Oxygen isotope exchange and isotopic fractionation during N_2O production by denitrification

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Stable isotopic analyses of N_2O may help in quantification of soil denitrification processes. N_2O reduction to N_2 during denitrification is associated with significant isotopic fractionation. Theoretically, this would allow the product ratio ($N_2O/(N_2+N_2O)$) to be calculated based on the isotopic signature of the remaining N_2O if the isotopic signature of the produced N_2O were precisely predictable. Oxygen isotopes are especially useful, in particular the ^{17}O excess, $\Delta(^{17}O)$, to quantify any oxygen isotope exchange between soil water and intermediate products (NO_2^-, NO). This significantly influences the $\delta(^{18}O)$ values of the N_2O produced. Previous studies showed this exchange to be nearly complete, up to 90% [1,2]. However, there are very few studies on the associated oxygen isotopic fractionation and its potential coupling to the magnitude of oxygen isotope exchange with soil water [2,3]. We hypothesize that for high oxygen exchange, the oxygen isotopic fractionation will show little variability.

In previous experiments, an ^{18}O-enriched tracer was applied to quantify the magnitude of oxygen exchange [1,2]. Such an approach does not permit determining any oxygen isotope fractionation. Here, we applied two novel experimental approaches: (1) waters of two different $\delta(^{18}O)$ values within the natural range (–1.5 and –14.8 ‰ relative to VSMOW) were used for rewetting the incubated soils and the oxygen exchange was calculated from comparing the relative isotope ratio difference between N_2O and H_2O for these two water treatments; (2) soils were amended with Chile Saltpeter characterized by a high ^{17}O excess (20.2 ‰) and the ^{17}O excess of the N_2O product was measured. Both approaches were applied simultaneously on the same soil samples, which allowed quantifying the oxygen isotope exchange with two independent methods at the same time. The N_2O reduction was inhibited with acetylene method and $\delta(^{18}O)$ values of the N_2O produced were measured to determine the oxygen fractionation during N_2O production.

Both methods showed nearly complete (95-99%) oxygen exchange with soil water for all soil types (loamy sand and silt loam), water contents (50 to 80% water-filled pore space), temperatures (8 and 22 ºC), and N_2O production rates. The oxygen isotope fractionation $\varepsilon(^{18}O, N_2O$-$H_2O)$, defined as the relative isotope ratio difference between product (N_2O) and substrate (soil water), was quite stable between 16 and 20 ‰ . This confirms that $\delta(^{18}O)$ values may be useful in determination of the product ratio. Moreover, the very low ^{17}O excess found in N_2O indicates that the hypothesis of soil denitrification contributing to the oxygen isotope excess of atmospheric N_2O can be rejected [4,5].

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