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Nitrogen Isotope Exchange Between NO and NO_2 and Its Implication for ^{15}N Variations in Tropospheric NO_x

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Nitrogen oxides (NO_x = NO + NO_2) are trace gases that have numerous sources that include vehicles, power plants, lightning, soil emissions, agriculture, and biomass burning. It is important to estimate the budgets of these emission sources because NO_x play an important role in air quality, climate, and human health. Analysis of the nitrogen stable isotope ratio ($^{15}N/^{14}N$) has been suggested as a useful method for partitioning NO_x sources, as emission sources often have characteristic $^{15}N/^{14}N$ ratios ("fingerprints"). However, the effects of chemical and physical processes on $^{15}N/^{14}N$ ratios of NO_x have not been researched in depth, which limits this isotopic technique. It has been suggested that the nitrogen isotope exchange between NO and NO_2 has an influence on the partitioning of ^{15}N between these two molecules. However, previous experimental and theoretical studies disagree about the value of this isotope exchange process. We have experimentally measured this isotope exchange process in which NO and NO_2 were equilibrated in a vacuum system and NO_2 was selectively removed from the system and measured for its $^{15}N/^{14}N$ ratio. Our experimental values agree exceptionally well with the theoretically predicted value, using corrections for anharmonicity. Using this data, we were able to model a diurnal cycle and seasonal changes in the distribution of $^{15}N/^{14}N$ ratios between NO and NO_2 resulting from nitrogen isotopic exchange. Future research will measure $^{15}N/^{14}N$ ratios of NO_x in ambient air to see if our predicted diurnal and seasonal change is correct.

Research advisor Greg Michalski writes: "Damian's research improves our understanding of a key component of air pollution, nitrogen oxide chemistry, and was published in the highly ranked peer reviewed journal Geophysical Research Letters*. This is a major accomplishment for an undergraduate and highlights the possibilities of undergraduate research here at Purdue."*

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