A novel method for trapping and analyzing $^{15}$N in NO for tracing NO sources

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$^{15}$N isotope tracing is an effective and direct approach to investigate the biological and chemical sources of nitric oxide (NO) in soil. However, NO is highly reactive and rapidly converted to nitrogen dioxide ($\text{NO}_2$) in the presence of ozone. Various chemical conversions of NO to the more stable solutes nitrite ($\text{NO}_2^-$) and nitrate ($\text{NO}_3^-$) have been proposed, which allow analyzing the $^{15}$N abundance without major fractionation. However, NO emissions from soils are usually small, posing major challenges to conversion efficiency and background contamination. Here we present a novel method in which NO is oxidized to $\text{NO}_2^-$ by chromium trioxide ($\text{CrO}_3$) prior to conversion to $\text{NO}_2^-$ and $\text{NO}_3^-$ in an alkaline hydrogen peroxide ($\text{H}_2\text{O}_2$) solution. Immediately following trapping, manganese dioxide ($\text{MnO}_2$) and 5M HCl are added to remove excess $\text{H}_2\text{O}_2$, and to adjust the pH to around 6.0-7.0, respectively. The resulting solution can be stored until analysis and is none-toxic, allowing to use a modified denitrifier method (Zhu et al., submitted), where $\text{NO}_2^-$ and $\text{NO}_3^-$ are reduced quantitatively to nitrous oxide ($\text{N}_2\text{O}$). Optimum NO conversion rates of > 90% even at extremely low initial NO concentration were obtained with 4% $\text{H}_2\text{O}_2$, 0.5 M NaOH, and 0.5 L min$^{-1}$ gas flow rate. In a laboratory test, using NO gas with different $^{15}$N signals produced from unlabelled and-labelled $\text{NO}_2^-$, we found an overall precision of 0.4‰ for unlabelled and 49.7‰ for NO enriched with 1.0 atom% $^{15}$N, respectively. This indicates that this method can be used for both natural abundance studies of NO, as well as in labelling studies tracing NO sources.

Zhu J, Yu L, Bakken LR, Mørkved PT, Mulder J, Dörsch P. Controlled induction of denitrification in Pseudomonas aureofaciens: a modified denitrifier method for $^{15}$N and $^{18}$O analysis in $\text{NO}_3^-$ from natural water samples by IRMS. Submitted.