Towards a global interpretation of dual nitrogen isotopes in natural water

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Abstract:

Modern anthropogenic activities have significantly increased nitrate concentrations in natural waters. Stable isotopes of nitrate (NO_3^-) offer a tool to deconvolute some of the these man-made changes in the nitrogen cycle. They are often graphically illustrated on a template designed to identify different sources and denitrification in groundwater. In the two decades since this template was developed, NO_3^- isotopes have been measured in a variety of ecosystems and through the nitrogen cycle, however the interpretation of NO_3^- isotopes has not advanced. This default is no longer helpful because it does not describe non-groundwater ecosystems well and encourages researchers to think solely about denitrification even in well oxygenated systems where denitrification is likely to have little to no influence on the nitrogen cycle. We propose a different scheme to encourage a better understanding of the nitrogen cycle and interpretation of NO_3^- isotopes. We use a mechanistic understanding of NO_3^- formation to place bounds on the oxygen isotope axis and provide a means to adjust for different environmental water isotope so data from multiple sites and times of year can be appropriately compared.

Background:

Stable isotopes in nitrate (NO_3^-) have been commonly measured for more than 4 decades (see Heaton (1986) and papers therein). Methods have evolved from off-line $AgNO_3$ precipitation, to chemical and microbial reduction to N_2O and subsequent CF-IRMS analyses. Since NO_3^- is a very common global pollutant and contributor to eutrophication in water (Vitousek et al. 1997), a key application of NO_3^- isotopes was to identify the NO_3^- source or sources. Through combining a number of individual studies, this lead to publication of a $\delta^{18}O\text{-}NO_3^-$ vs $\delta^{15}N\text{-}NO_3^-$ co-plot with suggested ranges for different ‘sources’ of NO_3^- (Kendall 1998). It has been modified a few times but the fundamental concept remained the same. It’s application for interpreting NO_3^- isotopes has become widespread but this figure is not really fit for this purpose and commonly over-interpolated. Here, we discuss the assumptions inherent in this figure and key improvements needed improved understanding of NO_3^- isotopes in the environment.

The figure was designed for interpreting groundwater data where NO_3^- isotope values of different NO_3^- sources are preserved except by (chemo)denitrification. Some researchers identified forests that receive a lot of nitrogen deposition export NO_3^- in streams and this does not retain the atmospheric deposition isotope values. This was early evidence that measured NO_3^- isotopes in surface water showed that they should not be used for source identification because of various biological alteration along their flowpath. As method improvements allowed more NO_3^- isotope data to be generated, a schematic figure that recognized biological processing of NO_3^- between its sources and sampling point needed to be developed. However, this commonly used figure encourages researchers to think only about one process, denitrification (Kendall 1998), although it may be uncommon in well oxygenated lake surfaces or streams and rivers. In this way, we need a better schematic figure that explicitly recognizes the differences between NO_3^- sources and processes that produce and consume NO_3^-.

Interpretation:

The “nitrogen axis” had been used as the primary differentiator between sources. However, given the wide range of possible $\delta^{15}N$ values in manure/sewage and soils (Craine et al. 2015), and the obvious fact that nitrogen will be biologically cycled in those systems, source identification cannot be done with boxes on a figure. Since the δ^{15}N scale is typically defined against atmospheric N_2, this means the data are already adjusted for the high levels of synthetic nitrogen produced and used globally. Measuring locally appropriate sources of nitrogen as potential initial δ^{15}N values would be a very useful contribution to each study instead of relying on the broad assumption that a single set of boxes, derived from a limited number of measurements and locally constrained, are globally appropriate.

The "oxygen axis" has groups that can be defined a priori: (i) high δ^{18}O values from NO_3^- produced in the atmosphere where the δ^{18}O value depends strongly on latitude (Michalski et al. 2012); and (ii) low δ^{18}O values where the δ^{18}O value depends strongly on the δ^{18}O of H_2O where the NO_3^- is formed (Snider et 2010). The δ^{18}O value of NO_3^- produced by nitrification, including nitrification of nitrogen ammonified from organic nitrogen, can be bounded in two ways. First, canonical two-step nitrification (from NH_4^+ over NH_2OH to NO_2^- to NO_3^-) adds one O atom from O_2 in the first step and one O atom from H_2O in each of the next two steps (Snider et al. 2010). In surface soils, the pore gas δ^{18}O-O_2 value is very likely near the atmospheric value of +23.5‰ (vs SMOW). In productive aquatic ecosystems, the diel variability of δ^{18}O-O_2 values can be large (e.g. Venkiteswaran et al. 2015, Wassenaar et al. 2010) though this range can be estimated by one set of diel samples during the most productive part of the year and analyzed via a variety of techniques (e.g., Barth et al. 2004; Wassenaar and Koehler 1999). Second, incubation experiments with various levels of δ^{18}O-H_2O indicate that the contribution of δ^{18}O-H_2O values to the final δ^{18}O-NO_3^- value is often greater than the minimum two-thirds and sometimes close to 1. Thus the range of δ^{18}O values of NO_3^- produced in situ can be bounded by knowledge of δ^{18}O-O_2 and δ^{18}O-H_2O values: a minimum of $^{3}/_{3} \times \delta^{18}$O-$H_2O$ and a maximum of $\frac{1}{2} \times \delta^{18}$O-$O_2 + \frac{2}{3} \times \delta^{18}$O-$H_2O$. These are the logical values that should be generated for each field site rather than a single catch-all approach. Globally, δ^{18}O-H_2O values of surface water vary widely but they can be predicted by latitude and databases such as waterisotopes.org though direct measurement is much simpler than NO_3^- isotopes. Additionally, to make data δ^{18}O-NO_3^- comparable between seasons and sites, displaying the data vs the δ^{18}O-H_2O value from the same sample rather than vs V-SMOW. This is akin to the way δ^{18}O-PO_4^{3-} values are plotted relative to their temperature-specific equilibrium point with δ^{18}O-H_2O (Davies et al. 2014, Paytan et al. 2002) in order to remove the influence of difference δ^{18}O-H_2O values (Fig. 1).

Only once the appropriate range of initial δ^{18}O-NO_3^- values has been determined can processes, such nitrification, denitrification, and NO_3^- assimilation be considered. Here, the δ^{18}O and δ^{15}N values of NO_3^- in the environment will be pulled in multiple directions at the same time. The magnitude of change depends on multiple factors that are difficult to statically display in a biplot: mineralization of organic nitrogen and subsequent nitrification may decrease δ^{18}O and δ^{15}N values of NO_3^-, ammonia and NO_3^- uptake and release by riverine periphyton and macrophytes may have differing impacts, and denitrification in riparian zones and anoxic river and lake sediments may increase δ^{18}O and δ^{15}N values of NO_3^- if there is residual NO_3^- to measure. In all cases, changes in the δ^{18}O and δ^{15}N values of NO_3^- are more complex that a single arrow for denitrification suggests (Kendall 1998).

At our sites in Canada, Kenya, and the United Kingdom, almost all data fall within the range of δ^{18}O-NO_3^- values produced in site from O_2 and H_2O values (Fig. 1). This means that without additional independent information, there are several possible explanations for the data that are more complex than simply assigning a source based on the δ^{15}N values. For example, varying contributions of the δ^{18}O-H_2O values, two or more sources of nitrogen, uptake and release of varying amounts of ammonia and NO_3^-, and denitrification in varying combinations may have produced the observed patterns in our data.

Recommendations:

In order to move beyond the simple source apportionment assumptions commonly made in NO_3^- isotope biplots and to explicitly acknowledge that there are a variety of processes that alter the $\delta^{15}N$ and $\delta^{18}O$ values of NO_3^- we recommend:

A. Measuring $\delta^{18}O$-H_2O values at the same time as $\delta^{18}O$-NO_3^- values and report $\delta^{18}O$-NO_3^- values vs $\delta^{18}O$-H_2O instead of V-SMOW to make appropriate comparisons with time and across sites;
B. Combining $\delta^{18}O$-H_2O and $\delta^{18}O$-O_2 values to develop appropriate site-specific ranges of $\delta^{18}O$-NO_3^- produced *in situ*; and
C. Measuring locally relevant $\delta^{15}N$ source values to significantly reduce the range of $\delta^{15}N$ values of nitrogen input to aquatic systems.

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Figure

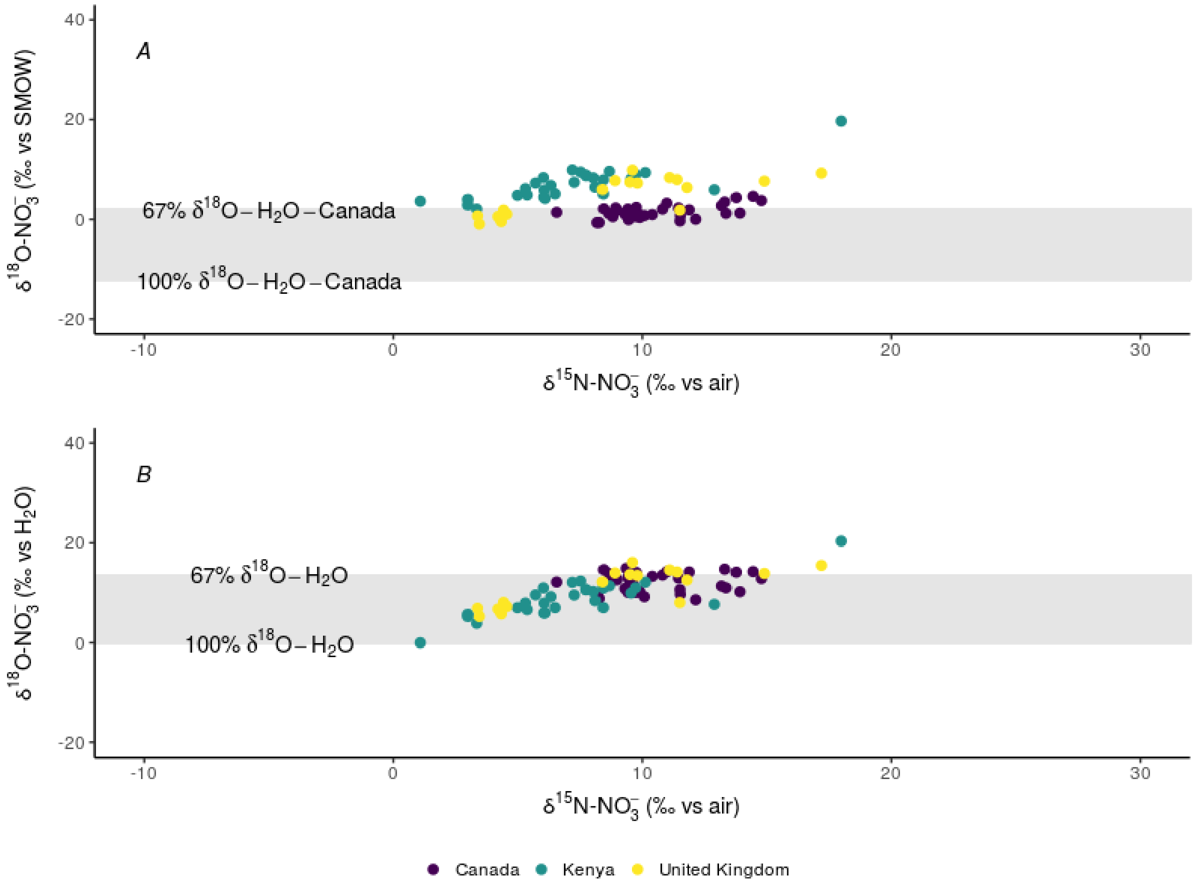

Fig. 1 (a): Nitrate isotope biplot of data from three sites in the middle of the Grand River, Ontario, Canada; 11 sites in the Nyando River, Kenya; eight sites in the Nzoia River, Kenya; five sites in the Sondu River, Kenya; eight sites in the River Lambourn near Boxford, United Kingdom; and 11 sites in the River Thames near Oxford, United Kingdom. The grey panel indicates NO_3^- produced with the maximum range of $\delta^{18}O\text{-}NO_3^-$ values based on a mixture of $\delta^{18}O\text{-}O_2$ and $\delta^{18}O\text{-}H_2O$ values for the Canadian sites. Comparisons are difficult between seasons at one site and still more difficult between sites because of the variability in $\delta^{18}O\text{-}H_2O$ since the $\delta^{18}O\text{-}NO_3^-$ axis is reported relative to the typical standard SMOW.

(b): Nitrate isotope biplot of the same data where the $\delta^{18}O\text{-}NO_3^-$ axis is reported relative to the ambient $\delta^{18}O\text{-}H_2O$ values in the river at the time of sampling, as per recommendation A. Here, data are more clearly expressed relative to the appropriate environmental conditions that recognize that nitrogen is biologically cycled and will be largely imprinted with the ambient $\delta^{18}O\text{-}H_2O$ value. A parsimonious interpretation here is that many data from Kenya and the UK exhibit the range of known contributions of the $\delta^{18}O\text{-}H_2O$ values, i.e. from two-thirds to one. Most Canadian and some Kenyan and UK data approach the theoretical maximum $\delta^{18}O\text{-}NO_3^-$ before a requirement of denitrification must be considered.

References

Barth JAC, Tait A, Bolshaw M (2004) Automated analyses of $^{18}O/^{16}O$ ratios in dissolved oxygen from 12-mL water samples. Limnol Oceanogr Meth 2:35–41, DOI: 10.4319/lom.2004.2.35

Craine JM, Elmore AJ, Wang L, Augusto L, Baisden WT, Brookshire EN, Cramer MD, Hasselquist NJ, Hobbie EA, Kahmen A, Koba K (2015) Convergence of soil nitrogen isotopes across global climate gradients. Scientific Reports 5:8280, DOI: 10.1038/srep08280

Davies CL, Surridge DWJ, Gooddy DC (2014) Phosphate oxygen isotopes within aquatic ecosystems: Global data synthesis and future research priorities. Sci Total Environ 496:563–575, DOI: 10.1016/j.scitotenv.2014.07.057

Heaton THE (1986) Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: A review. Chem Geol 59:87–102, DOI: 10.1016/0168-9622(86)90059-X

Kendall C (1998) Tracing Nitrogen Sources and Cycling in Catchments. In: Kendall C, McDonnell JJ (eds) Elsevier Science, Amsterdam, pp 519–576

Michalski G, Bhattacharya SK, Mase DF (2012) Oxygen isotope dynamics of atmospheric nitrate and its precursor molecules. In: Baskaram M (ed) Handbook of environmental isotope geochemistry, Springer, Berlin Heidelberg, pp 613–635

Paytan A, Kolodny Y, Neori A, Luz B (2002) Rapid biologically mediated oxygen isotope exchange between water and phosphate, Global Biogeochem Cy, 16, DOI: 10.1029/2001GB001430

Snider DM, Spoelstra J, Schiff SL, Venkiteswaran JJ (2010) Stable oxygen isotope ratios of nitrate produced from nitrification: ^{18}O-labelled water incubations of agricultural and temperate forest soils. Environ Sci Technol 44:5358–5364 DOI: 10.1021/es1002567

Venkiteswaran JJ, Schiff SL, Taylor WD (2015) Linking aquatic metabolism, gas exchange, and hypoxia to impacts along the 300-km Grand River, Canada. Freshwat Sci 34:1216-1232, DOI: 10.1086/683241

Vitousek PM, Aber JD, Howarth RW, Likens GE, Matson PA, Schindler DW, Schlesinger WH, Tillman DG (1997) Human alteration of the global nitrogen cycle: sources and consequences. Ecol Appl 7, 737-750, DOI: 10.1890/1051-0761(1997)007[0737:HAOTGN]2.0.CO;2

Wassenaar LI, Koehler G (1999) An On-Line Technique for the Determination of the $\delta^{18}O$ and $\delta^{17}O$ of Gaseous and Dissolved Oxygen. Anal Chem 71:4965–4968, DOI: 10.1021/ac9903961

Wassenaar LI, Venkiteswaran JJ, Schiff SL, Koehler G (2010) Aquatic community metabolism response to municipal effluent inputs in rivers quantified using diel $\delta^{18}O$ values of dissolved oxygen. Can J Fish Aquat Sci 67:1232-1246, DOI: 10.1139/F10-057