Investigating the N and O isotopic composition of NO_x

MEREDITH G. HASTINGS[1*], WENDELL W. WALTERS[1], JIAJUE CHAI[1], DAVID M. MILLER[1,2]

[1] Institute at Brown for Environment and Society and Department of Earth, Environmental, and Planetary Sciences, Brown University, Providence, RI 02912, USA (*correspondance: meredith_hastings@brown.edu)

[2] now at Environmental Defense Fund, Boston, MA, USA

Variability in the burden of nitrogen oxides (NO_x = $NO+NO_2$) is a first-order research question in atmospheric chemistry. NO_x concentrations play an important role in determining the oxidizing efficiency of the atmosphere via connections to ozone cycling and OH radical concentrations; NO_x is also the primary source of nitric acid, a major contributor to acid rain and global nitrogen deposition. NO_x is released by both anthropogenic and natural sources, which vary considerably in space and time. The isotopic composition of NO, NO_2 and/or NO_x offers a powerful tool for tracking the sources and chemistry of NO_x in the atmosphere.

Prior measurements of the nitrogen isotopic composition of NO_x have utilized a variety of methods for collecting NO and/or NO_2 as nitrate or nitrite for isotopic analysis, and testing of some of these methods (including active and passive collections) reveal inconsistencies in efficiency of collection, as well as issues related to changes in conditions such as humidity, temperature, and NO_x fluxes. We have recently developed and thoroughly verified techniques in the laboratory and field, to efficiently and accurately determine the $\delta^{15}N$ of NO_x ($NO + NO_2$) and the $\delta^{18}O$ (and for the first time, $\Delta^{17}O$) of NO_2. These techniques allow for high-time resolved observations (i.e. hourly), and the ability to collect in environments with highly variable NO_x sources and concentrations. Results from laboratory and field studies of vehicle emissions, agricultural soil emissions, and biomass burning, suggest very different $\delta^{15}N$-NO_x values and less variability than previous work, particularly for vehicle emissions. Preliminary results from urban air at two locations show distinct behavior in $\delta^{15}N$- and $\delta^{18}O$-NO_2 ($\Delta^{17}O$ measurements are underway); both sites have a similar NO_x source (vehicular traffic) but different environmental conditions. Our aim is to directly utilize the isotopic composition of NO_x to track emissions and photochemical cycling, promoting greater understanding of NO_x processing and impacts.