



Deciphering land-atmosphere interactions of reactive nitrogen using high-frequency isotope analysis

Emily M. Elliott (1), Lucy A. Rose (2), and Zhongjie Yu (1)

(1) University of Pittsburgh, Pittsburgh, Pennsylvania U.S.A., (2) University of Minnesota, St. Paul, Minnesota U.S.A.

Methodological advances in sample collection and isotopic analyses have facilitated an exponential increase in the measurement of reactive nitrogen (N) isotopes in atmospheric systems. Despite rapid advances in our production of new data, most prior studies have characterized NO_x emission and NO_3^- deposition dynamics on seasonal, annual, and longer time scales. In contrast, much less attention has focused on NO_3^- deposition dynamics over short time scales (e.g., individual storm events). Because NO_x emissions from certain sources, such as lightning and biogenic emissions, are highly transient, improved characterization of N emission and deposition dynamics on episodic time scales is needed to clarify the importance of these sources to atmospheric NO_3^- formation and deposition. Here we examine, on episodic time scales, shifts in the isotopic composition of rainwater nitrate and soil derived NO_x in two separate case studies.

We coupled the triple isotopic composition of NO_3^- ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$) in hourly precipitation samples with regional air mass back trajectory analysis to evaluate nitrate formation pathways, fractionation dynamics, and NO_x source contributions to precipitation NO_3^- at Fernow Experimental Forest (West Virginia, USA) during six growing season storms. $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ values in precipitation exhibited extreme variability, varying by up to 16‰, 26‰ and 9‰ respectively, over two hours during some events. The wide range of $\Delta^{17}\text{O}$ - NO_3^- values encompassed by the precipitation NO_3^- measured during these growing season storms, combined with the patterns in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^- over short time periods, demonstrate the dynamic nature of atmospheric NO_3^- formation and deposition during storm events and the utility of triple nitrate isotopes for evaluating N deposition sources and processes.

While soil NO emission is expected to be an important source driving the intra-precipitation variations of $\delta^{15}\text{N}$ - NO_3^- , $\delta^{15}\text{N}$ of soil-emitted NO is notoriously hard to measure and predict due to the high chemical reactivity of NO and the episodic and complex nature of soil NO-producing processes. Here we highlight a new NO collection approach that is capable of collecting soil-emitted NO for $\delta^{15}\text{N}$ analysis at time scale of minutes. Coupling this new method with a dynamic flux chamber system under both laboratory and field conditions, we show that transient, but pronounced variations in magnitude (up to nine-fold) and $\delta^{15}\text{N}$ (up to 36‰) of soil NO emission can be triggered by rewetting dry soils using different N substrates. These results collectively demonstrate the promising potential of high-frequency isotope analysis in characterizing the dynamic nature of soil NO emission, discerning microbial processes governing pulse soil NO emissions, and ultimately elucidating the complex land-atmosphere interactions of reactive N in natural and human-dominated ecosystems.