asymmetric N<sub>2</sub>O molecule) can be used to constrain the atmospheric N<sub>2</sub>O budget and to characterize N<sub>2</sub>O turnover processes including N<sub>2</sub>O reduction to N<sub>2</sub>. However, the use of this approach to study N<sub>2</sub>O dynamics in soils requires knowledge of isotopologue fractionation factors ( $\epsilon$ ) for the various partial processes involved, e.g. N<sub>2</sub>O production by nitrification or denitrification, N<sub>2</sub>O reduction by denitrification and diffusive transport. The aim of our study was to investigate whether isotopologue signatures of soil-emitted N<sub>2</sub>O can be used to estimate N<sub>2</sub>O reduction, and accordingly N<sub>2</sub> formation.

Two arable soils were fertilized with NO<sub>3</sub><sup>-</sup> and incubated anaerobically in a closed laboratory system until all NO<sub>3</sub><sup>-</sup> was converted to N<sub>2</sub>. Similar incubations were conducted with a water-saturated arable peat soil and sediment from a sandy aquifer.

The time courses of N<sub>2</sub>O and its isotopologues were monitored during the reaction progress of denitrification. N<sub>2</sub> production was estimated from  $^{15}\text{N}_2$  accumulation during parallel incubation experiments, where materials were fertilized with  $^{15}\text{N}$ -labelled NO<sub>3</sub><sup>-</sup>.

$\epsilon$  of the NO<sub>3</sub>-to-N<sub>2</sub>O step was derived from isotopologue signatures obtained from replicates where N<sub>2</sub>O reduction was absent under the presence of C<sub>2</sub>H<sub>2</sub>.  $\epsilon$  of N<sub>2</sub>O reduction to N<sub>2</sub> was estimated by modeling the time course of N<sub>2</sub>O and its isotopologues. For this purpose,  $\epsilon$  of the NO<sub>3</sub>-to-N<sub>2</sub>O step and production rates of N<sub>2</sub>O and N<sub>2</sub> were used as independent model parameters and  $\epsilon$  of N<sub>2</sub>O reduction to N<sub>2</sub> was estimated by fitting.

Fractionation factors of this study will be compared to literature data and the consequences for estimating N<sub>2</sub> fluxes based on N<sub>2</sub>O isotopologues will be discussed.

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