Increased nitrate and decreased $\delta^{15}N\text{-}NO_3^-$ in the Greenland Arctic after 1940 attributed to North American oil burning

Nathan J. Chellman
(Desert Research Institute, Division of Hydrologic Sciences, Reno, Nevada)
Correspondence to: Nathan.chellman@dri.edu

Meredith G. Hastings
(Brown University, Department of Earth, Environmental and Planetary Sciences and Institute at Brown for Environment and Society, Providence, Rhode Island)

Joseph R. McConnell
(Desert Research Institute, Division of Hydrologic Sciences, Reno, Nevada)

S1 Methods

Isotopic analysis was conducted at Brown University using the denitrifier method (Casciotti et al., 2002; Hastings et al., 2005; Kaiser et al., 2007; Sigman et al., 2001). The denitrifier method uses denitrifying bacteria that lack nitrous oxide reductase to convert dissolved NO_3^- to N_2O gas, which is then analyzed on a continuous flow isotope ratio mass spectrometer (ThermoFinnigan Delta V) to determine the isotopic composition. The analyte N_2O is passed, with a helium carrier gas, through a series of purification (removal of water, CO_2, and VOCs) and sample collection steps to a mass spectrometer which then measures the $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios of the sample (based on m/z 44, 45, and 46). The majority of samples in this study were run at 5 nmol nitrate, typically requiring 6 ml of sample, to conserve sample volume and allow for replicate measurements. Sample replicates were measured between runs to ensure that data is reproducible. On average, there were three replicates measured out of each run of 15 samples. The sample measurements were referenced against internationally recognized standards (IAEA-N3 and USGS34 for $\delta^{15}N$; IAEA-N3, USGS34, and USGS35 for $\delta^{18}O$) with assigned $\delta^{15}N$ and $\delta^{18}O$ values (Supplementary Table S1). Multiple nitrate standards, with similar concentrations to samples, are run with each set of samples. The sample $\delta^{15}N$ and $\delta^{18}O$ data are both corrected for the blank size (below detection for all runs included in this study) and the $\delta^{18}O$ data are additionally corrected for exchange with water during the denitrification process (assuming an average sample $\delta^{18}O$ of water value of -30‰ vs. VSMOW) (see correction scheme outlined in Kaiser et al., 2007).

The data was also corrected for the contribution of $^{14}N^{14}N^{17}O$ to the mass 45 signal measured on the mass spectrometer (Kaiser et al., 2007). Typically, it is assumed that the $\delta^{17}O$ and $\delta^{18}O$ of a compound will behave mass dependently, such that the $\delta^{17}O$ could be assumed from the $\delta^{18}O$ signal that is determined from the ratio of masses 46 and 44 (i.e. $^{14}N^{14}N^{18}O/^{14}N^{14}N^{16}O$). However, atmospheric nitrate contains an anomalous signature of $\delta^{17}O$ and $\delta^{18}O$, quantified as $\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$ (e.g., Michalski et al., 2003). The $\Delta^{17}O$ of nitrate was quantified for 18 samples distributed throughout the core using a sample size of 25 nmol nitrate. N_2O generated from the denitrifiers is further reduced to N_2

and O_2 in a gold tube heated to 780 C, with the O_2 subsequently measured at masses 32, 33, and 34 to determine $^{17}O/^{16}O$ and $^{18}O/^{16}O$ for the original sample nitrate. Reference materials USGS34 and USGS35 (at similar concentrations to the samples) were used to correct sample data with each run. The average $\Delta^{17}O$ (±1σ) for the 18 samples was 26.2(±2.6)‰, which compares well with the average value of 27.9(±0.9)‰ measured at lower resolution over the time period 1692-1976 C.E. by Alexander et al, 2004. The average value of 26.2‰ was used to correct the $\delta^{15}N$ data (see also Hastings et al., 2005). The average value is appropriate to use as the difference in $\delta^{15}N$ between using the lowest measured $\Delta^{17}O$ (21‰) and highest (31‰) is smaller than the typical reproducibility for replicate measurements (i.e., <0.5 ‰).

	$\delta^{15}N$ (‰ vs. N_2)	**$\delta^{18}O$ (‰ vs. VSMOW)**	**$\Delta^{17}O$ (‰)**
IAEA-N3	4.7	25.6	–
USGS34	-1.8	-27.9	-0.292
USGS35	2.7	57.5	21.6

Table S1- Assigned values for standards used in data correction (Böhlke et al., 2003).

Alexander, B., Savarino, J., Kreutz, K. J., and Thiemens, M. H., Impact of preindustrial biomass-burning emissions on the oxidation pathways of tropospheric sulfur and nitrogen, J. Geophys. Res. Atmos., 109, doi:10.1029/2003JD004218, 2004.

Böhlke, J. K., Mroczkowski, S. J., and Coplen, T. B., Oxygen isotopes in nitrate: new reference materials for O-18 : O-17 : O-16 measurements and observations on nitrate-water equilibration, Rapid Communications in Mass Spectrometry, 17, 1835-1846, 2003.

Casciotti, K. L., Sigman, D. M., Hastings, M. G., Bohlke, J. K., and Hilkert, A., Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method, Anal. Chem., 74, 4905-4912, 2002.

Hastings, M. G., Sigman, D. M., and Steig, E. J., Glacial/interglacial changes in the isotopes of nitrate from the Greenland Ice Sheet Project 2 (GISP2) ice core, Global Biogeochem. Cycles, 19, 2005.

Kaiser, J., Hastings, M. G., Houlton, B. Z., Roeckmann, T., and Sigman, D. M., Triple oxygen isotope analysis of nitrate using the denitrifier method and thermal decomposition of N2O, Anal. Chem., 79, 599-607, 2007.

Sigman, D. M., Casciotti, K. L., Andreani, M., Barford, C., Galanter, M., and Bohlke, J. K., A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater, Anal. Chem., 73, 4145-4153, 2001.