

Report for 2002MD12B: Investigation of Isotopic Methods for Identifying Atmospheric Deposition of Nitrate to the Chesapeake Bay Watershed

There are no reported publications resulting from this project.

Report Follows

Investigation of Isotopic Methods for Identifying Atmospheric Deposition of Nitrate to the Chesapeake Bay Watershed.

Research Objectives:

We have been developing methods to analyze $\Delta^{17}\text{O}$ of nitrate and are assessing whether these methods can be used to place limits on the amounts of nitrate that are derived from non-point atmospheric sources. The work builds upon that of G. Michalski and coworkers (2002) who have shown that a unique isotopic signature is present in atmospheric nitrate that is derived from NO_x - Ozone chemistry. This signature has the potential to be used as a tracer of atmospheric nitrate and also to place constraints on the magnitude of this source in a watershed. Our work has three goals: (1) to establish the capabilities for analyzing $\Delta^{17}\text{O}$ in nitrate at the University of Maryland, (2) to test whether this approach can be used to place constraints on the contribution of non-point atmospheric sources, and (3) to apply these methods to studies of the Chesapeake Bay Watershed. This work is the Ph.D. research of Katherine Cooney.

The research conducted to date has focused on developing and testing the techniques that will be required to measure the $\Delta^{17}\text{O}$ of nitrate in precipitation that falls to the Chesapeake Bay Watershed. The project has been divided into three parts: (1) sample collection, (2) nitrate extraction, and (3) isotopic analysis of extracted nitrate.

Sample Collection:

Precipitation samples are collected in HDPE bins that have been rinsed with 10% hydrochloric acid followed by numerous rinses of Millipore water. Due to relatively low concentrations of nitrate in precipitation, a minimum of 12-18 liters of rainwater or melted snow are needed in order to recover an adequate amount of nitrate for analysis. Collection bins are placed outside immediately before and collected at the end of rain events. Bins are also placed outside to catch falling snow, and at the end of the storm more snow is scooped into the bins using clean HDPE lids. Snow samples have also been collected in regular intervals following snow events. These snow samples have been collected in a time series so we could look for changes in concentrations and isotopic compositions in the snow packs. Whenever possible, the precipitation samples have been immediately frozen and kept in a frozen state until they are thawed and filtered prior to nitrate extraction.

Thus far, precipitation samples have been collected from five locations within the Chesapeake Bay Watershed, including College Park, Kensington, Laurel, Tacoma Park, and Urbana, MD. These samples will be used to collect a preliminary data set. Further sampling strategies will be devised after we evaluate this groundwork data.

Nitrate Extraction:

We carefully considered the techniques discussed in Silva et al. (2000) and Chang et al. (1999), and we consulted with Janet Hannon about the methods being used to extract nitrate at the USGS in Reston, Virginia. The preparation scheme detailed below utilizes aspects of all of these procedures. R. Carmody has processed test samples that are being used to verify various steps to

the method. K. Cooney is in the process of applying the technique to the natural precipitation samples.

Approximately 15 L of each natural precipitation sample is filtered through 0.4 μm polycarbonate membrane filters and poured or pumped into a clean container. Approximately 20mL of the each sample is syringe filtered through a 0.2 μm polycarbonate filter into acid soaked and Millipore water rinsed glass bottles with polyseal caps. This portion of the sample is used for ion chromatography.

The sample gravity drips through a series of two columns. The first is a cation exchange column loaded with AG50WX8 resin, in hydrogen form. This column is intended to protonate the DOC in the sample. The second column contains anion exchange resin (AG2X8 resin, in chloride form) onto which nitrate and other anions from the sample are collected. In order to determine the amount of anion exchange resin needed to accommodate the anions in the precipitation samples, concentration data on chloride, sulfate, and nitrate are obtained using ion chromatography. We are very thankful to Dr. Allen Davis for his willingness to let us use the Dionex DX100 Ion Chromatograph, housed in the Civil and Environmental Engineering Environmental Lab, and to Hunho Kim for training us to operate the instrument.

Once the nitrate is absorbed onto the anion exchange resin, nitrate and other ions are eluted from the column using a 0.25M KCl solution. We are able to track the elution of the nitrate peak using nitrate reducing solution and nitrite coloring solution. We learned to make and use these solutions from Janet Hannon at USGS. The nitrate is eluted using 5- or 10-mL aliquots of 0.25M KCL, and each "cut" is collected in a separate, clean test tube. Only the "cuts" containing nitrate are saved for continued processing. Other anions (e.g. sulfate), are removed by adding BaCl_2 to the solution. The precipitate (e.g. BaSO_4) is then separated from the KCl/ KNO_3 solution by filtering and the precipitate is saved and dried.

The next step is to eliminate the chloride from the KCl/ KNO_3 solution. This is accomplished by combining the nitrate-bearing eluant with AG MP-50 cation exchange resin in silver form. Potassium exchanges for silver on the resin's exchange sites, and the silver introduced to solution allows chloride to precipitate as $\text{AgCl}_{(s)}$. After stirring this mixture for one hour, and then allowing it to stand overnight, the resin and $\text{AgCl}_{(s)}$ is separated from the chloride-free solution by pouring the mixture into a large column. The solution is allowed to drain out into a clean graduated cylinder. After the resin and precipitate in the column have been rinsed and the rinse-water has been checked with the colorimetric test solutions to confirm that it is nitrate-free, the solution goes through a final clean-up column to insure that a pure precipitate will form when the sample solution is freeze-dried prior to isotopic analysis. At this stage, one must decide whether the final solid form of the sample should be AgNO_3 or KNO_3 . If AgNO_3 is desired, the solution is run through a 5-mL AG MP-50 resin (in silver form) column. If KNO_3 is desired, the sample solution is run through a 5-mL AG50WX8 resin (in potassium form) column. At this point the solutions are ready to be freeze-dried.

We are still working to establish freeze-drying techniques. Six freeze-dryer experiments have been undertaken. The most successful freeze-dryer experiments have involved two steps. First, 100mL of nitrate solution ($\text{KNO}_{3(aq)}$ or $\text{AgNO}_{3(aq)}$) was distributed among five 50-mL plastic

centrifuge tubes so that each tube contained approximately 20mL of solution. These tubes were placed in the freezer at an angle to produce greater surface area on the ice. After freezing, the caps on the tubes were removed. Each of the tubes was then covered with a Kimwipe secured with a rubber band. Then, the tubes with frozen nitrate solution were placed in a 900-mL freeze-dryer flask and freeze-dried. The second freeze-drying stage involved transferring the KNO_3 or AgNO_3 from the plastic centrifuge tubes to a pre-weighed glass vial by pipetting a few milliliters of Millipore water into each tube to dissolve the nitrate, and then pipetting this solution into the glass vial. This vial containing more concentrated nitrate solution was then frozen, placed in the freeze-dryer flask, and freeze-dried.

Preliminary tests using the continuous flow isotope ratio mass spectrometer (CF-IRMS) and elemental analyzer overseen by Jay Kaufman show that the measured $\delta^{18}\text{O}$ of the freeze-dried KNO_3 is within error of the $\delta^{18}\text{O}$ of the reagent KNO_3 that had been dissolved and freeze-dried.

Nitrate Pyrolysis and Isotopic Analyses:

The final step in our analytical protocol is the conversion of nitrate to molecular oxygen for isotopic analysis. Potassium nitrate and silver nitrate are converted to molecular oxygen for isotopic analysis using methods that are modified from techniques used at the University of California, San Diego. The manifold that we use for the vacuum pyrolysis of silver and potassium nitrate is described in Figure 1. This system consists of a Platinum resistance furnace in a vacuum chamber that is heated by a 10 volt 15 amp DC current. KNO_3 and AgNO_3 decompose to O_2 and NO_2 when heated in vacuum. The O_2 is purified by condensing the NO_2 in a liquid nitrogen-cooled trap. O_2 is then separated from the frozen NO_2 by freezing it onto a molecular sieve substrate that is kept at liquid nitrogen temperature. The purified O_2 is then introduced to a gas-source mass spectrometer for isotopic analysis.

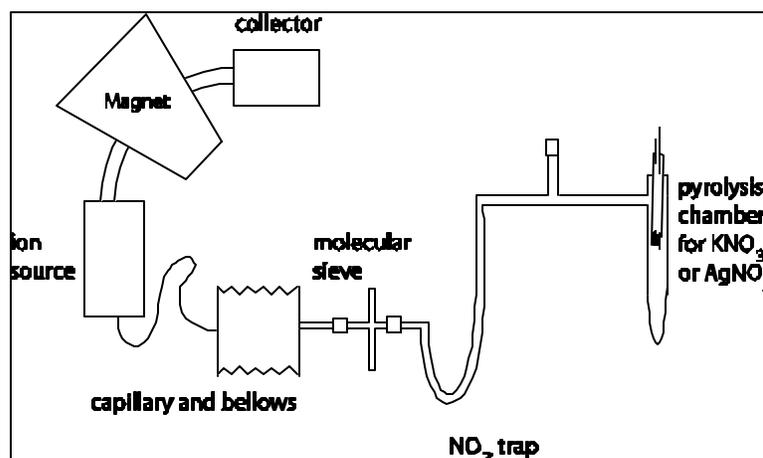


Figure 1. Schematic diagram of nitrate pyrolysis manifold and mass spectrometer. Nitrate samples are wrapped in silver foil and placed in the pyrolysis chamber which is evacuated overnight. The sample is heated using a platinum resistance furnace to generate NO_2 and O_2 . O_2 is purified by condensing NO_2 in a liquid nitrogen-cooled trap and then by transferring the O_2 onto a liquid nitrogen-cooled molecular sieve trap. This purified O_2 is then introduced to the Delta plus gas-source mass spectrometer for determination of its oxygen isotopic composition. The gas is introduced through the capillary to the ion source where it is ionized and accelerated by a voltage potential. The ion beams are separated according to mass by the magnet and the intensities of the ion beams are measured by an array of Faraday collectors. The isotopic abundances of the gas are measured by isotope ratio measurement relative to a standard.

Figure 2 presents the results of our $\Delta^{17}\text{O}$ analyses of nitrate standard materials that have been previously analyzed at UCSD by Greg Michalski and coworkers (2002). We have good agreement between our methods and theirs and have better reproducibility for $\Delta^{17}\text{O}$ than reported by Michalski et al. (2002) which we attribute to the design of our pyrolysis cell which is internally heated.

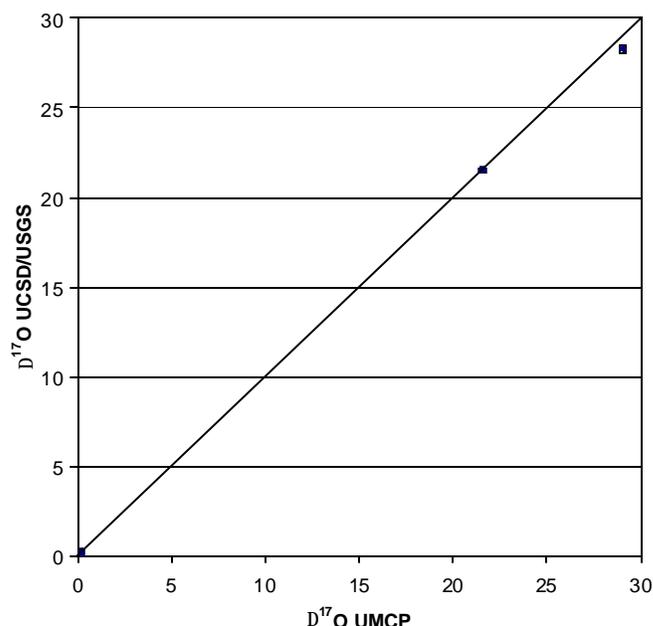


Figure 2 illustrates the $\Delta^{17}\text{O}$ values that we have measured for thermal decomposition of two nitrate standards that are reported in Michalski et al (2002) and one nitrate sample that Michalski sent to us. The standards fall within error of a slope 1 line indicating a good correspondence between labs. The third sample yielded higher $\Delta^{17}\text{O}$ at UMCP that is outside of analytical uncertainty and thought to reflect a blank contribution in the UCSD/USGS data that is not present in the UMCP preparation procedure.

Planned work:

In the next year, we will (1) verify the nitrate extraction procedures by analyzing the resulting KNO_3 or AgNO_3 from the test experiments on the CF-IRMS. From the isotopic measurements of these test experiments, we will be able to identify any fractionation that is occurring in the nitrate extraction process and any blank contribution. We will (2) continue to evaluate our techniques for measuring $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ on the CF-IRMS and $\Delta^{17}\text{O}$ using the dual-inlet isotope ratio mass spectrometer. In addition, we will (3) continue to collect precipitation samples using more guided sampling strategies and (4) proceed to apply nitrate extraction and analysis procedures to the collected precipitation samples. We can then (5) further assess how to apply these isotopic tools to studies on the atmospheric deposition of nitrate to the Chesapeake Bay Watershed.

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