Triple-isotopologue Analysis of $N_2$ as a Tracer of the Global Nitrogen Cycle

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The uncertainty of the global nitrogen budget highlights the importance of a better understanding of the fixed-nitrogen inventory. High-precision measurements of $^{14}\text{N}^{14}\text{N}$, $^{14}\text{N}^{15}\text{N}$ and $^{15}\text{N}^{15}\text{N}$ in $N_2$ can provide new constraints on this inventory. We report the first measurements of these species in tropospheric $N_2$ and in $N_2$ generated from denitrification and discuss the potential uses of $N_2$ “triple-isotopologues” to improve our understanding of the nitrogen cycle.

The $N_2$ triple-isotopologue distribution, expressed as $\Delta_{30}$, describes enrichment in $^{15}\text{N}^{15}\text{N}$ of $N_2$ relative to that predicted by chance. It reflects isotopic ordering through N-N bond breaking and formation during nitrogen fixation and denitrification. The $\Delta_{30}$ parameter is analogous to $\delta^{15}\text{N}$ in that it corresponds to chemical transition among N-bearing compounds. However, unlike $\delta^{15}\text{N}$, $\Delta_{30}$ is insensitive to the total $^{15}\text{N}/^{14}\text{N}$ ratio in the reservoirs.

We present $\Delta_{30}$ values of $N_2$ analyzed on a high-resolution isotope ratio mass spectrometer (the Nu instruments Panorama). The analytical accuracy was verified with laboratory Knudsen diffusion experiments. The $\Delta_{30}$ values of $N_2$ from soils and pure cultures of denitrifiers vary between +16.9 and +18.9‰, which indicate large kinetic isotopic effects during denitrification and probably reflect the isotopic signatures of enzymes that catalyze N-N bond formation. Enrichment in $^{15}\text{N}^{15}\text{N}$ was also observed in tropospheric $N_2$ ($\Delta_{30} = +19.05 \pm 0.12\%$o, 1σ), which likely inherits its value from the nitrogen lost from biosphere. Overall, our results suggest that the degree of isotopic ordering of tropospheric $N_2$ may be applied to reflect the relative contributions of global natural $N_2$ sources.

Keywords: global nitrogen cycle, $N_2$ triple isotopologues, denitrification