



## The Use of Stable Isotopes to Constrain the Nitrogen Cycle

Krystin Riha

PhD Candidate

Nitrogen (N) is a crucial element which is essential for life and is necessary for all organisms to live and grow. However, N compounds have also been acknowledged for their many detrimental impacts on the environment. Human activities have dramatically altered the global N cycle, currently human fix  $N_2$  at the same rate as biotic  $N_2$  fixation through anthropogenic activities including: energy production (fossil fuel combustion), production of synthetic fertilizers, and cultivation of legumes and other crops. And, driven by energy and food production for an ever growing world population, anthropogenic N fixation is projected to increase 60% by 2020 (mainly in developing countries), therefore causing a fertilizing effect on global ecosystems and changing ecosystem function in ways we still do not understand. This dissertation aims to resolve sources of reactive N and its fate in the environment using stable isotopes abundances.

The use of nitrogen and triple oxygen isotopes of nitrate ( $NO_3^-$ ) have been used to infer changes in the nitrogen biogeochemical cycle (e.g.  $NO_3^-$  source appointment, processing, and atmospheric chemistry). However, analytical and isotopic approaches come with their caveats many of which are overlooked. The recent isotopic analysis method which employs the use of denitrifying bacteria coupled with subsequent gold tube thermal decomposition has several shortcomings and adaptations have been made to: simultaneously analyze nitrogen and oxygen isotopes, discuss detection limits, determine the isotopic effects of sample preparation as well as improve calibration curves to encompass the full range of environmental samples and eliminate the need for extrapolation and improper corrections. One way to determine the sources of nitrogen input to these environments is through the use of multiple isotope analysis ( $\delta^{15}N$ ,  $\delta^{18}O$  and  $\Delta^{17}O$ ). However, the commonly used 'dual isotope' approach for  $NO_3^-$  source appointment is based off of limited studies conducted in forested and coastal ecosystems and is not conclusive of all ecosystem  $NO_3^-$  values. Poor separation also occurs between  $NO_3^-$  sources, particularly atmospheric and nitrification, as well as misinterpretation of  $NO_3^-$  values due to fractionation occurring during  $NO_3^-$  processing. However, many N biogeochemical studies still employ this approach which can lead to inconclusive or incorrect results. Improvements to the dual isotope approach presented in this dissertation included isotopic constraints of  $NO_3^-$  sources including atmospheric samples from a variety of locations across the globe, more large set of fertilizer  $NO_3^-$  samples, modeled nitrification  $NO_3^-$   $\delta^{18}O$  values, and inclusion of an alternative dual isotope approach using  $\Delta^{17}O$  which allows for better source separation. These  $NO_3^-$  source constraints were employed in a case study to determine the effects of urbanization on the coupled nitrogen hydrologic cycle in the semi-arid urban city of Tucson, AZ. It was found that, contrary to an abundant amount of literature, variations in atmospherically derived  $NO_3^-$  was not controlled by changes in  $NO_x$  chemistry but rather by shifts in meteorological conditions and atmospheric chemistry. Urban runoff was found to have a consistently high fraction of atmospheric  $NO_3^-$  (range 0-80%, mean = 38%), substantially higher than previous N studies in forested catchments. The degree of atmospheric  $NO_3^-$  in these stream samples changes over the course of the storm events suggesting different pools of nitrate are being mobilized by changing hydrologic conditions. The isotope data suggests that type of drainage substrate, such as concrete or vegetated washes, influences N cycling within the individual watershed.

*Refreshments at 3:00pm*

*Room 2201/HAMP*

**Thursday, April 18, 2013**

**3:30 p.m.**

**Room 1252, HAMP Bldg.**