Interpreting isotopic composition of atmospheric nitrogen deposition using a multiple model approach

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Introduction

Isotopic analyses provide information on sources and processes affecting precipitation (Sjostrom & Welker 2009) and nitrogen (N) deposition. Excess N alters ecosystems through eutrophication, acidification, modified biodiversity, and disrupted biogeochemical cycles (Fenn et al. 2011). Over 600 hundred precipitation samples from 9 sites (Fig 1) will be analyzed for precipitation and N isotopic composition to understand patterns of N deposition in the northwestern US. Here, we illustrate how modeling can further inform precipitation samples, their isotopic composition, and refine deposition patterns. Data presented are from 15 National Atmospheric Deposition Program (NADP) samples from the Snowy Range site (WY00) in southern Wyoming. All samples are from the summer of 2000. This poster begins integrating modeling and isotopic approaches to understand N deposition.

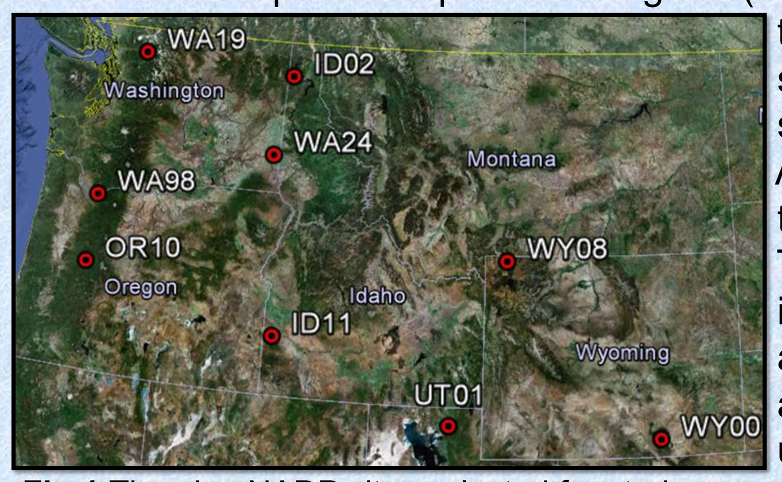


Fig 1 The nine NADP sites selected for study

The Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model tracks air mass movement which can be used to determine source areas of precipitation and N deposition. HYSPLIT uses archived EDAS meteorological data to track from where the precipitation came that produced the samples analyzed (Draxler & Hess 1998). Storm track trajectories were ran for 72 hours prior to when precipitation occurred. Table 1 illustrates different categories (synoptic patterns) of source areas determined with back trajectories. Each color represents a different day during which precipitation occurred.

Isotopic Trends of NADP Precipitation Samples

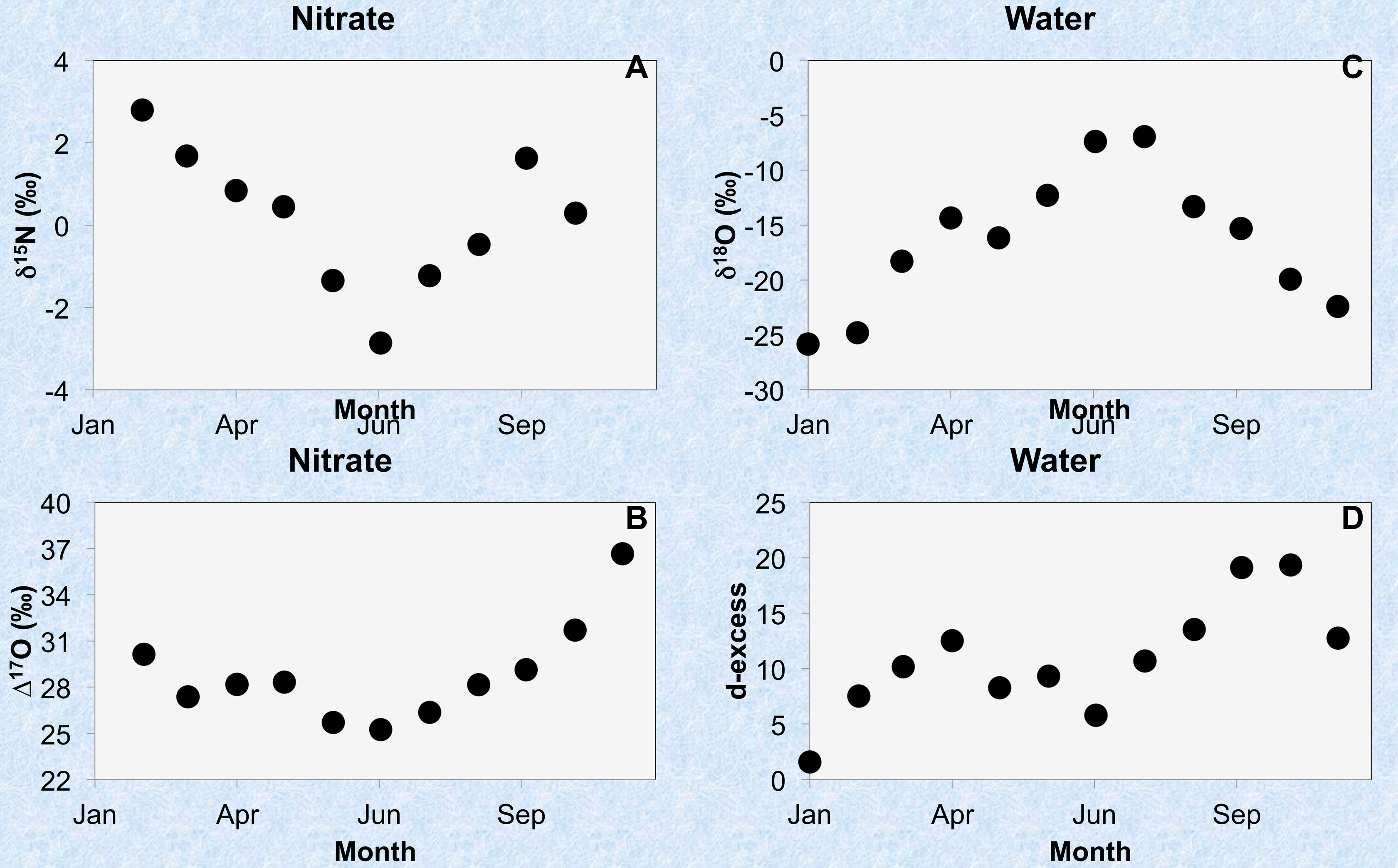
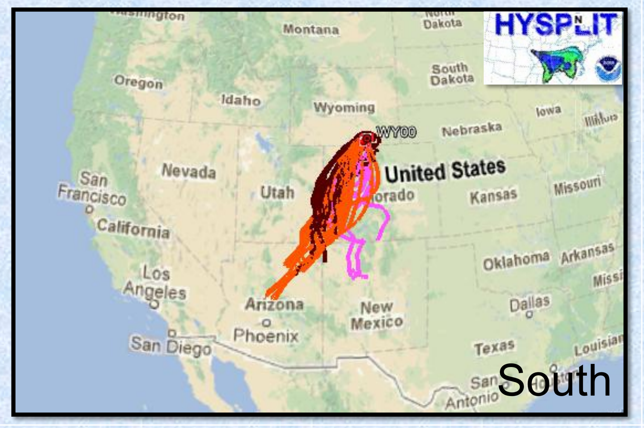
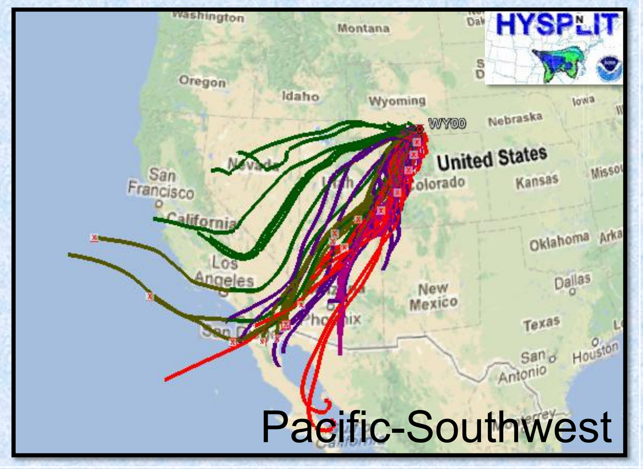
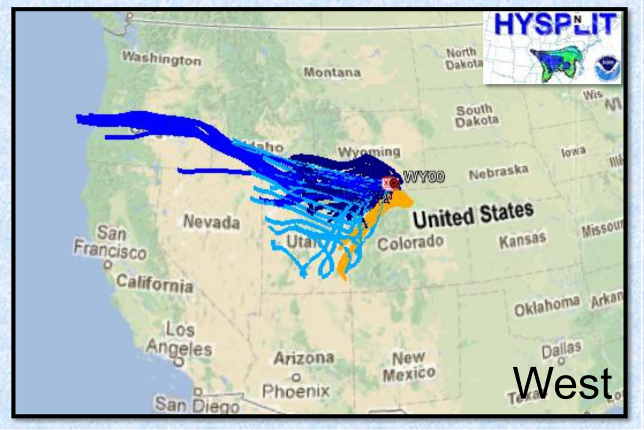
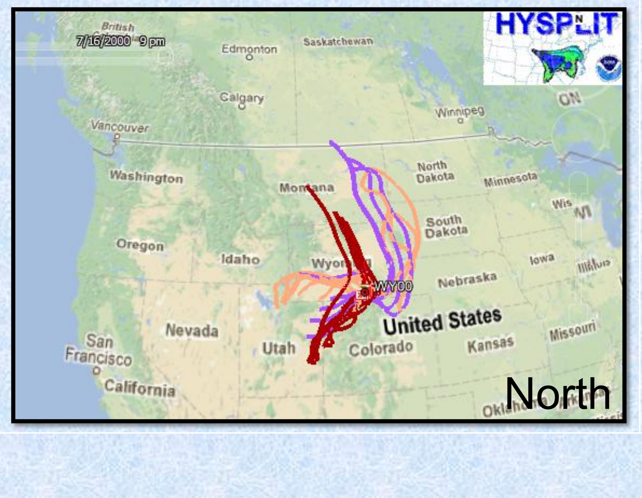


Fig 2 Seasonal trends were observed in isotopic composition of NADP samples. The nitrate $\delta^{15}N$ values decreased in warmer months likely due to increased biogenic N sources (Elliott et al. 2007, Fig 2A). The $\Delta^{17}O$ values decreased in warmer months indicating a greater role of oxidants other than ozone in nitrate formation (Alexander et al. 2009, Fig 2B). The $\delta^{18}O$ values of water increased during warmer months which may indicate an effect of warmer temperatures, changes in evapotranspiration, and/or changes in the origin of precipitation (Araguas-Araguas e al. 2000, Fig 2C). The deuterium-excess (d-excess) values indicated shifts in the area and/or conditions (such as relative humidity) of precipitation's origin (Gat 1996, Araguas-Araguas e al. 2000, Fig 2D). Seasonal trends do not however identify sources which necessitates atmospheric modeling.

Back-trajectory Modeling

Table 1 Synoptic patterns observed in NADP samples from WY00

Synoptic Patterns	n	Concentration: NH_4^+ (mg/L)	Concentration: NO_3^- (mg/L)	Water Isotopes: $\delta^{18}O$	Water Isotopes: d-excess	Nitrate Isotopes: $\delta^{15}N$	Nitrate Isotopes: $\Delta^{17}O$
 South	3	0.21 (±0.05)	1.85 (±0.53)	-6.1 (±0.9)	9.0 (±5.8)	-1.8 (±1.3)	26.3 (±1.0)
 Pacific-Southwest	4	0.07 (±0.06)	0.61 (±0.04)	-14.6 (±4.5)	9.9 (±3.7)	1.5 (±1.4)	26.0 (±1.6)
 West	4	0.64 (±0.58)	3.28 (±3.44)	-7.9 (±7.5)	2.4 (±7.4)	-2.5 (±1.4)	25.8 (1.6)
 Pacific Northwest	1	0.12	0.61	-15.7	12.1	-2.3	26.1
 North	3	0.18 (±0.10)	1.05 (±0.37)	-10.5 (±2.1)	10.4 (±1.9)	-2.7 (±1.1)	25.5 (±0.6)

Chemical-Transport Modeling

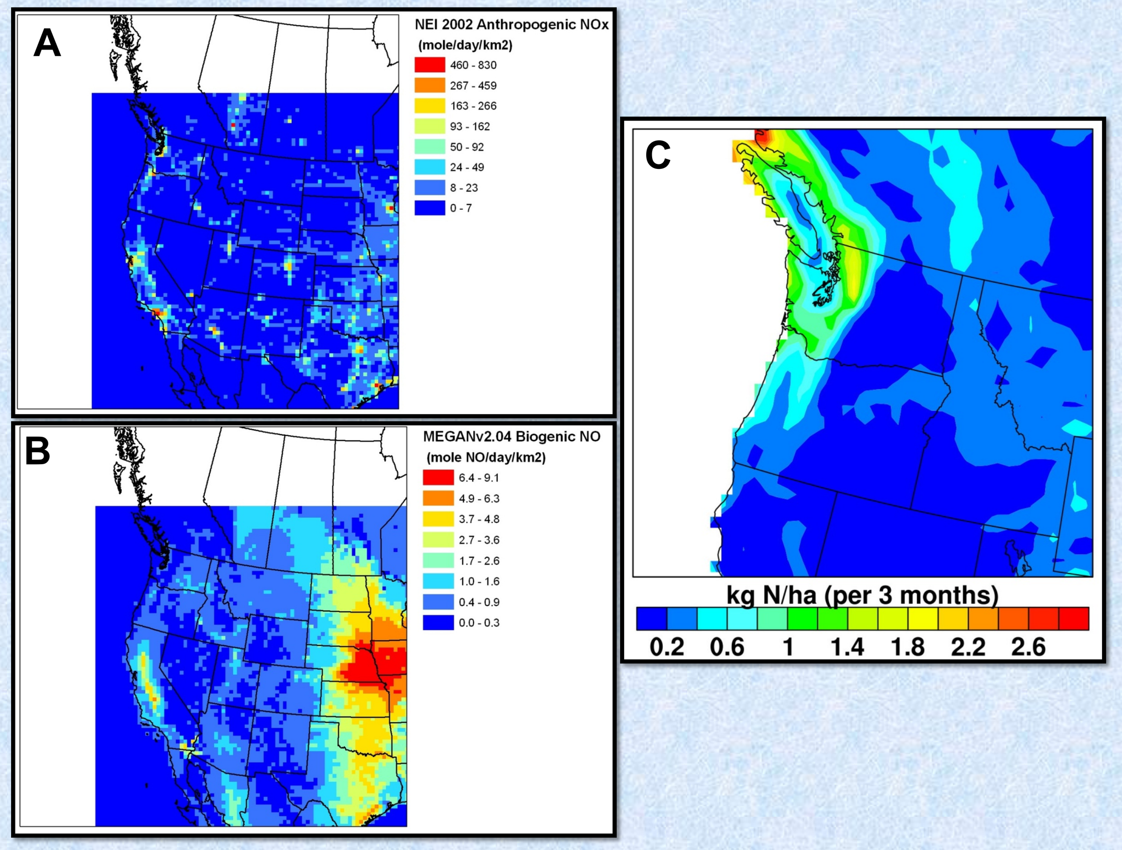


Fig 3 The Community Multi-scale Air Quality model (CMAQ) is a chemical transport model created by the EPA to model air quality (Byun & Schere 2006). Using the anthropogenic emission inventory from the US EPA and MEGAN biogenic emission estimates as input, CMAQ can model atmospheric chemical transformations and transport and predict concentrations of interested compounds in the atmosphere, such as ozone and nitrate, and their deposition rates. Here plots of anthropogenic NO_x emissions (Fig 3A), biogenic NO_x emissions (Fig 3B), and N deposition (Fig 3C) from CMAQ are shown from simulations of summertime conditions. CMAQ runs with different N source categories turned off can determine which sources are important to a site and serve as a comparison to isotopic results.

Back Trajectory Modeling Trends

- Higher concentrations of both N compounds (ammonium and nitrate) occurred in trajectories originating over inland areas (South, West, North).
- Higher nitrate $\delta^{15}N$ values coincided with trajectories from areas predominantly south of the site (South, Pacific Southwest).
- Lower water $\delta^{18}O$ values were observed in trajectories originating over the Pacific (Pacific Southwest, Pacific Northwest)
- West trajectories have much greater variability than any other type of trajectory
- No noticeable trends were observed in $\Delta^{17}O$ of nitrate or d-excess in this summer season dataset. These two isotopic measurements may be more relevant for trends between seasons instead of within seasons.

Future Directions

We will employ two additional modeling strategies to further decipher patterns in N deposition in the northwestern US: CMAQ-Adjoint and synoptic classification. The CMAQ Adjoint model allows for sensitivity analysis of a receptor location, such as one of our NADP sites, which allows more quantitative modeling of what sources and areas contributed to deposition (Hakami et al. 2007). Adjoint modeling is expected to corroborate HYSPLIT and CMAQ information.

Synoptic weather classification will provide a way to categorize the mean state of the atmosphere for each sample (Sheridan 2002). This includes the mean air flows which determine where precipitation and N travel from their area of origin. We will classify the atmospheric conditions for the NADP samples into synoptic patterns in order to discern N deposition patterns that can be applied beyond our sample time period.

References

Alexander, B, MG Hastings, DJ Allman, J Dachs, JA Thornton, SA Kunasek (2009). Quantifying atmospheric nitrate formation pathways based on a global model of the oxygen isotopic compsotion ($\Delta^{17}O$) of atmospheric nitrate. Atmospheric Chemistry and Physics Discussions, 9, 11185-11220.

Araguas-Araguas, L, K Froehlich, K Rozanski (2000). Deuterium and oxygen-18 isotope composition of precipitation and atmospheric moisture. Hydrological Processes, 14, 1341-1355.

Byun, D, KL Schere (2006). Review of the governing equations, computational algorithms, and other compoenents of the Models-3 Community Multiscale Air Quality (CMAQ) modeling system. Applied Mechanics Reviews, 59, 51-77.

Draxler, RR, GD Hess (1998). An overview of HYSPLIT_4 modelling system for trajectories, dispersion and deposition. Australian Meteorological Magazine, 47, 295-308.

Elliott, EM, C Kendall, SD Wankel, DA Burns, EW Boyer, K Harlin, DJ Bain, TJ Butler (2007). Nitrogen isotopes as indicators of NO_x source contributions to atmospheric nitrate deposition across the Midwestern and Northeastern United States. Environmental Science & Technology, 41, 7661-7667.

Fenn, ME, KF Lambert, TF Blett, DA Burns, LH Pardo, GM Lovett, RA Haeuber, DC Evers, CT Driscoll, DS Jeffries (2011). Setting limits: using air pollution thresholds to protect and restore U.S. ecosystems. Issues in Ecology, Report Number 14.

Gat, JR (1996). Oxygen and hydrogen isotopes in the hydrologic cycle. Annual Review of Earth and Planetary Sciences, 24, 225-262.

Hakami, A, DK Henze, JH Seinfeld, K Singh, A Sandu, S Kim, D Byun, Q Li (2007). The adjoint of CMAQ. Environmental Science & Technology, 41, 7807-7817.

Scheridan, SC (2002). The redevelopment of a weather-type classification scheme for North America. International Journal of Climatology, 22, 51-88.

Sjostrom, DJ, JM Welker (2009). The influence of air mass source on the seasonal isotopic composition of precipitation, eastern USA. Journal of Geochemical Exploration, 102, 103-112

Welker, JM (2012). ENSO effects on $\delta^{18}O$, $\delta^{2}H$ and d-excess values in precipitation across the U.S. using a high-density, long-term network (USNIP). Rapid Communications in Mass Spectrometry, 26, 1893-1898.

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