



Causes of ^{15}N site preference in N_2O produced via biological denitrification

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There is much current interest in the use of the isotopic composition of N_2O , including site-specific $\delta^{15}\text{N}$ (i.e., the $^{15}\text{N}/^{14}\text{N}$ ratios of the central or terminal positions, expressed as $\delta^{15}\text{N}^\alpha$ and $\delta^{15}\text{N}^\beta$ respectively) and $\delta^{15}\text{N}^{bulk}$ (the integrated N isotope value) to understand sources of this important greenhouse gas, particularly biological nitrification and denitrification. Since the chemistry of these processes is very different, the site preference ($\text{SP} = \delta^{15}\text{N}^\alpha - \delta^{15}\text{N}^\beta$) and $\delta^{15}\text{N}^{bulk}$ of N_2O has been proposed as an identifier of N_2O production pathways. However, recent field observations and laboratory studies of biological N_2O production, while showing considerable variation in $\delta^{15}\text{N}^{bulk}$ and SP, do not yet indicate there are clear isotopic signatures of N_2O from nitrification versus denitrification. Mechanisms driving the variability of $\delta^{15}\text{N}^{bulk}$ and SP values of biologically produced N_2O need to be better understood before we are able to robustly constrain the atmospheric N_2O budget using $\delta^{15}\text{N}^{bulk}$ and SP.

In the absence of N_2O consumption, the $\delta^{15}\text{N}^{bulk}$ value of N_2O from denitrification will be a function of the $\delta^{15}\text{N}$ of the initial nitrate and the isotopic fractionation associated with the rate controlling step/s of its reduction to N_2O . On the other hand, the SP of N_2O from denitrification is determined where the site equivalence of each N atom is lost, i.e. the reduction of NO (or NO_2^-) to N_2O . A useful way to explore the reaction mechanism is to determine whether these isotope effects are dependent on substrate concentration, in this case nitrate. Another reason to consider the effects of nitrate concentration is that denitrification occurs in terrestrial and aquatic environments where nitrate concentrations are highly variable, however published lab studies to date only consider denitrification under relatively high nitrate conditions.

We investigated the $\delta^{15}\text{N}$ values of N_2O produced by the denitrifier *P. aureofaciens* at nitrate concentrations ranging from 0.03 mg/L to 2000 mg/L at which the total conversion was $< 15\%$ of the initial nitrate. The bulk ^{15}N enrichment factor (ε) increased with production rate when the $[\text{NO}_3^-]_{\text{initial}}$ varied between 25 mg/L to 844 mg/L, but was constant below this $[\text{NO}_3^-]_{\text{initial}}$ range (here referred to as low nitrate). The maximum production rate and observed enrichment factors were reached at $[\text{NO}_3^-]_{\text{initial}} \sim 1000$ mg/L and remained constant up to 2000 mg/L (here referred to as high nitrate). Results were $\varepsilon = -23.7 \pm 2.9\%$, (n=12) at low nitrate, and constant at $\varepsilon = -44.0 \pm 1.9\%$, (n=8) at high nitrate. $\delta^{15}\text{N}^\alpha$ and $\delta^{15}\text{N}^\beta$ values relative to air N_2 (we measure tropospheric N_2O to have $\delta^{15}\text{N}^\alpha$ and $\delta^{15}\text{N}^\beta$ values of $+27.2\%$, and -14.6% , respectively relative to air N_2) were $-11.4 \pm 2.5\%$, (n=11) and $-27.5 \pm 3.7\%$, (n=11) at low nitrate, and $-35.7 \pm 2.1\%$, (n=7) and $-48.3 \pm 3.1\%$, (n=7) at high nitrate. We found significant dependences of isotope effects on nitrate availability: ε decreased and SP increased as nitrate concentration decreased. Implications of these results with respect to denitrification mechanism and the causes of SP during N_2O production will be discussed.