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Isotope fractionation factors of N_2O production and reduction by denitrification: b. Modeling data from soil incubation under N_2-free atmosphere

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Quantifying denitrification in arable soils is crucial in predicting the microbial consumption of nitrogen fertilizers as well as N_2O emissions. Stable isotopologue analyses of denitrification substrates ($\delta^{15}N_{NO3}$,$\delta^{18}O_{NO3}$) and products ($\delta^{15}N_{N2O}$, $\delta^{18}O_{N2O}$and SP_{N2O} = Site Preference, i.e. difference in $\delta^{15}N$ between the central and peripheral N positions of the asymmetric N_2O molecule) can help to distinguish production pathways and to identify N_2O reduction to N_2. However, such interpretations are often ambiguous due to insufficient knowledge on isotopic fractionation mechanisms and wide differences in isotope fractionation factors determined by various studies for N_2O production and reduction.

Here we present an original approach to determine fractionation factors associated with denitrification. This determination is based on simultaneous modeling of both reaction steps (N_2O production and reduction) and comparison of the results with experimental data from a laboratory incubation experiment carried out under N_2-free atmosphere. During the incubations N_2O and N_2 concentrations were measured continuously, hence the reduced fraction ($N_2/(N_2+N_2O)$) was calculated directly from measured gas fluxes. Various modeling approaches have been applied to estimate the ranges of isotopic fractionation factors controlling the isotopic signatures of soil-emitted N_2O. Initially, assumed isotope fractionation factors and the Rayleigh equations describing isotopic fractionation were used to calculate the theoretical $\delta^{15}N$, $\delta^{18}O$and SP values for emitted N_2O. Afterwards, the best fit fractionation factors for N_2O production and reduction were determined by comparing modeled and measured values.

For two analyzed arable soils (clay and sandy loam), the isotopic fractionation factors were very consistent. For N_2O production mean net isotope effects of $\eta^{15}N_{N2O-NO3}\sim$ -41‰ , $\eta SP_{N2O-NO3}\sim$ 2‰ and $\eta^{18}O_{N2O-H2O}\sim$ +40‰ have been found. For N_2O reduction mean net isotope effects of $\eta^{15}N_{N2-N2O}\sim$ +1‰ , $\eta SP_{N2-N2O}\sim$ -7‰ and $\eta^{18}O_{N2-N2O}\sim$ -5‰ have been found. When compared to previous reports these results show significantly lower fractionation for $\delta^{15}N$ and $\delta^{18}O$values during N_2O reduction, which is most likely due to enhanced experimental approach that largely eliminates laboratory artifacts.