The isotopic composition of precipitation nitrate reflects the processes involved in its formation. Silver nitrates prepared from Maryland precipitation were thermally decomposed to gases for mass spectrometric analyses. Nitrate $\delta^{15}$N ranged from $-5.1 \pm 0.5\%$ to $+5.9 \pm 0.5\%$ ($1\sigma$), $\delta^{18}$O ranged from $+42.6 \pm 0.5\%$ to $+81.9 \pm 0.5\%$, and $\Delta^{17}$O ranged from $+15.33 \pm 0.05\%$ to $+31.71 \pm 0.05\%$. Precipitation samples were re-analyzed for $\delta^{15}$N and $\delta^{18}$O using a method in which bacteria convert nitrate to N$_2$O for analyses, and $\delta^{15}$N ranged from $-3.6 \pm 0.2\%$ to $+7.1 \pm 0.2\%$ and $\delta^{18}$O ranged from $+61.6 \pm 0.3\%$ to $+86.8 \pm 0.3\%$. Differences between the methods were attributed to organic contaminants in the silver nitrates. Nitrate $\delta^{15}$N, $\delta^{18}$O, and $\Delta^{17}$O were highest in the winter and lowest in the summer. Ion concentrations, storm track data, and the $\delta^{34}$S of precipitation sulfate were used for interpretations. Most likely, $\delta^{15}$N varied due to seasonal changes in the NO$_x$ photo-stationary state, and $\delta^{18}$O and $\Delta^{17}$O varied due to changes in oxidation chemistry.
A STABLE ISOTOPE INVESTIGATION OF PRECIPITATION NITRATE

By

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1. Introduction

1.1. Atmospheric nitrate

Gas-phase nitric oxide, NO, and nitrogen dioxide, NO$_2$, referred to as NO$_x$, play a major role in atmospheric chemistry and are smog-forming air pollutants. Globally, NO$_x$ abundances range from a few parts per trillion in remote areas to greater than 100 parts per billion in urban areas (EHHALT et al., 2001). While there are constant emissions of NO$_x$ from automobiles, coal-fired power plants, soils, and lightning channels, NO$_x$ undergoes chemical transformations to nitric acid (HNO$_3$) or nitrate (NO$_3^-$) on the order of a day. Within a week, atmospheric nitrate is delivered to the Earth’s surface via dry or wet deposition.

The approximately five-fold increase in NO$_x$ emissions since pre-Industrial times translates to larger quantities of atmospheric nitrate (JAWORSKI et al., 1997; PROSPERO et al., 1996) and represents a major perturbation to nitrogen cycling in the atmosphere and biosphere (VITOUSEK et al., 1997). Nitric acid is a significant component of acid rain (GALLOWAY and LIKENS, 1981) and contributes to increased acidity in surface waters (e.g., MURDOCH and STODDARD, 1992). The deposition of atmospheric NO$_3^-$ also has an effect on soil processes and plant biodiversity (e.g., GOULDING et al., 1998). In addition, since nitrogen is frequently the limiting nutrient in surface waters of estuarine and coastal environments (RYTHER and DUNSTAN, 1971), atmospheric NO$_3^-$ affects the productivity of these ecosystems (e.g., PAERL, 1985) and contributes to eutrophication and algal blooms (JAWORSKI et al., 1997; VITOUSEK et al., 1997 and references therein). Furthermore, atmospheric NO$_3^-$...
contaminates drinking water, and the consumption of water with elevated NO$_3^-$ concentrations may have negative effects on human health, such as links to infant methemoglobinemia, or “blue baby” disease, and gastric cancer (BRUNINGFANN and KANEENE, 1993).

Properly managing NO$_3^-$ loading to land and water requires constraints on atmospheric deposition relative to other NO$_3^-$ delivery pathways, such as applications of fertilizers or manure, effluent from waste-water treatment plants, and microbial production via nitrification. If atmospheric deposition delivers an appreciable portion of the total NO$_3^-$, then other relevant concerns become how and where the precursor NO$_x$ originated.

1.2. Stable isotopes

Stable isotopes provide a tool to distinguish atmospheric nitrate from nitrate formed by non-atmospheric processes. Isotopes are atoms of an element that have the same number of protons, or atomic number, but different sums of protons and neutrons, or mass numbers. There are two stable nitrogen isotopes, $^{14}$N and $^{15}$N, and three stable oxygen isotopes, $^{16}$O, $^{17}$O, and $^{18}$O. Whereas unstable isotopes undergo radioactive decay, stable isotopes maintain their numbers of protons and neutrons over time. In a neutral atom, the number of protons determines the number of electrons. The number and distribution of electrons in an atom’s orbitals largely determines its chemical properties, and therefore isotopes exhibit similar behavior and occupy the same place on the periodic table. Even so, there are subtle variations in the properties of isotopes that lead to compounds having slightly different isotopic
compositions. Natural variations in N and O isotope ratios are typically smaller than a few percent and are reported in delta (δ) notation with units of parts per thousand, or per mil (‰).

\[ \delta = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000 \text{‰} \]

By convention, R is the ratio of a less abundant isotope over the most abundant isotope. Atmospheric N\textsubscript{2} has a constant $^{15}$N/$^{14}$N of 1/272 (Copley et al., 1992; Junk and Svec, 1958; Mariotti, 1983). Nitrogen isotope ratios are typically expressed in δ notation as the ‰ difference from the atmospheric N\textsubscript{2} reference, AIR.

\[ \delta^{15}N = \left( \frac{^{15}N/^{14}N_{\text{sample}}}{^{15}N/^{14}N_{\text{AIR}}} - 1 \right) \times 1000 \text{‰} \]

Nitrate oxygen isotope ratios are typically reported relative to Vienna Standard Mean Ocean Water, VSMOW, which has an absolutely calibrated $^{18}$O/$^{16}$O of 0.0020052 ± 0.00000045 (Baertschi, 1976) and $^{17}$O/$^{16}$O of 0.0003799 ± 0.0000008 (Li et al., 1988).

\[ \delta^{18}O = \left( \frac{^{18}O/^{16}O_{\text{sample}}}{^{18}O/^{16}O_{\text{VSMOW}}} - 1 \right) \times 1000 \text{‰} \]

\[ \delta^{17}O = \left( \frac{^{17}O/^{16}O_{\text{sample}}}{^{17}O/^{16}O_{\text{VSMOW}}} - 1 \right) \times 1000 \text{‰} \]

Plotting δ$^{18}$O versus δ$^{17}$O for most terrestrial compounds forms an array, often referred to as the mass-dependent fractionation line, which is shown in Figure 1. The theoretical basis for the mass-dependent fractionation line is presented in section 2.2. The oxygen isotope compositions of several atmospheric compounds plot off the mass-dependent fractionation line. The parameter, Δ$^{17}$O, shown graphically in Figure 1, is the difference between a measured δ$^{17}$O value and the δ$^{17}$O value predicted on
the basis of the mass-dependent fractionation line. Whereas most terrestrial compounds have $\Delta^{17}O$ values close to zero, several atmospheric compounds have non-zero $\Delta^{17}O$ values. Of the atmospheric compounds that have been measured, ozone, $O_3$, exhibits the largest $\Delta^{17}O$ values.

**Figure 1:** Non-mass dependent isotope effects observed in atmospheric trace compounds as published by Brenninkmeijer and coworkers (2003). Tropospheric refers to compounds collected within the lowest 10-15km of the atmosphere while stratospheric refers to compounds collected from the top of the troposphere to 50km above ground level.

Ozone in the troposphere, the lowest 10-15km of the atmosphere, takes part in a number of atmospheric chemical reactions involving nitrogen oxides (see section 2.1). Michalski and coworkers (2003) showed that during these processes non-mass dependent oxygen atoms can be transferred from ozone to nitrogen oxides, resulting in atmospheric nitrate with $\Delta^{17}O$ values as high as $30\%$ (Figure 2). The other oxidants involved in NO$_x$ oxidation have $\Delta^{17}O$ values significantly closer to zero.
Since ozone plays a greater role in NO\textsubscript{x} oxidation in the winter than in the summer, the $\Delta^{17}$O of atmospheric nitrate is higher in the winter and lower in the summer. The seasonal variation of the $\Delta^{17}$O of atmospheric nitrate was reproduced successfully by Michalski and others (2003) using an isotopic model coupled to a photochemical box model (Figure 2).

![Figure 2: Measurements (open squares) and model predictions (circles) for aerosol nitrate in La Jolla, CA as published by Michalski and colleagues (2003). Described simply, their model showed that lower $\Delta^{17}$O values in the summer and higher $\Delta^{17}$O values in the winter were the result of seasonal changes in the role of ozone on NO\textsubscript{x} oxidation.](image)

### 1.3. Research Overview

Atmospheric deposition provides a pathway of delivering non-mass dependent nitrate to the Earth’s surface. Measuring the $\Delta^{17}$O of NO\textsubscript{3}\textsuperscript{-} in surface waters may allow us to address the significance of NO\textsubscript{3}\textsuperscript{-} deposited from the atmosphere (non-zero $\Delta^{17}$O) relative to other NO\textsubscript{3}\textsuperscript{-} delivery pathways ($\Delta^{17}$O close to zero). However, in order to use $\Delta^{17}$O as a tool in watershed studies, it is necessary to be able to analyze nitrate isotopes accurately and precisely and to understand potential variations in atmospheric nitrate isotope ratios.
One technique commonly used to analyze nitrate stable isotopes involves the thermal decomposition of prepared silver nitrates. There are numerous challenges associated with the isolation and purification of nitrate salts. Since NO$_3^-$ is a universal solute, nitrate salts cannot be precipitated from solution. Instead, all non-nitrate compounds must be removed from solution, without removing any nitrate in the process, and then solutions are freeze-dried to produce nitrate salts. One of the most challenging aspects is removing organic contaminants. While activated carbon and various resins can be used to extract organic compounds from solution, these treatments can also adsorb NO$_3^-$\textsuperscript{-}. In addition to the possibility of isotope fractionation associated with adsorption, losing significant quantities of nitrate during the wet chemical procedure is not favorable for samples with relatively low NO$_3^-$ concentrations, such as precipitation.

One of our first research objectives was to set up techniques at the University of Maryland to produce contaminant-free nitrate salts that preserved the isotope ratios of precipitation NO$_3^-$\textsuperscript{-}. We established a set of techniques at the University of Maryland based on published methods (Chang et al., 1999; Silva et al., 2000) and the techniques used by researchers at the US Geological Survey in Reston (J. Hannon, personal communication). Silver nitrates prepared from precipitation samples were analyzed for $\Delta^{17}$O using thermal decomposition techniques set up at the University of Maryland and for $\delta^{15}$N and $\delta^{18}$O in the laboratory of M. Fogel at the Carnegie Institution of Washington. Despite our efforts to minimize organic contaminants, there was evidence that the prepared silver nitrates were impure. Before we could
interpret the results, we needed to examine the effects of organic contamination on measured isotope ratios.

We were offered the opportunity to re-analyze our samples using an innovative technique developed at Princeton University that avoids issues of organic contamination. Instead of preparing salts that can be decomposed to produce gases, the new approach uses denitrifying bacteria to convert NO$_3^-$ directly to N$_2$O for mass spectrometric analyses. We analyzed nitrate isotopes using both the AgNO$_3$/decomposition and denitrifier methods. A comparison of the two methods is a major outcome of this research.

Our study of atmospheric nitrate focused on a set of precipitation samples collected in Frederick, Maryland. Reasons for selecting Frederick as the site for sample collection are included in section 4.1. Since precipitation nitrate only represents a portion of the total atmospheric nitrate, we had to consider the effects of in-and-below cloud scavenging processes on nitrate isotope ratios. Other potential influences on the isotopic signature of precipitation NO$_3^-$ include the isotopic composition of precursor NO$_x$, physical-chemical mechanisms that influence the partitioning of isotopes between atmospheric compounds, and NO$_x$ oxidation pathways. In addition to analyzing $\delta^{15}$N, $\delta^{18}$O, and $\Delta^{17}$O of NO$_3^-$ and considering the relationships between these parameters, we also collected meteorological data, determined the source regions of air masses, measured the major ion concentrations, and analyzed the $\delta^{34}$S of precipitation sulfate. Evaluating isotope ratios in the context of these other parameters allowed us to determine the major influences on the isotope ratios of precipitation nitrate.
2. Background

2.1. Tropospheric NO\textsubscript{x} Budget

Although long-range transport of NO\textsubscript{x} is limited by its short chemical lifetime, the regions that generate NO\textsubscript{x} are not necessarily the regions where NO\textsubscript{3}\textsuperscript{−} deposition occurs (e.g., Vitousek et al., 1997). Similar to the way upstream activities affect downstream water quality, emissions of NO\textsubscript{x} from certain regions can lead to the deposition of atmospheric NO\textsubscript{3}\textsuperscript{−} and environmental consequences in distant areas. Thus, investigations of atmospheric NO\textsubscript{3}\textsuperscript{−} require knowledge of the processes that generate, transform, transport, and remove reactive nitrogen compounds.

2.1.1. NO\textsubscript{x} Formation Processes

There are numerous processes by which NO\textsubscript{x} enters the troposphere, the lower 10-15 km of the atmosphere where most weather occurs. The Intergovernmental Panel on Climate Change (IPCC) reported that the major processes that contribute to the global NO\textsubscript{x} budget, in order of decreasing significance, are fossil-fuel combustion, biomass burning, microbial production in uncultivated and cultivated soils, lightning, emission from aircraft, transport from the stratosphere, which begins above the troposphere and continues to around 50 km above ground level, and atmospheric NH\textsubscript{3} oxidation (Ehhalt et al., 2001). The IPCC lists aircraft separately because, at 8 to 12 km above ground level, aircraft emit NO\textsubscript{x} directly to the free troposphere, where NO\textsubscript{x} has a disproportionately large effect on greenhouse gas concentrations (Ehhalt et al., 2001). For the purposes of this discussion, aircraft emissions are considered part of
fossil fuel combustion processes. Fuel combustion sources of NO\textsubscript{x} in the United States are estimated to be 40-45% from transportation, 30-35% from power plants, and approximately 20% from industrial sources (SEINFELD and PANDIS, 1998). The relative contributions of NO\textsubscript{x} from these processes vary regionally and seasonally (KASIBHATLA et al., 1993; LEVY et al., 1999; PENNER et al., 1991). Figure 3 illustrates the major processes that introduce NO\textsubscript{x} to the troposphere.

Figure 3: Illustration of the major NO\textsubscript{x} formation processes. Fossil fuel combustion by coal-fired power plants, industries, and automobiles, microbial production during nitrification and denitrification in cultivated and uncultivated soils, lightning, and biomass burning account for the majority of NO\textsubscript{x} entering the troposphere.

In the formation of NO\textsubscript{x} at high-temperatures, N is derived from atmospheric N\textsubscript{2} (thermal NO\textsubscript{x}) or organic N (fuel NO\textsubscript{x}). Processes that produce thermal NO\textsubscript{x}
include lightning discharges and high-temperature industrial processes. Automobile engines also produce mostly thermal NO\textsubscript{x} due to low concentrations of organic N in petrol (typically negligible) and high engine temperatures (>2000\textdegree C). The production of thermal NO\textsubscript{x} can be explained by the Zel’dovich mechanism (ZEL'DOVICH et al., 1947). Molecular oxygen thermally decomposes to form ground state atomic oxygen, O(\textsuperscript{3}P), by

\[ \text{O}_2 + \text{heat} \rightarrow 2\text{O(}^{3}\text{P)}. \]  

Atmospheric nitrogen reacts with atomic oxygen to produce NO and atomic nitrogen by

\[ \text{N}_2 + \text{O(}^{3}\text{P}) \rightarrow \text{NO} + \text{N}, \]  

and then molecular oxygen reacts with atomic nitrogen to produce NO and atomic oxygen by

\[ \text{O}_2 + \text{N} \rightarrow \text{NO} + \text{O(}^{3}\text{P)}. \]  

Under certain conditions and to a lesser extent, a third reaction contributes to NO formation by

\[ \text{N} + \text{OH} \rightarrow \text{NO} + \text{H}. \]  

At high temperatures, N\textsubscript{2} and NO exist in chemical equilibrium. The most common reaction of NO back to N\textsubscript{2} is

\[ \text{NO} + \text{N} \rightarrow \text{N}_2 + \text{O(}^{3}\text{P)}. \]  

The equilibrium concentration of NO decreases as the temperature decreases. If N\textsubscript{2} and NO remain in equilibrium at low temperatures, then the amount of NO produced would be minor. However, the amount of time required to achieve chemical equilibrium increases as the gas cools. When the rate of the gas cooling is
approximately equal to the rate of gas approaching chemical equilibrium, the concentration of NO “freezes out.”

Coal-fired power plants typically generate fuel NO$_x$. Combustion in coal-fired power stations generally occurs at temperatures too low to generate sufficient amounts of thermal NO$_x$ (1300-1400°C), but there are significant quantities of nitrogen in coal (1.0 to 1.2% N). Fuel NO$_x$ is produced by a number of reactions involving the conversion of organic N to reactive N (e.g., N, NH, HCN) and subsequent oxidation by an oxygen-containing radical (e.g., OH) to form NO. Since temperatures of biomass burning and forest fires are generally too low to produce thermal NO$_x$, the N is likely derived from organic material and can therefore be classified as fuel NO$_x$.

Bacteria produce microbial NO$_x$ during nitrification (conversion of NH$_4^+$ to NO$_2^-$ followed by the oxidation of NO$_2^-$ to NO$_3^-$) and denitrification (reduction of NO$_3^-$ to NO$_2^-$ followed by the conversion of NO$_2^-$ to N$_2$ and trace amounts of N$_2$O and NO$_x$). Atmospheric NH$_3$ oxidation can also generate small quantities of NO$_x$ (Kohlmann and Poppe, 1999). Ammonia enters the atmosphere by a number of processes, including the decomposition of animal waste, emissions from fertilized and unfertilized soils, industrial emissions (especially biomass burning), and natural emissions from vegetation and oceans (e.g., Dentener and Crutzen, 1994). Within several hours, NH$_3$ undergoes heterogeneous reactions to produce aerosols. While the predominant reaction is between NH$_3$ and sulfuric acid (H$_2$SO$_4$) to produce NH$_4$HSO$_4$ and (NH$_4$)$_2$SO$_4$, NH$_3$ also reacts with nitric acid (HNO$_3$) to produce NH$_4$NO$_3$ (e.g., Stelson and Seinfeld, 1982). To a much lesser extent, NH$_3$ can
undergo gas-phase degradation. Kohlmann and Poppe (1999) considered the 27 reactions known to be involved in NH₃ degradation and reported that NH₃ oxidation was a source of NOₓ under high NOₓ conditions (>1ppb) and a sink under low NOₓ conditions (<1ppb). Small amounts of tropospheric NOₓ are also the result of reactive nitrogen compounds being transported from the stratosphere.

2.1.2. Tropospheric NOₓ Transformations

Atmospheric NOₓ oxidation products, termed NOₓ, include HNO₃, nitrous acid (HONO), nitrate radical (NO₃), dinitrogen pentoxide (N₂O₅), peroxyacetic acid (HNO₄), aerosol NO₃⁻ of various sizes, peroxyacetyl nitrate “PAN” (RC(O)OONO₂), alkyl nitrate (RONO₂), and peroxyalkyl nitrate (ROONO₂), where R represents an organic group. The chemical transformations involving NOₓ are highly complex. In particular, transformations to organic nitrates are not straightforward (A THERTON and PENNER, 1988; 1990). The explanation provided here is simplified to include only the processes that dominate NOₓ chemistry, according to current understanding (e.g., SEINFELD and PANDIS, 1998).

Daytime NOₓ chemistry is strongly affected by photolysis. Within a few minutes, NOₓ introduced to the troposphere photochemically equilibrates. Nitric oxide quickly reacts with ozone, O₃, to produce NO₂ by

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2. \quad (6)
\]

Then, nitrogen dioxide photolyzes to produce ground state atomic oxygen, O(^3P), by

\[
\text{NO}_2 + \text{hv} (\lambda<434\text{nm}) \rightarrow \text{NO} + \text{O}^3\text{P}, \quad (7)
\]
and $O(^3P)$ reacts with $O_2$ and a third molecule required to absorb energy, called a moderator, $M$, to regenerate $O_3$ by

$$O_2 + O(^3P) + M \rightarrow O_3 + M,$$

(8)

and the NO$_x$ cycle (reactions 6-8) continues. Cycling between NO and NO$_2$ also occurs, to a lesser extent, via the reaction of NO and $O(^3P)$ to form NO$_2$ by

$$NO + O(^3P) + M \rightarrow NO_2 + M,$$

(9)

and the reaction of NO$_2$ and $O(^3P)$ to produce NO and $O_2$ by

$$NO_2 + O(^3P) \rightarrow NO + O_2.$$

(10)

Other atmospheric compounds relevant to the NO$_x$ cycle are the result of the photolysis of ozone, which produces $O(^3P)$ or excited state atomic oxygen, $O(^1D)$ by

$$O_3 + h\nu (\lambda < 310\,nm) \rightarrow O(^3P) + O_2,$$

or

(11a)

$$O_3 + h\nu (\lambda < 463\,nm) \rightarrow O(^1D) + O_2.$$ (11b)

Once formed, $O(^1D)$ generally collides with another atmospheric compound (most often $N_2$ or $O_2$) and transfers its excess energy to the other compound to form $O(^3P)$ by

$$O(^1D) + M \rightarrow O(^3P) + M.$$ (12)

Since $O(^3P)$ quickly reacts with $O_2$ and $M$ to regenerate ozone (reaction 8), reactions 11a and 11b generally have no net effect. However, a significant exception occurs when $O(^1D)$ reacts with water vapor to produce the highly reactive hydroxyl radical, OH, by

$$O(^1D) + H_2O \rightarrow 2OH.$$ (13)

Once formed, OH reacts with volatile organic compounds (VOCs) to produce the peroxy radical ($HO_2$) and a number of organic peroxy radicals ($RO_x$, where again
R represents an organic group). The oxidation of carbon monoxide, CO, provides an example of HO₂ formation. Carbon monoxide reacts with OH to form CO₂ and atomic hydrogen by

\[ \text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}. \]  

(14)

Atomic oxygen reacts with molecular oxygen to produce HO₂ by

\[ \text{H} + \text{O}_2 \rightarrow \text{HO}_2, \]  

(15)

and then HO₂ can subsequently oxidize NO to NO₂ by

\[ \text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}. \]  

(16)

Methane, CH₄, reacts with OH to produce CH₃, the methyl radical by

\[ \text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}. \]  

(17)

Methyl radical reacts with molecular oxygen to produce the methyl peroxy radical, an example of an organic peroxy radical, by

\[ \text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2, \]  

(18)

and then CH₃O₂ can subsequently oxidize NO to NO₂ by

\[ \text{NO} + \text{CH}_3\text{O}_2 \rightarrow \text{NO}_2 + \text{CH}_3\text{O}. \]  

(19)

The general form for reactions involving the oxidation of NO by organic peroxy radicals is

\[ \text{NO} + \text{RO}_x \rightarrow \text{NO}_2 + \text{RO}_{x-1}. \]  

(20)

Although more complex VOCs than CO and CH₄ dominate the chemistry of the polluted troposphere, the same rules apply: The oxidation of VOCs generates HO₂ and ROₓ, which subsequently oxidize NO to NO₂ according to reactions 16 and 20, and the oxidation of NO by HO₂ regenerates OH.
Considerable cycling between NO and NO₂ occurs until there is a termination reaction, which, during the day, is production of HNO₃ by

\[ \text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}. \quad (21) \]

In addition, reaction of NO₂ with O₃ produces the nitrate radical, NO₃, by

\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2, \quad (22) \]

and, to a much lesser extent, by

\[ \text{NO}_2 + \text{O}^3\text{P} + \text{M} \rightarrow \text{NO}_3 + \text{M}. \quad (23) \]

The nitrate radical is irrelevant in daylight chemistry because NO₃ is quickly destroyed by photolysis by

\[ \text{NO}_3 + \text{hv} (\lambda < 700 \text{ nm}) \rightarrow \text{NO} + \text{O}_2, \text{ or} \]
\[ \text{NO}_3 + \text{hv} (\lambda < 580 \text{ nm}) \rightarrow \text{NO}_2 + \text{O}^3\text{P}, \quad (24a, 24b) \]

and by reaction with NO by

\[ \text{NO}_3 + \text{NO} \rightarrow 2\text{NO}_2. \quad (25) \]

At night, photolysis ceases and a different set of atmospheric processes begins to dominate the NOₓ cycle. The presence of appreciable levels of NO₃ provides another pathway for NOₓ removal. Nitrate radical reacts with NO₂ and a third molecule to produce dinitrogen pentoxide, N₂O₅, by

\[ \text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}. \quad (26) \]

Although N₂O₅ can decompose by

\[ \text{N}_2\text{O}_5 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_3 + \text{M}, \quad (27) \]

the majority of N₂O₅ undergoes heterogeneous reaction with water in aerosols or cloud droplets to produce HNO₃ by

\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O}_{(s)} \rightarrow 2\text{HNO}_3. \quad (28) \]
Other reactions determined to be relevant in nighttime chemistry and HNO₃ production involve reaction of NO₃ with organic molecules (e.g., RUSSELL et al., 1985), such as formaldehyde, HCHO, by

\[
\text{NO}_3 + \text{HCHO} \rightarrow \text{HNO}_3 + \text{HO}_2 + \text{CO}, \quad (29)
\]

and organic aldehydes, RCHO, by

\[
\text{NO}_3 + \text{RCHO} \rightarrow \text{HNO}_3 + \text{RCO}_3. \quad (30)
\]

There are seasonal variations in NOₓ chemistry. During the summer, the conversion of NO to NO₂ is more rapid because of higher abundances of O₃ relative to NOₓ. In addition, increased solar insolation accelerates the rate of O(¹D) production (e.g., reaction 11b). Higher O(¹D) and H₂O concentrations in the summer lead to increased OH production by reaction 13, and elevated OH speeds up termination reaction 21. As a result, daylight chemistry (pathway #1 in Figure 4) dominates HNO₃ production. During the winter, conversion of NO to NO₂ is less efficient due to lower O₃/NOₓ, and nighttime chemistry by reactions 26-30 (including pathways #2 and #3 in Figure 4) becomes more important.
2.1.3. Removal of NO\textsubscript{x} from the Troposphere

Although the removal of NO\textsubscript{x} by chemical transformations occurs on the order of a day, the product HNO\textsubscript{3} typically remains in the atmosphere for days to a week until scavenged by dry or wet deposition (Figure 5). The lifetime of HNO\textsubscript{3} is shorter during wet periods because of more frequent washout of reactive nitrogen compounds. Typically, the lifetime of HNO\textsubscript{3} in the lower troposphere limits long-range transport of reactive nitrogen. The potential for transport increases when NO\textsubscript{x} gets vented during storms to the upper troposphere, where transformation of NO\textsubscript{x} to HNO\textsubscript{3} and the subsequent removal of HNO\textsubscript{3} occur at slower rates. In areas far from
the location of precursor NO$_x$ production, the photolysis of HNO$_3$ can regenerate NO$_x$ by

$$\text{HNO}_3 + \text{hv} \rightarrow \text{NO}_2 + \text{OH}. \quad (31)$$

![Diagram of NO$_x$ removal](image)

**Figure 5:** Illustration of the removal of NO$_x$ from the troposphere. Gas phase and aqueous phase nitric acid and aerosol nitrate are removed via dry and wet deposition.

In this sense, HNO$_3$ serves as a reservoir of NO$_x$. In addition to HNO$_3$, there are other important reservoir species, including aerosol NO$_3^-$ and, to a greater extent, organic nitrates. In the polluted troposphere, aerosol NO$_3^-$ exists primarily in the fine-mode (<1µm diameter) as ammonium nitrate aerosol, NH$_4$NO$_3$(s/aq), which forms when HNO$_3$ reacts with ammonia by

$$\text{HNO}_3 + \text{NH}_3 \rightarrow \text{NH}_4\text{NO}_3(\text{s/aq}), \quad (32)$$
Some NH$_4$NO$_3$(s) can be transported away from polluted areas. Over the oceans, fine-mode aerosol NO$_3^-$ dissociates by

$$\text{NH}_4\text{NO}_3(\text{s/aq}) \rightarrow \text{HNO}_3 + \text{NH}_3,$$  \hspace{1cm} (33)

and forms coarse-mode sea-salt aerosol NO$_3^-$ (>1µm diameter) by

$$\text{HNO}_3 + \text{NaCl} \rightarrow \text{NaNO}_3(\text{s}) + \text{HCl},$$  \hspace{1cm} (34)

and conversion to coarse-mode aerosol NO$_3^-$ increases dry and wet deposition rates (SPOKES et al., 2000).

Another class of compounds, organic nitrates, can transport reactive nitrogen even farther from NO$_x$-generating regions. The most abundant organic nitrate species, peroxyacetyl nitrate, PAN, forms by the reaction of peroxyacetyl radical, CH$_3$CO-O$_2$ with NO$_2$ and a third molecule by

$$\text{CH}_3\text{CO-O}_2 + \text{NO}_2 + M \rightarrow \text{PAN} + M.$$  \hspace{1cm} (35)

Since PAN does not photodissociate in the troposphere or dissolve readily in precipitation, its primary destruction mechanism is thermal decomposition by

$$\text{PAN} + \text{heat} \rightarrow \text{CH}_3\text{CO-O}_2 + \text{NO}_2.$$  \hspace{1cm} (36)

Consequently, the chemical lifetime of PAN is strongly temperature dependent, ranging from approximately 30 minutes at 25°C to eight hours at 0°C to many months in the upper troposphere (SEINFELD and PANDIS, 1998). In polluted areas with high hydrocarbon-to-NO$_x$ ratios, nearly one-fourth of NO$_x$ can be transformed to PAN and other organic nitrates (ATHERTON and PENNER, 1988). While some organic nitrates get dry deposited, appreciable amounts can be transported to remote regions, and chemical transport models have demonstrated the importance of PAN on global NO$_y$ distributions (KASIBHATLA et al., 1993).
In brief, NOx from various processes enters the troposphere and transforms to HNO3, aerosol NO3−, and organic nitrates. Although small quantities of tropospheric NOy compounds enter the stratosphere during rare storm events, the vast majority of NOy ultimately gets deposited to the Earth’s surface. Although short chemical lifetimes typically limit transport of NOx, HNO3, and aerosol NO3− in the lower troposphere, the venting of NOx to the upper troposphere and the formation of PAN permit the movement of NOy significant distances from the locations of NOx introduction prior to being deposited as atmospheric NO3−.

2.2. Isotope Fractionation

The various NOy species introduced in the previous section can be considered pools of nitrogen (N) and oxygen (O), and each pool can be characterized by N and O isotopic compositions. This chapter describes the physical-chemical mechanisms that influence the partitioning of isotopes between pools and introduces isotope terminology. Molecules that differ only in their isotopic compositions, called isotopologues, have different energies associated with atomic motions, such as vibrations, rotations, and translations. From a quantum mechanical perspective, these energies are quantized into distinct levels. Using statistical mechanics, a total partition function, Q, can be derived to quantify the total energy of motion over all energy states, where \( E_i \) is the total energy and \( g_i \) is the degeneracy of state \( i \), \( k_B \) is Boltzmann constant, and \( T \) is temperature, by

\[
Q = \sum_i g_i e^{-\frac{E_i}{k_B T}}.
\]
Exact determinations of $Q$ require solutions of the Schrödinger equation (waves that describe the quantized energy). A molecule’s total energy is the sum of its internal energy, $E_{\text{int}}$, and translational energy, $E_{\text{tr}}$. Since the contribution of gravitational forces on a molecule’s potential energy is small, $E_{\text{int}}$ is mostly the energy associated with the potential for interactions within the molecule. Electronic interactions have the greatest potential energy. There are also minor interactions between nuclei and between electrons and nuclei, which are influenced by the masses of the nuclei and the electrons. When all the potentials for interactions are considered, the equation for $E_{\text{int}}$ cannot be solved for most molecules. The Born-Oppenheimer (B-O) approximation considers motions of nuclei, relative to electrons, to be insignificant and allows for the cancellation of some energy terms. As a result of the B-O approximation, the potential energy surfaces for isotopologues are treated as identical and the principal differences for $E_{\text{int}}$’s arise primarily because of how the masses of the nuclei affect the energies associated with stretching, compressing, and rotating atoms relative to their optimal distance. A molecule’s $E_{\text{tr}}$ is the energy associated with the movement of the center of the mass in three-dimensional space and can be determined by solving the translational Schrödinger equation. Isotopologues have different $E_{\text{tr}}$’s due to the effect of mass on molecular velocities. Compared to the light isotopologue, heavy isotopologues have lower $E_{\text{int}}$’s and $E_{\text{tr}}$’s, and thus $Q$’s.

Energy differences between isotopologues result in isotope fractionation, the general term used to describe the processes that cause isotopes to selectively partition into certain pools and are described using partition function ratios. Vibrational
quanta are significantly larger than rotational or translational quanta. Vibrations have characteristic frequencies that depend on the masses of the atoms and the forces, such as bonds, opposing atomic motion. Every substance has a characteristic vibrational energy in their lowest energy state, or zero point energy (ZPE). When a heavier isotope replaces a lighter isotope, the ZPE lowers. When substances undergo isotope exchange, heavier isotopes tend to concentrate in the substance that experiences the greatest shift in ZPE upon substitution. Fractionation processes can be categorized as equilibrium or kinetic. Equilibrium isotope effects (EIEs) occur when there is complete isotope exchange between pools, and these effects are mainly driven by changes in $E_{\text{int}}$ upon isotopic substitution. Kinetic isotope effects (KIEs) are generally associated with one-directional processes and involve incomplete isotope exchange. Kinetic isotope effects can be driven by differences in the $E_{tr}$ of isotopologues or by specific features of the reaction paths (e.g., the transition state).

2.2.1. Equilibrium isotope effects

Most observed EIEs can be adequately explained by shifts in zero-point vibrational energies that accompany isotope exchange, although 2\textsuperscript{nd}-order effects may involve non-vibrational, non-mass-dependent mechanisms (Bigeleisen, 1998). When a heavier isotope replaces a lighter isotope, the energy shift can be represented as the ratio of the partition functions of the heavy and light isotopologues, $Q^*$ and Q. (Asterisks signify terms for heavy isotopologues.) Urey (1947) and Bigeleisen and Mayer (1947) described ways to calculate partition function ratios ($Q^*/Q$)'s from vibrational frequencies, and their simplifying assumptions allow the calculation of
equilibrium constants for isotope exchange reactions. Several reviews of their approaches were useful in preparing this summary (CHACKO et al., 2001; MATSUHISA et al., 1978; RICHET et al., 1977; SCHAUBLE, 2004; YOUNG et al., 2002).

To a reasonable approximation, \((Q^*/Q)\)’s can be calculated from taking the product of the component partition function ratios for vibrational (vib), translational (tr), and rotational (rot) energies.

\[
(Q^*/Q) = (Q^*/Q)_{vib} (Q^*/Q)_{rot} (Q^*/Q)_{tr}.
\]

Other terms can be included to account for anharmonic vibrations, \(Q^*/Q)_{anharb},\) rotational-vibrational interactions, \((Q^*/Q)_{rot-vib},\) and rotational stretching energies \((Q^*/Q)_{rot-str}\) (RICHET et al., 1977). Theoretically, there should also be a partition function included for electronic energy associated with excited energy states, \((Q^*/Q)_{el},\) but the general practice is to assume this energy is negligible.

Determinations of \((Q^*/Q)_{vib}\) require inputs of vibrational frequencies for the isotopologues. For relatively common isotopic compounds, vibrational frequencies are often obtained using spectroscopy, which involves the measurement of the differences between ground state and excited state energies or two excited state energies. Zero-point vibrational frequencies are then calculated from the spectroscopic data using equations that describe the shape of molecules’ potential energy surfaces (HERZBERG, 1950). For rarer isotopic compounds, vibrational frequencies are typically calculated from the frequencies of the common forms. Other techniques involve the use of empirical force-field and \textit{ab initio} quantum-mechanical force-field models (see SCHAUBLE, 2004 for a review).
Exact equations used to calculate \((Q^*/Q)_{\text{vib}}\) and \((Q^*/Q)_{\text{rot}}\), and, if included, \((Q^*/Q)_{\text{anh}}, (Q^*/Q)_{\text{rot-vib}}, \text{and } (Q^*/Q)_{\text{rot-str}}\) depend on the expression used for molecules’ PE surfaces. Although there are several parameters that influence \(Q_{\text{tr}}\), all of the terms cancel in the calculation of \((Q^*/Q)_{\text{tr}}\) except the mass term, where \(M^*\) and \(M\) are the molecular masses of the molecules with heavy and light isotopic compositions, respectively. The expression commonly referred to as the “classical” part of the total partition function is

\[
(Q^*/Q)_{\text{tr}} = \left(\frac{M^*}{M}\right)^{\frac{3}{2}}.
\]

Molecules can also be characterized by a reduced partition function, \(f\), which excludes the “classical” term. Where \(r\) is the number of atoms being exchanged, \(f\) is determined by

\[
f = (Q^*/Q)\left(\frac{M}{M^*}\right)^{\frac{3r}{2}}.
\]

Closely related to \(f\)'s are \(\beta\)-factors, which have been tabulated for many compounds (RICHET et al., 1977) and are calculated by

\[
\beta = f^{\frac{1}{r}}.
\]

For isotope exchange reactions, \((Q^*/Q)\)'s and \(\beta\)-factors can be used to predict the equilibrium partitioning of isotopes between compounds. When two substances \(\text{IX}\) and \(\text{IY}\) exchange the two isotopes \(^1\text{I}^*\) (heavy) and \(^1\text{I}\) (light) and \(a\) and \(b\) are stoichiometric coefficients, the isotope exchange reaction is given by

\[
a\text{IX} + b\text{I}^*\text{Y} \leftrightarrow a\text{I}^*\text{X} + b\text{IY}.
\]
The equilibrium constant, $K_{eq}$, can be written in terms of the Q’s of the products over the reactants and in terms of the $(Q^*/Q)$’s as

$$K_{eq} = \frac{(Q_{IX}^*)^a (Q_{IY}^*)^b}{(Q_{IX})^a (Q_{IY})^b} = \frac{(Q^*/Q)_{IX}^a}{(Q^*/Q)_{IY}^b}.$$  

As a result of equilibrium isotope exchange, the compounds IX and IY will have different isotope ratios, which can be expressed as $R$’s or in δ notation. The equilibrium fractionation factor $\alpha_{eq}$ can be determined experimentally by measuring the isotope ratios of the two compounds at equilibrium, or theoretically. The equations used to calculate $\alpha_{eq}$ from measured isotope ratios and theoretical β-factors are

$$\alpha_{EIE,(IX\leftarrow IY)} = \frac{R_{IX}}{R_{IY}} \frac{\delta_{IX} + 1000}{\delta_{IY} + 1000} = \frac{\beta_{IX}}{\beta_{IY}}.$$  

When a and b are unity, $K_{eq}$ is equivalent to $\alpha_{eq}$. There are small differences between $K_{eq}$ and $\alpha_{eq}$ for reactions when more than one atom is exchanged. Temperature (T) largely affects the magnitude of $\alpha_{eq}$, but the relationship between T and $\alpha_{eq}$ is not simple (Criss, 1991). In general, $\alpha_{eq}$ decreases as temperature increases, but, for most substances, the T dependence of $\alpha_{eq}$ cannot be described with a single equation over a broad range of T’s. For particular T ranges, ln$\alpha_{eq}$ varies continuously from a function of $T^{-1}$ (at low T) to $T^{-2}$ (at high T). At infinite high temperatures, $\alpha_{eq}$ is unity.
2.2.2. Kinetic isotope effects

Compared to equilibrium isotope exchange, kinetic isotope effects (KIEs) result from a wider range of mechanisms, many of which have not been fully described in the isotope literature. KIE’s are often described using ratios of the reaction rate constants (k’s). The ratio of the k’s of light and heavy isotopologues determines the kinetic isotope fractionation factor, $\alpha_{\text{kin}}$, by

$$\alpha_{\text{kin}} = \frac{k}{k^*}.$$  

Isotopologues have different reaction rate constants (k’s) due to the effect of molecular masses on translational energies ($E_{\text{tr}}$’s). Whereas the effect of atomic masses on internal energy ($E_{\text{int}}$) is a purely quantum mechanical phenomena, the effect of molecular masses on $E_{\text{tr}}$ can also be explained using classical mechanics. The quantum mechanical parameter, $E_{\text{tr}}$, in the translational Schrödinger equation is derived from the classical expression for average translational kinetic energy (KE).

In the classical description, KE relates to temperature (T) by the Boltzmann constant ($k_B$) and is a function of molecular mass (M) and average translational velocity (v) by

$$KE = \frac{3}{2} k_B T = \frac{1}{2} M v^2.$$  

At a given temperature, the relationship between the M’s and v’s of two isotopologues is

$$\frac{v^*}{v^2} = \frac{M}{M^*}.$$  

According to collision theory, higher molecular or translational velocities translate to higher collision frequencies and faster reaction rates. As a result, light
isotopologues tend to have higher reaction rate constants than heavy isotopologues. KIEs occur when there is incomplete isotope exchange during non-reversible reactions, such as dissociation, and reactions in which the reaction products move away from the starting pool, such as evaporation or diffusion.

Fractionations associated with dissociation have been explained by a transition state theory (Bigeleisen, 1949; Bigeleisen and Wolfsberg, 1958). The rates of chemical reactions often depend on single “rate-limiting” or “rate-determining” steps, which only occur when a molecule possesses enough energy to achieve an activated complex. In this transition state, the distance between atoms reaches a maximum and the bond can break to permit the formation of products. When a substance becomes activated, the activated complex can either be deactivated or dissociated. The probability of a molecule exceeding the energy barrier, or activation energy, can be determined using statistical mechanics by evaluating the \((Q^* / Q)\)'s of the reactants and the activated complexes of the isotopologues. The reaction rate constants for dissociation can also be calculated using a quantum mechanical model, such as the Rice-Ramsperger-Kassel-Marcus (RRKM) theory (Marcus, 1952; 1965). Although the light isotopologue reacts faster than heavy isotopologues in most cases, there are exceptions that may be related to a phenomenon called the “tunnel effect,” in which molecules tunnel through the energy barrier rather than surpassing it (Bigeleisen, 1949).
2.2.3. Fractionation networks

Fractionations associated with networks, such as those involving geochemical, biological, or atmospheric processes, have been described by some workers as “kinetic.” These networks can include both equilibrium isotope effects and kinetic isotope effects, and the fractionation associated with them can produce net isotope effects that reflect the total processing of a material through the network (e.g., (Hayes, 2001). Every reaction has an intrinsic fractionation factor ($\alpha_{eq}$ or $\alpha_{kin}$). An intrinsic isotope effect, $\epsilon_{intrinsic}$, can be calculated by

$$\epsilon_{intrinsic} = (\alpha_{intrinsic} - 1) \times 1000\% \approx \ln \alpha_{intrinsic} \times 1000\%$$

The isotopic compositions of different pools in nature reflect the various reactions that the molecules in the pools undergo. The net isotope effect, $\epsilon_{net}$, can be defined as

$$\epsilon_{net} = (\alpha_{net} - 1) \times 1000\% \approx \ln \alpha_{net} \times 1000\%$$

In applying this approach to atmospheric nitrogen chemistry, there are three ways that isotope fractionation affects the isotopic composition of atmospheric N and O pools: source effects, sink effects, and isotope exchange between different pools (Brenninkmeijer et al., 2003; Kaye, 1987; Mauersberger et al., 2003; Thiemens, 1999; Weston, 1999). Source effects refer to the phenomenon of gases with distinctive isotopic compositions being introduced to the atmospheric from various sources. Sink effects include the wide range of mechanisms that affect isotopic compositions during removal reactions, such as chemical transformations, phase changes, and photolysis.
2.2.4. Non-mass dependent isotope effects

Although the processes described thus far occur due to a wide range of mechanisms, the fractionations are driven primarily by the influence of mass on the properties of isotopologues. There are several known examples of non-mass parameters influencing fractionation processes. There are 2nd-order isotope effects associated with shifts in nuclear shape and size upon isotopic substitution (Bigeleisen, 1998). Nuclear field shifts affect electronic partition function ratios \( \frac{Q^*}{Q} \), which are not considered in the approaches of Urey (1947) and Bigeleisen and Mayer (1947). Although these effects could make a minor effect on equilibrium isotope effects for heavy isotope systems, such as uranium, nuclear field effects are most likely irrelevant in light stable isotope studies.

Another instance of non-mass-dependent (NMD) isotope effects is associated with the effects of nuclear spin on certain chemical reaction rates (Turro, 1983). Spin refers to an intrinsic property of charged particles that possess magnetic moments. Whereas all electrons possess spin, only odd-mass nuclei, such as \(^{13}\)C and \(^{17}\)O, have spin. During certain reactions involving radicals, the spins of two unpaired electrons, or radical pairs, can orient so that the spins cancel (singlet state) or add to unity (triplet state). Hyperfine interactions between the magnetic moments of electrons and those of odd-mass nuclei can cause changes in nuclear and electron spin that affect the rates of intersystem crossings between the singlet and triplet states. Since certain “self-reactions” only occur when radical pairs are in the singlet state, occurrences of intersystem crossings ultimately affect reaction rates and lead to
magnetic kinetic isotope effects. These effects are very small and are limited to reactions that occur in confined spaces over sufficient time-scales, including certain aqueous-phase photochemical reactions.

Non-mass dependent isotopic compositions also occur in meteorites and meteoritic material (CLAYTON et al., 1973; HULSTON and THODE, 1965). The parameter “Cap Delta 17,” $\Delta^{17}$O, was defined as the deviation of a measured $\delta^{17}$O value from the $\delta^{17}$O value predicted on the basis of a mass-dependent reference array (MDRA). The slope of the MDRA is the three-isotope coefficient, $\theta$. Matsuihisa and others (1978) defined the slope of the MDRA, “three-isotope coefficient,” $\theta$, for the oxygen isotope system as

$$\theta = \frac{\ln \alpha_{17O/16O}}{\ln \alpha_{18O/16O}} \approx \frac{m^{17}O - m^{16}O}{m^{18}O - m^{16}O}$$

Early definitions used the linear approximation of the MDRA of

$$\delta^{17}O = \theta \times \delta^{18}O,$$

and defined $\Delta^{17}$O as

$$\Delta^{17}O = \delta^{17}O - \theta \times \delta^{18}O.$$  

More recent studies have defined the MDRA as

$$\delta^{17}O = ((1 + \delta^{18}O/1000)^\theta - 1) \times 1000,$$

and defined $\Delta^{17}$O as

$$\Delta^{17}O = \delta^{17}O - ((1 + \delta^{18}O/1000)^\theta - 1) \times 1000.$$  

Early hypotheses assumed that chemical processes could not produce large NMD anomalies and suggested that the “strange” oxygen isotopic compositions observed in meteorites resulted from nuclear processes involving the production of
isotopes. However, the assumption that ruled out chemical effects was invalidated by the laboratory experiments of Heidenreich and Theimens (1983), in which O$_3$ generated by electrical discharge exhibited large NMD isotopic compositions. Since their discovery, there has been considerable work dedicated to continuing laboratory experiments, identifying other terrestrial and extraterrestrial compounds with anomalies, understanding the nature of NMD effects in ozone and other gas-phase compounds, and revisiting questions on the origin of meteoritic NMD compositions (BRENNINKMEIJER et al., 2003; THIEMENS, 1999; THIEMENS et al., 2001; WESTON, 1999).

More detailed investigations on the reactions that generate and destroy O$_3$ and other potential reactions with NMD effects followed the electrical discharge experiments of Heidenreich and Theimens (1983). Other reactions involving O$_3$ were shown to exhibit unconventional isotope behavior, including O$_3$ production via O$_2$ photolysis (MORTON et al., 1990; THIEMENS and JACKSON, 1987; 1988), O$_3$ destruction by photolysis (BHATTACHARYA and THIEMENS, 1988; VALENTINI, 1987; WEN and THIEMENS, 1991), and O$_3$ destruction by thermal decomposition (BHATTACHARYA and THIEMENS, 1988; WEN and THIEMENS, 1991). Other laboratory experiments investigated potential effects associated with reactions of oxygen-bearing compounds other than O$_3$, including the production of CO$_2$ by reaction of CO+O(3P) (BHATTACHARYA and THIEMENS, 1989), reaction of CO+OH (ROCKMANN et al., 1998), CO$_2$ destruction by photolysis (BHATTACHARYA et al., 2000), isotope exchange between CO$_2$ and O(1D) (JOHNSTON et al., 2000; WEN and THIEMENS,
formation of H$_2$O$_2$ by reaction of H with O$_2$ (SAVARINO and THIEMENS, 1999), and the formation of sulfate (SAVARINO et al., 2000).

Other investigators searched for natural compounds with “strange” oxygen isotopic compositions. Whereas most terrestrial compounds have $\Delta^{17}$O values of zero, many atmospheric trace gases exhibit positive $\Delta^{17}$O signatures. The greatest anomalies in Earth’s atmosphere are observed in tropospheric O$_3$ (JOHNSON and THIEMENS, 1997; KRANKOWSKY et al., 1995) and stratospheric O$_3$ (KRANKOWSKY et al., 2000; MAUERSBERGER et al., 2001). Other compounds with NMD oxygen isotope signatures include CO (ROCKMANN et al., 1998), stratospheric CO$_2$ (ALEXANDER et al., 2001; ALEXANDER et al., 2002; BOERING et al., 2004; LAMMERZAHL et al., 2002; THIEMENS et al., 1991; THIEMENS et al., 1995), N$_2$O (KAISER et al., 2004; ROCKMANN et al., 2001), sulfate (LEE et al., 2001), and nitrate (MICHALSKI et al., 2003). Anomalous isotopic compositions are also transferred to the Earth’s surface via deposition of these atmospheric compounds. Oxygen isotope measurements of nitrate in desert deposits (MICHALSKI et al., 2003), perchlorate in desert soils (BAO and GU, 2004), and sulfate in numerous deposits (BAO et al., 2000), such as desert varnishes (BAO et al., 2001), Antarctic dry-valley soils (BAO et al., 2000), ash beds (BAO et al., 2003), and desert gypcretes (BAO et al., 2001), reveal non-zero $\Delta^{17}$O.

After two decades of investigations, the physical-chemical origin of $\Delta^{17}$O in O$_3$ and other trace atmospheric compounds remains a topic of considerable debate. The reaction identified as being primarily responsible for the O$_3$ anomaly is the recombination reaction between O$_2$, O($^3$P), and a third body, M. Characteristics of ozone metastable states affect their lifetimes, which affect ozone formation rates.
Some hypotheses ascribe the NMD compositions of $O_3$ partially to symmetry-induced kinetic isotope effects, SIKIEs (GAO and MARCUS, 2001; GAO and MARCUS, 2002; HATHORN and MARCUS, 1999; HATHORN and MARCUS, 2000). Described simply, the symmetry of activated complexes that form when $O(^3P)$ collides with $O_2$ can affect the rates of $O_3$ formation. Others have pointed to non-symmetry mechanisms that influence the lifetimes of metastable states (JANSSEN et al., 1999; MAUERSBERGER et al., 1993). There may also be dependency on the third-body that reacts with the activated complex to stabilize $O_3$ (GUENTHER et al., 2000). Recently, Babikov and colleagues devised a quantum mechanical model, which incorporates several non-statistical parameters and calculates the positions and lifetimes of different metastable states (BABIKOV et al., 2003; BABIKOV et al., 2003; BABIKOV et al., 2003).

There are also several explanations associated with NMD effects observed during photodissociation. One of the proposed mechanisms stems from the finding that the photodissociation of $^{12}CO_2$ and $^{13}CO_2$ by 185nm radiation to form $O$ and CO with different oxygen isotope effects (BHATTACHARYA et al., 2000). Occurrences of intersections between the potential energy surfaces of pre-dissociative and dissociative states affect the rates of reactions. Another mechanism, called “self-shielding,” occurs as a result of isotopologues having slightly different absorption spectra due to shifts in the vibrational frequencies upon isotopic substitution. Photodissociation of the more abundant isotopologue causes saturation, thus shielding the remaining molecules of the same absorption spectra from radiation. As a result, a zone forms where the less abundant isotopologue(s) increase their relative
significance. “Self-shielding” has been recently invoked to explain the anomalies observed in meteorites (CLAYTON, 2002; LYONS and YOUNG, 2005).

Atmospheric nitrate and sulfate have positive $\Delta^{17}$O values due to the transfer of oxygen atoms from ozone during the oxidation of NO$_x$ and SO$_2$, respectively (LYONS, 2001). Since the oxygen atoms in nitrate formed by non-atmospheric processes are typically derived from H$_2$O and/or atmospheric O$_2$, which have $\Delta^{17}$O values close to zero, nitrate that exhibits NMD isotopic compositions can be traced back to an atmospheric origin.
3. Previous investigations

3.1. Techniques used to analyze nitrate isotopes

Since the mass spectrometric improvements of McKinney and others (1950), numerous techniques have been developed to analyze nitrate isotope ratios. The first technique used to analyze the $\delta^{15}$N of nitrate involves collecting NO$_3^-$ on anion exchange resin, eluting NO$_3^-$ from the resin, using an alloy to reduce NO$_3^-$ to NH$_3$, distilling the NH$_3$ into an acidic solution, and reacting the distillate with NaBrO under vacuum conditions to produce N$_2$ (Hoering, 1955 and references therein). The gas then passes over heated copper and copper oxide and through a liquid nitrogen trap to remove CO, which has an interfering mass spectrum (Hoering, 1955). The purified N$_2$ is then introduced to a mass spectrometer and the relative intensities of ions with mass to charge ratios (m/z) of 28 and 29 are compared to a working N$_2$ standard.

Combustion techniques are also used to produce N$_2$ for isotope analyses. There are a suite of “off-line” methods in which nitrate salts (often KNO$_3$) are combusted in sealed tubes to produce N$_2$, which gets purified and concentrated prior to analyses (Kendall and Grim, 1990 and references therein). “On-line” techniques include thermally decomposing nitrate salts in a thermal-conversion elemental analyzer (TC/EA) or elemental analyzer (EA) (Stickrod and Marshall, 2000) to generate and purify N$_2$ for continuous flow isotope ratio mass spectrometric (CF-IRMS) analyses.

Other methods include reducing NO$_3^-$ to NH$_3$ using Devarda’s alloy, distilling the NH$_3$ into H$_2$SO$_4$, adding sodium tetraphenylborate, $(C_6H_5)_4B\text{Na}$ to the distillate
and combusting the precipitated \((C_6H_5)_4BNH_4\) in an EA to produce \(N_2\) for CF-IRMS (SAKATA, 2001). Recent analytical developments include the denitrifier method in which denitrifying bacteria convert \(NO_3^-\) to \(N_2O\) for CF-IRMS analyses of \(m/z\) 44, 45, and 46 (SIGMAN et al., 2001).

The first method developed to analyze the \(\delta^{18}O\) of nitrate was derived from the technique developed by Rittenberg and Ponticorvo (1956) to measure oxygen isotope ratios of organic compounds. The modification of this technique reported by Amberger and Schmidt (1987) involves the combustion of \(KNO_3(s)\) with \(Hg(CN)_2\) at 550°C to produce \(CO_2\) for isotopic analyses. The \(\delta^{18}O\) of \(NO_3^-\) is calculated from the relative intensities of singly charged \(CO_2^+\) ions with \(m/z\) 44 \((^{12}C^{16}O^{16}O)\), 45 \((^{12}C^{16}O^{17}O, ^{13}C^{16}O^{16}O)\), and 46 \((^{12}C^{16}O^{18}O, ^{13}O^{16}O^{17}O, ^{12}C^{17}O^{17}O)\) relative to a working \(CO_2\) standard. Other combustion techniques used to generate \(CO_2\) for isotope analysis include sealed-tube thermal decomposition of \(AgNO_3\) with \(AgCN\) (WASSENAAR, 1995) or graphite at 850°C (SILVA et al., 2000) and reaction of \(KNO_3\) with guanidine hydrochloride (\(NH_2C(NH)NH_2\cdotHCl\)) at 590°C (BRAUER and STRAUCH, 2000). Révész and coworkers (1997) developed a method to determine both \(\delta^{15}N\) and \(\delta^{18}O\) that involved heating \(KNO_3\) with catalyzed graphite in an evacuated sealed tube at 520°C for 24 hours to produce \(CO_2\), \(K_2CO_3\), and \(N_2\). The fraction of oxygen as \(CO_2\) and \(K_2CO_3\) and the fractionation factor between \(CO_2\) and \(K_2CO_3\) were constrained, and the \(\delta^{18}O\) of the nitrate could be determined from the \(CO_2\) mass-spectrometric measurements.

“On-line” techniques involve using a TC/EA to produce and purify \(CO\) for CF-IRMS analyses (KORNEXL et al., 1999). The \(\delta^{18}O\) of \(NO_3^-\) is calculated from the
intensities of singly charged CO$^+$ ions with m/z 28 ($^{12}$C$^{16}$O), 29 ($^{13}$C$^{16}$O, $^{12}$C$^{17}$O), and 30 ($^{13}$C$^{17}$O, $^{12}$O$^{18}$O) relative to a CO reference gas. The denitrifier method can also be used to measure the $\delta^{18}$O of NO$_3^-$ (Casciotti et al., 2002).

There have been significant standardization issues associated measurements of the $\delta^{18}$O of NO$_3^-$ over the past decade (Bohlke et al., 2003; Kornexl et al., 1999). Until 2003, there were two internationally distributed reference materials IAEA-N3 (also known as RM8549 (NIST) and IAEA-NO-3) and USGS-32 (also known as RM8558 (NIST)), both of which have $\delta^{18}$O values close to atmospheric O$_2$. As shown by Révész and Böhlke (2002), the absence of a reference with a $\delta^{18}$O value distinct from the $\delta^{18}$O of atmospheric O$_2$ prevented researchers from addressing blanks and scale-compression issues, leading to inaccurate determinations of $\delta^{18}$O.

Three KNO$_3$ samples were analyzed by three “off-line combustion” techniques (Amberger and Schmidt, 1987; Révész et al., 1997; Silva et al., 2000) and one “on-line combustion” technique (Kornexl et al., 1999). One sample had a $\delta^{18}$O value near the “mid-point” of the $\delta^{18}$O scale (approximately +21 to +25‰), while the other two samples had $\delta^{18}$O values significantly higher and lower than the “mid-point.” All four techniques yielded similar results for the KNO$_3$ sample with $\delta^{18}$O near the “mid-point.” However, for the KNO$_3$ samples with significantly lower and higher $\delta^{18}$O values, the results for the “off-line combustion” techniques were closer to the mid-point than the values obtained by “on-line combustion.” Révész and Böhlke (2002) reported that $\delta^{18}$O scale for the “off-line combustion” techniques was compressed to 0.33 to 0.68 times the scale of “on-line combustion” technique and attributed the scale contraction to oxygen exchange between CO$_2$ and the glass tubes.
in “off-line combustion” techniques. For the high $\delta^{18}$O sample, which had a measured value of 54.2‰ using “on-line combustion” (assuming $\delta^{18}$O of IAEA-NO3 = +22.7‰), the differences between the measured values for the “off-line combustion” techniques were as large as 17‰.

Published $\delta^{18}$O values for IAEA-NO-3 include +22.7‰ (REVESZ et al., 1997), +22.9‰ (SILVA et al., 2000), +23.6‰ (MICHALSKI et al., 2002), +25.3‰ (KORNEXL et al., 1999) and +25.6‰ (BOHLKE et al., 2003). These values differ by more than reported analytical precision and are likely due to variable contraction of the $\delta^{18}$O scale in different preparation methods (e.g., REVESZ and BOHLKE, 2002). Nitrate reference materials with widely varying $\delta^{18}$O have only recently become available (BOHLKE et al., 2003). USGS-34 (KNO3) was produced by the equilibration of HNO3 with $^{18}$O-depleted water, and preliminary analyses yield $\delta^{18}$O and $\delta^{17}$O values of -27.9‰ and -14.8‰, respectively (BOHLKE et al., 2003). USGS-35 (NaNO3) was obtained by purification of nitrate ores deposits from the Atacama Desert, and preliminary results for $\delta^{18}$O and $\delta^{17}$O are +57.5‰ and +51.5‰, respectively (BOHLKE et al., 2003).

### 3.2. Stable isotope investigations of atmospheric nitrate

The isotopic composition of atmospheric NO$_3^-$ has been of scientific interest for over half a century. The first wave of studies considered the nitrogen isotopes of precipitation NO$_3^-$ to test and form hypotheses on atmospheric chemistry. The long-standing hypothesis that atmospheric NO$_3^-$ was principally formed from the electrical fixation of atmospheric N$_2$, was challenged by several investigators, including
Hutchinson (1944; 1954), who pointed out that there was insufficient evidence linking rainwater NO₃⁻ concentrations to lightning events. Hoering (1957) conducted laboratory experiments on NO₃⁻ formed by electrical fixation and reported δ¹⁵N values of +1.4‰ for nitrogen fixed between platinum electrodes and -0.5‰ for nitrogen fixed between tungsten electrodes. Hoering (1957) also analyzed NO₃⁻ from rain collected on the rooftop of the University of Arkansas chemistry building and reported a range of -7.2‰ to +3.4‰. Hoering’s data provided evidence that electrical nitrogen fixation was not solely responsible for the production of atmospheric NO₃⁻.

Meanwhile, increasing evidence showed that the primary pathway of atmospheric nitrate formation was neither electrical discharge nor the atmospheric oxidation of ammonia (e.g., ROBINSON and ROBBINS, 1970 and references therein). Nearly two decades after the first δ¹⁵N measurements of precipitation NO₃⁻, isotope studies on atmospheric NO₃⁻ resumed (FREYER, 1978; FREYER, 1978; MOORE, 1974; MOORE, 1977; WADA, 1975). The isotopic evidence supported the hypothesis that precipitation NO₃⁻ was the result of the “washout” of NOₓ, which either dissolved directly into droplets or formed HNO₃ or aerosol NO₃⁻ which subsequently dissolved into rain (HEATON, 1986). Researchers also measured the δ¹⁵N of atmospheric NO₂ (MOORE, 1974; MOORE, 1977), barnyard NO₂ (MOORE, 1977) automobile exhaust NO₂ (FREYER, 1978; HEATON, 1987; HEATON, 1990; MOORE, 1977), coal-fired power plant exhaust NO₂ (HEATON, 1987; 1990), gaseous HNO₃ (FREYER, 1991), cloud-water NO₃⁻ (GARTEN, 1992), throughfall NO₃⁻ collected beneath a forest canopy (GARTEN, 1992), and aerosol NO₃⁻ (FREYER, 1991; MOORE, 1974; MOORE, 1977). Various methods were also used to sample the dry deposited NO₃⁻ for the purposes of
\[ \delta^{15}N \] analyses, including accumulation on an inclined Perspex sheet (Heaton, 1987) and an artificial tree (Garten, 1996).

The next wave of investigators used stable isotopes to distinguish atmospheric NO\(_3^–\) from NO\(_3^–\) produced by non-atmospheric processes. Nitrogen isotope ratios alone were used to investigate atmospheric deposition to such ecosystems as coastal waters (Fogel and Paerl, 1993) and forests (Nadelhoffer and Fry, 1994). Other studies capitalized from the use of nitrogen and oxygen isotope ratios, the “dual-isotope approach.” Atmospheric NO\(_3^–\) (Durka et al., 1994; Voerkelius, 1990) has significantly higher \( \delta^{18}O \) values than NO\(_3^–\) produced by non–atmospheric processes, including synthetic production of nitrate fertilizer (Amberger and Schmidt, 1987; Wasenaar, 1995) and nitrification in soils (Mayer et al., 2001), manure and ammonium fertilizers (Wasenaar, 1995), and septic systems (Araavena et al., 1993). Oxygen isotope ratios of NO\(_3^–\) are established during nitrate formation because NO\(_3^–\) does not exchange oxygen atoms with water at pH values typical in nature (Bunton et al., 1952; Hall and Alexander, 1940; Klein and Fiedel, 1950; Titani and Goto, 1939). Microbial processes can significantly alter isotope ratios and interfere with efforts to discriminate between NO\(_3^–\) sources (Mariotti et al., 1981). Although denitrification considerably shifts the isotope ratios of residual NO\(_3^–\) towards higher \( \delta^{15}N \) and \( \delta^{18}O \) (Araavena and Robertson, 1998; Bottcher et al., 1990; Mewis et al., 1999), reservoirs of NO\(_3^–\) affected by denitrification (e.g., groundwater NO\(_3^–\)) typically remain distinguishable from atmospheric NO\(_3^–\) (Campbell et al., 2002; Schiff et al., 2002; Spoelstra et al., 2001).
The contribution of atmospheric NO$_3^-$ relative to non-atmospheric NO$_3^-$, particularly “microbial NO$_3^-$” formed via nitrification, can be addressed, at least qualitatively, using the “dual-isotope approach” and isotope mass balance determinations (KENDALL, 1998). Such techniques have been applied to NO$_3^-$ studies in rivers (BATTAGLIN et al., 2001; CHANG et al., 2002; MAYER et al., 2002), tributaries in forested watersheds (BURNS and KENDALL, 2002; DURKA et al., 1994; PARDO et al., 2004; SCHIFF et al., 2002; SPOELSTRA et al., 2001; WILLIARD et al., 2001) and alpine watersheds (CAMPBELL et al., 2002), snowmelt (BURNS and KENDALL, 2002; CAMPBELL et al., 2002; KENDALL et al., 1996; OHTE et al., 2004) and desert nitrate deposits (BOHLKE et al., 1997).

A discovery by Michalski and coworkers (2003) advanced the ability to use isotopes to differentiate atmospheric and non-atmospheric NO$_3^-$. Whereas the $\delta^{17}$O and $\delta^{18}$O of nitrate formed by non-atmospheric pathways exhibit the approximate relationship $\delta^{17}$O = 0.52 $\times$ $\delta^{18}$O, Michalski and others (2003) reported that this relationship was not observed in atmospheric NO$_3^-$. The $\Delta^{17}$O (\(\equiv \delta^{17}$O - 0.52 $\times$ $\delta^{18}$O) also showed a strong seasonal pattern that could be modeled according to changes in atmospheric chemistry. The $\Delta^{17}$O of nitrate has been used to investigate the contribution of atmospheric NO$_3^-$ in arid ecosystems (MICHALSKI et al., 2004) and desert nitrate deposits (MICHALSKI et al., 2004).

Meanwhile, others utilized the isotopic composition of atmospheric NO$_3^-$ to better understand the processes involved in its formation. Several researchers considered the $\delta^{15}$N of precipitation NO$_3^-$ to assess the relative contribution of different NO$_x$ emitters to regional air masses (HASTINGS et al., 2003; RUSSELL et al.,
1998; Xiao and Liu, 2002). Other recent studies used the $\delta^{15}$N of size-segregated aerosol NO$_3^-$ (Yeatman et al., 2001; Yeatman et al., 2001; Yeatman et al., 2001), the $\delta^{18}$O of precipitation NO$_3^-$ (Hastings et al., 2003), and the $\delta^{18}$O and $\Delta^{17}$O of aerosol NO$_3^-$ (Michalski et al., 2003) to address questions on particular atmospheric processes. Complementary studies include measurements of the $\delta^{15}$N and $\delta^{18}$O NO$_3^-$ in snow and ice cores (Freyer et al., 1996; Hastings et al., 2004; Heaton et al., 2004) and the $\delta^{15}$N of atmospheric NO$_3^-$ deposition to ombrotrophic Sphagnum mires (Bragazza et al., 2005). Comprehensive studies on the $\delta^{15}$N, $\delta^{18}$O, and $\Delta^{17}$O of precipitation NO$_3^-$ are in progress (Elliott et al., 2004; Hastings et al., 2004), but there is minimal published data on the relationship between these parameters.

### 3.3. Summary of related findings

#### 3.3.1. $\delta^{15}$N of NO$_x$ from different processes

There is evidence that different processes produce NO$_x$ with characteristic $\delta^{15}$N values. Conventional isotope theory (Urey, 1947) predicts that equilibrium isotope effects are small at the high temperatures required to produce thermal NO$_x$. Freyer (1978) and Heaton (1987), predicted that the $\delta^{15}$N of NO$_x$ produced from anthropogenic fuel combustion would be close to 0‰ because the $\delta^{15}$N of atmospheric N$_2$ was 0‰ (by definition) and the $\delta^{15}$N of organic nitrogen in coal ranged from -2 to +3‰. The results of Heaton (1990) did not support the hypothesis that anthropogenic NO$_x$ was necessarily close to 0‰. When vehicle engines were operating under heavy load with high NO$_x$ concentrations the $\delta^{15}$N was -2‰, but
under reduced load (engine at idle), the $\delta^{15}\text{N}$ was significantly lower (-7 to -13‰). NO$_x$ from coal-fired power stations, in contrast, exhibited a range of $\delta^{15}\text{N}$ values from +6 to +13‰ (Heaton, 1990).

Heaton (1990) explained the results on NO$_x$ from automobile exhaust as reflecting different degrees of chemical equilibrium. Equilibrium would be kinetically limited by the high energy required to break the triple bond of N$_2$. If $^{14}\text{N}^{14}\text{N}$ reacted more quickly than $^{15}\text{N}^{14}\text{N}$, then the $^{15}\text{N}/^{14}\text{N}$ of NO$_x$ would be lower than atmospheric N$_2$. In Heaton’s experiments, under heavy load, advancing the spark ignition led to higher peak temperatures and longer reaction times, which brought the reaction closer to equilibrium (higher concentrations of NO$_x$). Under reduced load, there could be a greater kinetic isotope effect leading to more negative $\delta^{15}\text{N}$ values. For NO$_x$ produced in coal-fired power stations, Heaton (1990) hypothesized that if $^{14}\text{NO}$ was destroyed faster than $^{15}\text{NO}$ then the remaining NO would be progressively enriched in $^{15}\text{N}$. In coal fired power plants, the majority of organic nitrogen would be converted to fuel NO$_x$. While isotope fractionation is unlikely during the production of fuel NO$_x$, if $^{14}\text{NO}$ converts back to N$_2$ faster than $^{15}\text{NO}$, then the NO$_x$ remaining in the exhaust would have higher $\delta^{15}\text{N}$ values (Heaton, 1990).

With the exception of data from a nitric acid production plant with highly depleted $\delta^{15}\text{N}$ values (Heaton, 1987), there are no published reports of the $\delta^{15}\text{N}$ of NO$_x$ produced by non-utility or manufacturing industries. Depending on the fuel sources and temperatures of combustion, the $\delta^{15}\text{N}$ of NO$_x$ from industries could represent a combination of thermal and fuel NO$_x$. There are also no data on the $\delta^{15}\text{N}$
of NO\textsubscript{x} from biomass burning. Since most would be fuel NO\textsubscript{x}, it may be reasonable to assume that similar considerations explained by Heaton (1990) for power plants could apply for the $\delta^{15}$N of NO\textsubscript{x} from biomass burning.

The isotopic composition of microbial NO\textsubscript{x} potentially differs from thermal or fuel NO\textsubscript{x}. Biological processes typically favor compounds with lower $^{15}$N/$^{14}$N (Delwicke and Steyn, 1970; Mariotti et al., 1981), and it has been hypothesized that NO\textsubscript{x} released from soils have low $^{15}$N/$^{14}$N (Heaton, 1986; Moore, 1977). Since the $\delta^{15}$N of NO\textsubscript{x} from soils has yet to be directly measured, the idea that NO\textsubscript{x} from soils have negative $\delta^{15}$N remains speculative.

It has been hypothesized that the $\delta^{15}$N of NO\textsubscript{x} produced by lightning reflects the composition of atmospheric N\textsubscript{2}. The temperature at the core of a lightning channel can exceed 20,000°C (Malan, 1963). During lightning, the “freeze-out” of NO\textsubscript{x} occurs due to a rapid drop in density (Goldenbaum and Dickerson, 1993) or temperature (Stark et al., 1996). The electrical discharge experiments by Hoering (1957) that were described in section 3.2 produced NO\textsubscript{x} with $\delta^{15}$N values close 0‰. Additional electrical discharge experiments took place in the laboratory of J. Farquhar at the University of Maryland as part of N. Bao’s 2003 summer project (unpublished results). The experiments were conducted inside a glass apparatus that was filled with air (N\textsubscript{2}, O\textsubscript{2}, Ar, CO\textsubscript{2}, and other trace gases) and a pool of water. An external device heated the water to produce water vapor inside the apparatus. There were five experiments during which the internal atmosphere was sparked for three, six, 12, 24, and 72 hours. At the end of the experiments, HNO\textsubscript{3} was collected from the apparatus,
converted to AgNO₃, and analyzed by mass spectrometry using the techniques described in section 4.3.

The results of these tests showed that the δ¹⁵N of the NOₓ varied with the number of hours of sparking (Figure 6). These results are preliminary but are included here to show that there could be a wider range of δ¹⁵N produced by electrical discharge than previously reported. The experiments by Hoering (1957) and members of Farquhar’s lab group used corona discharges. It should be noted that arc discharges more accurately simulate lightning (Wang et al., 1998). To date, measurements of the δ¹⁵N of NOₓ produced by arc discharge are not present in the literature.

Figure 6: The δ¹⁵N of nitrate scavenged from a glass apparatus used for corona discharge experiments. These tests were completed in the laboratory of J. Farquhar as part of N. Bao’s 2003 summer project (unpublished data). Wet chemical treatments were conducted by K. Cooney and mass spectrometric analyses were made in the laboratory of M. Fogel at the Carnegie Institution of Washington.
3.3.2. $\delta^{15}$N of atmospheric nitrogen compounds

Atmospheric NO$_y$ compounds undergo complex reactions and isotope fractionation occurs during atmospheric processes, including chemical conversions, photolysis, isotope exchange, and phase changes (Kaye, 1987). Analyses of the $\delta^{15}$N of several NO$_y$ species and NO$_3^-$ in dry and wet deposition show that different pools have measurably different isotope ratios (Freyer, 1991; Heaton, 1987; Moore, 1974; 1977; Yeatman et al., 2001; Yeatman et al., 2001). Moore (1977) showed that $\delta^{15}$N values for precipitation NO$_3^-$ were significantly lower than aerosol NO$_3^-$ and that “clean air” NO$_x$ in Boulder, Colorado had lower $\delta^{15}$N values than precipitation NO$_3^-$. The results of Freyer (1978; 1991) in Jülich, Germany agreed that $\delta^{15}$N values are lower for precipitation NO$_3^-$ than aerosol NO$_3^-$. Despite isotope fractionation between the two pools, both aerosol NO$_3^-$ and precipitation NO$_3^-$ in Jülich exhibited seasonal variation with higher $\delta^{15}$N values in the winter and lower $\delta^{15}$N values in the summer. Measurements of HNO$_3$(g) in Jülich showed a narrow range of $\delta^{15}$N values (-2 to -3‰) that was lower than aerosol NO$_3^-$. (Freyer, 1991). Although there were too few samples to be statistically significant, HNO$_3$(g) did not exhibit apparent seasonal variation.

Most measurements of the $\delta^{15}$N of precipitation NO$_3^-$ obtained by all methods fall in the range of -10 to +5‰ (Heaton et al., 2004). The slightly different ranges observed at individual sites are believed to be actual signatures of precipitation NO$_3^-$ at the sites, not analytical differences. The seasonal variation in the $\delta^{15}$N of precipitation NO$_3^-$ observed by Freyer and coworkers (1991) in Jülich, Germany has also been identified in other locations, such as Pretoria, South Africa (Heaton,
1987). Explanations for variations in the $\delta^{15}$N of precipitation NO$_3^-$ include changes in the sources of precursor NO$_x$ (e.g., RUSSELL et al., 1998) and seasonal variations in the NO$_x$ photo-stationary state (FREYER et al., 1993).

3.3.3. $\delta^{18}$O and $\Delta^{17}$O of atmospheric nitrate

Precipitation nitrate measured using nitrate salt/decomposition methods exhibited relatively large ranges of $\delta^{18}$O values. Throughfall precipitation collected beneath a forest canopy in Bavaria, Germany had a range of $\delta^{18}$O values from +52.5 to +73.4‰ (DURKA et al., 1994; VOERKELIUS, 1990). Throughfall precipitation NO$_3^-$ in Leading Ridge, Pennsylvania and Fernow, West Virginia had a wider range of $\delta^{18}$O from +17 to +76‰, (WILLIARD et al., 2001). In Sault Ste. Marie, Ontario, Canada, the $\delta^{18}$O of precipitation NO$_3^-$ ranged from +35 to +59‰ (SPOELSTRA et al., 2001), while in Toronto, Ontario, Canada, the $\delta^{18}$O of throughfall and precipitation NO$_3^-$ ranged from +30 to +54‰ (SCHIFF et al., 2002). In Loch Vale, Colorado, the $\delta^{18}$O of precipitation NO$_3^-$ ranged from +40 to +70‰ (CAMPBELL et al., 2002), and in New Hampshire, the $\delta^{18}$O of precipitation NO$_3^-$ ranged from +47 to +77‰ (PARDO et al., 2004).

Rain NO$_3^-$ from Bermuda analyzed using the denitrifier method yielded a narrower range of $\delta^{18}$O values between +60.3 and +86.5‰ (HASTINGS et al., 2003). The $\delta^{18}$O of snow NO$_3^-$ from Summit Greenland analyzed using denitrifying bacteria ranged from +65.2 to 79.6‰ (HASTINGS et al., 2004). Other results obtained using the denitrifier method include precipitation NO$_3^-$ from across the northeastern and mid-Atlantic U.S with $\delta^{18}$O values ranging from +60 to +90‰ (ELLIOTT et al., 2004)
and precipitation NO$_3^-$ in Princeton, NJ with $\delta^{18}$O values ranging from $+57.2$ and $+90.5\%$ (HASTINGS et al., 2004).

The first reported $\Delta^{17}$O measurements of atmospheric NO$_3^-$ were on aerosols in La Jolla, CA. Prepared AgNO$_3(s)$ was thermally decomposed to O$_2$ for dual-inlet IRMS of $\Delta^{17}$O values were calculated using the linear approximation ($\Delta^{17}$O = $\delta^{17}$O – $0.52 \times \delta^{18}$O). The results showed a range of 20-30.8‰ (MICHALSKI et al., 2003). Reports on the $\Delta^{17}$O of precipitation NO$_3^-$ from Princeton, NJ determined by bacterial conversion of NO$_3^-$ to N$_2$O followed by the decomposition of N$_2$O to O$_2$ similarly gave a range of $+19.7$ to $+30.8\%$ (HASTINGS et al., 2004). Both $\delta^{18}$O and $\Delta^{17}$O exhibit seasonal variation with the highest values in the winter and the lowest values in the summer. Seasonal variation in oxygen isotope ratios has been previously explained by changes in the primary oxidants involved in converting NO$_x$ to atmospheric NO$_3^-$ (HASTINGS et al., 2003; MICHALSKI et al., 2003)
4. Methods

4.1. Sample collection

Several sample collection strategies were considered and the National Atmospheric Deposition Program (NADP) operation manual (DOSSETT and BOWERSOX, 1999) was consulted prior to establishing the sampling protocol. First, rather than collecting on a daily, weekly, or monthly basis, samples were collected on a precipitation event basis, which permitted the characterization of each sample with storm tracks. Second, since collectors were only placed outside for the duration of the storms, bulk deposition collectors were used in place of sophisticated wet-deposition-only collectors. Third, rather than analyzing a few samples from several different sites, the majority of the samples were collected from a single site. A residential site in Frederick, MD was chosen as the primary collection location, because this site was not close to any point source NOx emitters (e.g., coal-fired power stations) or high-traffic roads and was a convenient place for the frequent collection of large volumes of sample.

Precipitation samples were collected between February 2002 and May 2004 in Frederick, Maryland. Precipitation samples were collected in poly-ethylene bins (approximately 50cm by 34cm) (Figure 7) that had been washed, rinsed with deionized water and 10% hydrochloric acid, and triply rinsed with ultra-pure deionized water (the typical cleaning sequence used for the entire procedure described here). The material of the bins and the strict cleaning procedure were consistent with the NADP protocol (DOSSETT and BOWERSOX, 1999). Similar bulk
precipitation collection devices have been used for previous investigations of nitrate isotopes (e.g., Hoering, 1957; Paerl, 1985; Willard et al., 2001). Several pre-cleaned collection bins were placed outside immediately before and collected directly after rain, snow, thunderstorm, and mixed precipitation events. In order to recover adequate amounts of nitrate for isotopic analyses, the preferred amount of rainwater or melted snow collected for each storm was 12-20 liters.

Figure 7: Photograph of snow collection in Frederick, Maryland on February 16, 2003 at 8:00pm. The poly-ethylene bins were approximately 34cm by 50cm. During snow storms, poly-ethylene lids were placed in between the bins. Snow on the lids was transferred into the bins at the end of the storms.

Typically, the precipitation samples were immediately transferred to clean high-density poly-ethylene (HDPE) bottles, frozen, and kept in a frozen state until
thawed and filtered prior to ion extraction. On a few occasions, the samples remained unfiltered in the covered collection bins at approximately 20°C for 24-48 hours prior to being frozen. J. Spoelstra and others (2004) recently investigated the effect of storage on nitrate concentrations and the δ¹⁸O and δ¹⁵N of nitrate in bulk precipitation samples. The precipitation samples collected in their experiment were divided into three aliquots. Control aliquots were immediately filtered and frozen, while filtered and unfiltered aliquots were stored in covered but not air tight bottles at 25-28°C for two weeks. The results of their investigation showed that the nitrate concentrations and δ¹⁸O and δ¹⁵N values for the frozen and unfrozen (filtered or unfiltered) aliquots were statistically indistinguishable.

4.2. Collection of meteorological and storm track data

Unedited meteorological data was obtained through the National Oceanic and Atmospheric Administration’s (NOAA) National Climate Data Center (NCDC) for Frederick, Maryland (http://www.ncdc.noaa.gov/oa/ncdc.html). The weather station was approximately five miles from the site of precipitation collection. Data available through the NCDC included weather type (drizzle, rain, thunderstorm, vicinity thunderstorm, snow, unknown precipitation, breeze, haze, and fog), precipitation intensity (light, moderate, heavy), relative humidity, wind speed, wind direction, and precipitation totals. Data was recorded approximately every 20 minutes. If less than 0.01 inches of precipitation fell during a 20 minute time period, the quantity of precipitation records as 0 inches. As a result, simply adding the individual precipitation quantities would not yield the total amount of precipitation. The NCDC
data was used to determine the starting and ending times for precipitation events and the precipitation types.

Storm track trajectories were calculated using the National Oceanic and Atmospheric Administration’s (NOAA) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (http://www.arl.noaa.gov/ready/hysplit4.html). Back trajectories were calculated at 500, 1000, and 1500 meters above ground level for 24 hours. The starting times for the back trajectories were chosen as six hours prior to the starting times of the precipitation events, thus predicting the region of the air mass 30 hours prior to the precipitation event.

4.3. AgNO₃/decomposition method

The protocol used to extract nitrate from the water samples and prepare silver nitrate for isotopic analyses incorporated aspects of Chang et al. (1999), Silva et al. (2000) and unpublished methods used by J. Hannon and others at the USGS in Reston, Virginia. The wet chemical procedure involved filtration, anion exchange, elution of anions from the anion exchange resin, nitrate purification, conversion to silver nitrate, and freeze-drying. Isotope analyses involved separate procedures: “on-line” decomposition to N₂ and CO followed by CF-IRMS for δ¹⁵N and δ¹⁸O and “off-line” decomposition to O₂ for dual-inlet IRMS for Δ¹⁷O.

4.3.1. Wet chemical techniques

The procedure used to isolate nitrate ions was similar to the methods used in early investigations of precipitation nitrate in which cation exchange resin in the H⁺
form was used to collect \( \text{NH}_4^+ \), anion exchange resin in the \( \text{Cl}^- \) form was used to extract nitrate, and potassium chloride was used to elute nitrate from the resin (Garten, 1992; Garten, 1996; Hoering, 1957; Moore, 1974; Moore, 1977). Hoering (1957) speculated that his results could have been affected by the contamination of organic matter that was not effectively removed during the wet chemical techniques. Many researchers have discussed the presence of organic matter in their nitrate samples, and there have been numerous methods described to reduce organic contaminants (e.g., Chang et al., 1999; Haberhauser and Blochberger, 1999; Silva et al., 2000; Spoelstra et al., 2001; Wasenaar, 1995). The techniques chosen to minimize contamination in this study were developed by Chang and others (1999) for waters with low nitrate concentration and have been used by numerous other studies (e.g., Battaglin et al., 2001; Chang et al., 2002; Pardo et al., 2004). Despite incorporating the modifications recommended by Chang et al. (1999), there is evidence that organic contaminants were not adequately removed, as discussed later.

Three to 22 liters of each precipitation sample were filtered using GF/F type and 0.4\( \mu \)m polycarbonate membrane filters. Each filtered sample was transferred to a clean lowboy with a spigot and gravity dripped through a series of two columns that were packed with analytical grade resins, which were carefully treated prior to use (for more details, see Appendices A and B). The first column was loaded with AG50WX-8 cation exchange resin in the \( \text{H}^+ \) form (100-200 mesh), which was intended to protonate and/or adsorb dissolved organic carbon (DOC) (Chang et al., 1999). The second column was filled with AG2X-8 anion exchange resin in the \( \text{Cl}^- \)
form (100-200 mesh), which was used to extract anions (e.g., nitrate and sulfate) from the precipitation samples (Chang et al. 1999). This particular anion exchange resin was chosen over AG1X-8 because it has a similar strong selectivity for nitrate but a weaker selectivity for DOC (Chang et al., 1999).

The solution that passed through the two columns was periodically tested for the presence of nitrate using prepared colorimetric test solutions (for more details, see Appendix C). It was important to verify that the nitrate was quantitatively retained on the anion exchange column to prevent isotope fractionation (e.g., Garten, 1992). If the solution that passed through the column contained nitrate, the sample was discarded.

After the entire sample had passed through the columns, the AG50WX-8 resin from the cation exchange column was transferred to a clean centrifuge tube, frozen, and freeze-dried. While AG50WX-8 in the H\(^+\) form does not contain any nitrogen, as the sample passed through the cation exchange column, precipitation NH\(_4^+\) replaced H\(^+\) on some of the exchange sites. Therefore, the N\(_2\) produced by heating the AG50WX-8 resin partially filled with precipitation NH\(_4^+\) would reflect the nitrogen isotopic composition of the precipitation NH\(_4^+\) (Lehmann et al., 2001). Therefore, the freeze-dried AG50WX-8 resin for each sample was saved in the freezer for possible future analyses.

Anions were then eluted from each anion exchange column using 0.25M potassium chloride solution (J. Hannon 2002, personal communication). Elution of nitrate from the AG2X-8 column was monitored by periodically analyzing drops of solution from the column for the presence of nitrate using colorimetric test solutions.
Typically, quantitative recovery of nitrate (and sulfate) was recovered using 145-225mL 0.25M KCl solution.

The next steps in the process involved the purification of nitrate and were derived from the techniques of Silva and colleagues (2000) and J. Hannon and coworkers (personal communication). It was determined that sulfate was quantitatively recovered within the first 50mL of 0.25 M KCl solution put through each column. This portion of the sample was acidified using 2-3 drops of 1M HCl to obtain a pH of 2-3, and 0.75 ml 0.5M BaCl₂ solution was added to precipitate BaSO₄(s). After thoroughly mixing and allowing the samples to stand overnight, the BaSO₄(s) was then removed using a 0.2µm nylon filter. The BaSO₄(s) was carefully transferred using Millipore water from the filter into a clean glass vial, placed in a drying oven at approximately 60°C, and saved for sulfate sulfur isotope analyses (see section 4.6). The approximately 50mL of solution was added back to the rest of the sample.

Next, chloride was removed by a technique modified from J. Hannon and others at the USGS, Reston that used AG MP-50 cation exchange resin converted from the H⁺ form to the Ag⁺ form (for more details, see Appendix D). Each sample was added to an appropriate amount of the specially prepared resin. The cations in solution (e.g., K⁺, H⁺, and Ba⁺²) replaced the Ag⁺ ions retained on the resin, and the freed Ag⁺ ions combined with the Cl⁻ ions to form AgCl(s). AG MP-50 has a capacity for 1.5meq/mL. When the exchange sites were predominantly filled with Ag⁺, it was assumed that there were 1.5 moles of Ag⁺ per milliliter resin. Since one mole of Ag⁺ was required per mole of Cl⁻ in the sample, the amount of AG MP-50 (Ag⁺) needed
could be calculated from the amount of Cl\(^-\) in each sample, which was the sum of the amounts of Cl\(^-\) from the 0.25M KCl, 0.5M BaCl\(_2\), and 1M HCl solutions. Due to the cost of the AG MP-50 (Ag\(^+\)) resin, for some of the samples, only a portion of each sample was added to AG MP-50 (Ag\(^+\)) and taken through the remainder of the chemistry. For example, 75mL KCl/KNO\(_3\) solution (plus Millipore water added during transfer steps) was added to 14mL AG MP-50 (Ag\(^+\)). Each solution was then separated from the resin/AgCl\(_{\text{s}}\) mixture and put through a column filled with 5mL AG MP-50 (Ag\(^+\)) to maximize the exchange of the other cations for Ag\(^+\) ions. At the end of the wet chemical method, only Ag\(^+\) and NO\(_3^-\) should have been present in significant quantities. The result of freeze-drying the solutions should have been nearly pure AgNO\(_3\) crystals. As described later, there were potentially two sources of contamination that made the silver nitrates impure.

4.3.2. Measurements of the \(\delta^{15}\)N and \(\delta^{18}\)O of precipitation nitrate

The \(\delta^{15}\)N and \(\delta^{18}\)O analyses were conducted at the Geophysical Laboratory of the Carnegie Institution of Washington, overseen by M. Fogel. Four aliquots (approximately 0.5mg) of each prepared silver nitrate were weighed into a silver capsules. Using methods derived from Kornexl, Gehre, and others (1999), each sample was dropped into a Thermal Conversion Elemental Analyzer (TC/EA), which consisted of a high temperature furnace and a gas chromatograph (GC). The furnace, heated to 1450°C, was composed of a glassy carbon tube placed inside a ceramic tube and filled with glassy carbon and graphite. The high temperature reaction of AgNO\(_3\) with graphite produced mainly N\(_2\) and CO. A stream of He carried these gases
through a gas chromatograph (GC) at 90°C and into a continuous flow isotope ratio mass spectrometer (CF-IRMS).

Although the gases were prepared according to the same TC/EA parameters, it was necessary to analyze N₂ and CO during separate runs. Duplicate samples were run for both δ^{15}N and δ^{18}O. For nitrogen isotope analysis, purified N₂ was carried by He flow into the mass spectrometer, where the gas was ionized. Accelerated by a voltage potential, singly charged N₂⁺ ions were separated by mass to charge ratio (m/z) and directed into Faraday cups. The δ^{15}N of nitrate was calculated from the relative intensities of singly charged N₂⁺ ions with m/z of 28 (^{14}N^{14}N) and 29 (^{15}N^{14}N) compared to a working N₂ standard.

For oxygen isotope analysis, purified CO was introduced to the mass spectrometer, ionized, and separated according to m/z. The δ^{18}O of nitrate was calculated from the intensities of singly charged CO⁺ ions with m/z 28 (^{12}C^{16}O), 29 (^{13}C^{16}O, ^{12}C^{17}O), and 30 (^{13}C^{17}O, ^{12}O^{18}O) relative to a CO reference gas. The δ^{18}O of IAEA-NO-3, USGS-34, and USGS-35 were measured and compared to published values to determine a calibration curve. The offset correction varied on a day-to-day basis. There are discrepancies in the literature for the δ^{18}O of these reference materials. The results reported here for TC/EA-CF-IRMS analyses are calibrated using the values recently reported by Böhlke and coworkers (BÖHLKE et al., 2003):

δ^{18}O (IAEA-NO-3) = +25.6‰, δ^{18}O (USGS-34) = -27.9‰, and δ^{18}O (USGS-35) = +57.5‰.
4.3.3. Determinations of the $\Delta^{17}$O of precipitation nitrate

The techniques used to measure $\Delta^{17}$O at the Stable Isotope Laboratory at the University of Maryland, College Park were modified from thermal decomposition methods developed at the University of California, San Diego (Michalski et al., 2002). The procedure used by G. Michalski and colleagues at UCSD involved placing the silver capsules into quartz reaction tubes that were attached to a borosilicate glass line. The reaction tubes were externally heated by a ceramic resistance heater (520°C) that slid over them. In order to eliminate the potential for exchange between the sample O$_2$ and the quartz glass, this part of the technique was modified at UMCP.

Prepared silver nitrate (4-6mg) was weighed into silver foil capsules, and the capsules were pinched closed and folded. Each sample was loaded individually into a platinum furnace that was enclosed in a vacuum apparatus. Under vacuum conditions, the samples were heated by supplying the platinum furnace with 13 amps/1.8volts of DC current for three minutes to generate molecular oxygen by

$$\text{AgNO}_3 \rightarrow \frac{1}{2} \text{O}_2 + \text{NO}_2 + \text{Ag(s)} (+ \text{trace quantities of NO and N}_2).$$

During the reaction, a dewar filled with liquid nitrogen was placed around the reaction chamber to minimize exchange with the glass walls. The evolved gases were then passed through a U-shaped liquid nitrogen-cooled trap to condense NO$_x$, and O$_2$ was frozen onto 5A molecular sieve substrate in a liquid nitrogen-cooled finger. After closing a valve between the cold finger and the U-trap and reaction chamber, the finger was thawed and the O$_2$ was frozen onto 5A molecular sieve in a second cold finger. The second cold finger filled with molecular sieve was thawed to room
temperature and the purified O₂ was introduced into the sample bellows of a Delta Plus gas source mass spectrometer. Meanwhile, a standard gas was introduced into the standard bellows.

The sample and standard gases alternated being introduced through a capillary to the ion source, where the gases were ionized and accelerated by a voltage potential. The ion beams were separated by a magnet according to m/z and collected by an array of Faraday collectors. The intensities of the O₂⁺ ions with m/z ratios of 32 (¹⁶O¹⁶O), 33 (¹⁷O¹⁶O), and 34 (¹⁸O¹⁶O, ¹⁷O¹⁷O) were measured, and the 34/32 and 33/32 ratios were determined. The average of the isotope ratios determined for each sample gas was compared to the isotope ratios of the standard gas to determine the δ¹⁷O and δ¹⁸O of the samples relative to the standard gas. The δ¹⁷O was then calculated using the equation

$$\delta^{17}O = \delta^{17}O - 1000 * ((1 + \delta^{18}O/1000)^{0.52} - 1).$$

Several additional steps were included in the Δ¹⁷O protocol to maximize accuracy and precision. Each time the reaction chamber was open to load a new sample, the seal was re-greased to ensure that maximum vacuum conditions would be produced. Once the decomposition line had been evacuated to 5mtorr by a mechanical pump, several traps were cooled to liquid nitrogen temperatures and the line continued to be evacuated by a diffusion pump. During the evacuation of the line, the cold fingers filled with molecular sieve were wrapped with heating tape and heated to 220°C for one hour. This protocol removed water from the surfaces and minimized the potential for a memory effect.
4.3.4. Quality assurance tests

J. Hannon of the USGS, Reston discovered an issue associated with the use of AG MP-50(Ag\(^+\)) to remove chloride from the samples and produce AgNO\(_3\) (2003 personal communication). The method used by J. Hannon differed slightly from the procedure described above. Columns filled with AG 50W X8 (H\(^+\)) were not used prior to the anion exchange columns; AG 1X anion exchange resin was used in place of AG 2X; and the final step involved the use of AG 50W X8 (K\(^+\)) to produce KNO\(_3\) instead of AG MP-50 (Ag\(^+\)) to produce AgNO\(_3\). When the standards USGS-34 (KNO\(_3\), \(\delta^{18}O = -27.9\permil\)) and USGS-35 (NaNO\(_3\), \(\delta^{18}O = +57.5\permil\)) were dissolved in deionized water, put through the wet chemical procedure, and isotopically analyzed, the \(\delta^{18}O\) values for USGS-34 were higher and the \(\delta^{18}O\) values for USGS-35 were lower than the published values. There was also a greater difference in the measured \(\delta^{18}O\) values when less nitrate salt was dissolved, processed, and analyzed. There were no observed differences in the measured \(\delta^{15}N\) values. In addition, when deionized water was put through the chemical procedure (blank experiment), the freeze-dried result was a fluffy tan colored solid. The solid was analyzed using an elemental analyzer and had the following composition: 15%S, 27%C, and 0.15%N. J. Hannon concluded that a small, constant amount of AG MP-50 resin, which has a matrix of styrene divinylbenzene with a sulfonic acid functional group (R-SO\(_3^-\)), was being leached into the sample during the chloride removal step. Donna Hardy of Bio-Rad’s Technical Support Group verified the potential for the sulfonic acid functional group to leach from the resin (personal communication).
To address these issues at the University of Maryland, standards were put through the wet chemical procedure. Two aliquots of the USGS-34 standard and two aliquots of USGS-35 standard were dissolved in 75mL of 0.25M KCl solution, added to 14mL of the prepared AG MP-50 (Ag⁺) resin, dripped through a 5mL column of AG MP-50 (Ag⁺) resin, freeze-dried, and analyzed. A blank experiment was also conducted in which 75mL of the 0.25M KCl solution was taken through the identical procedure as the samples.

To test for the presence of organic matter, the prepared silver nitrates, including dissolved standards and the precipitation nitrate samples, were analyzed for % carbon and C/N using an elemental analyzer coupled to CF-IRMS in the laboratory of M. Fogel at the Carnegie Institution of Washington. The presence of carbon would provide evidence of organic matter in the silver nitrates. Dissolved organic matter generally contains 40% oxygen. Thus, the presence of organic compounds would indicate a likely source of non-nitrate oxygen contaminating the samples.

4.4. Denitrifier method

Several samples were analyzed using a technique that uses denitrifying bacteria to prepare N₂O for isotopic analyses (Casciotti et al., 2002; Sigman et al., 2001). The analyses were overseen by J. Kaiser. The techniques used to revive freeze-dried denitrifying bacteria, Pseudomonas aureofaciens, prepare a nutrient broth, and inoculate the broth were conducted by G. Cane at Princeton University. After growing for six days, the bacteria were ready to harvest. The medium was tested for the presence of nitrite because nitrite indicates the bacterial culture is not
usable. The prepared solution was divided into 40mL tubes and centrifuged. The medium was then concentrated 10-fold and 0.1mL of 6.0 M ammonium sulfate, (NH₄)₂SO₄ was added. Then, 2mL of concentrated bacteria were pipetted into 20mL vials, which were sealed and purged for six hours by bubbling He through the vials. The appropriate amount of precipitation samples to contribute 15 nanomoles of N was added to each bottle. The vials were then incubated overnight. The next day, 0.1mL of 10N sodium hydroxide, NaOH, was injected into each bottle to end the biological reaction. The N₂O produced by the bacteria were injected into a gas-bench for purification and concentration prior to mass-spectrometric analyses of m/z 44, 45, and 46. From ⁴⁵N₂O/⁴⁴N₂O and ⁴⁶N₂O/⁴⁴N₂O, it was possible to calculate the δ¹⁵N and δ¹⁸O of nitrate (Casciotti et al., 2002; Sigman et al., 2001).

4.5. Measurements of ion concentrations

Nitrate/nitrite concentrations in the precipitation samples were analyzed in the laboratory of D. Sigman at Princeton University. An auto-sampler was used to inject 100µL of the water samples into an acidic medium containing vanadium III heated to 80-90°C. Nitrite and nitrate were reduced to NO, which was carried by a stream of He to a chemi-luminescence NOₓ analyzer (Braman and Hendrix, 1989). The measurement of standard solutions ranging from 1.79 to 60.35µM permitted the calibration of peak area versus concentration. Periodic measurement of the standard solutions throughout the run verified the consistency of the system. Reproducibility was better than 0.2µM (1σ), which was typical for this apparatus (Hastings et al., 2003).
Nitrate and sulfate concentrations were determined using ion chromatography (IC) in the Environmental Engineering Laboratory at the University of Maryland, overseen by A. Davis. Hunho Kim and Houng Li assisted with the operation of the Dionex DX-100 ion chromatograph. Calibration solutions were prepared from chloride, nitrate, and sulfate stock solutions of known concentrations. The intermittent analysis of check standards showed that sulfate concentration data was reproducible during all IC runs within 5µM (1σ). Two batches of nitrate concentration data had precision better than 5µM (1σ). However, the last batch of nitrate concentration data, which included a large number of samples, was inaccurate because nitrate and chloride were eluted at the same time from the aging column.

Ammonium concentrations were measured at Geophysical Laboratory of the Carnegie Institution of Washington managed M. Fogel using conventional phenol hypochlorite colorimetric techniques (SOLORZANO, 1969). A pipette was used to transfer 0.7mL of each sample into snap cap sample vials. An oxidizing solution was prepared by adding four parts alkaline solution (100g sodium citrate and 5g NaOH in 500mL pure water) to one part 1.5 N hypochlorite solution (bleach). First, 0.1 mL phenol solution (20g phenol in 200mL 95% v/v ethyl alcohol) was added and the mixture was vortexed. Then, 0.1 nitroprusside solution (1g sodium nitroprusside in 200mL pure water) was added to the sample tubes and the solution was mixed. Next, 0.25mL of the oxidizing solution was added and the mixture was vortexed prior to covering the sample tubes with aluminum foil and allowing the solutions to incubate for at least one hour. The solutions turned varying shades of blue, and optical densities of the solutions were measured using a spectrophotometer (670nm).
Standard solutions of known NH$_4^+$ concentrations were used to construct a calibration curve so that the NH$_4^+$ concentrations of the samples could be calculated from the absorbance data.

4.6. Determinations of the $\delta^{34}S$ of precipitation sulfate

Analyses of the $\delta^{34}S$ of precipitation sulfate were overseen by D. Ernest and A.J. Kaufman at the Stable Isotope Laboratory of the University of Maryland College Park. Approximately 0.5mg of dried BaSO$_4$ crystals were weighed into tin capsules. The capsules were dropped into an Elemental Analyzer to produce SO$_2$ for continuous flow mass spectrometric analyses. Most of the samples were run in duplicate. Duplicate NBS-127 sulfate standards were analyzed before and after each set of six samples to calculate the 1 $\sigma$ reproducibility, which was typically better than 0.5‰, and the offset from the sulfur isotope reference, VCDT, which is based on a troilite (FeS) from Canon Diablo meteorite, CDT (KROUSE and COPLEN, 1997). Sulfur isotope ratios are reported relative to VCDT in delta notation.

$$\delta^{34}S = \left( \frac{^{34}S/^{32}S}_{\text{sample}} - 1 \right) \times 1000 \text{‰}$$
5. Results

5.1. Meteorological and storm track data

Data from the National Climate Data Center revealed that a variety of storms were sampled (Table 1). The samples are organized and numbered in order of the date of sample collection. The start and end times for the precipitation events showed that the storms varied in length from a few hours to greater than a day. Precipitation types included rain (RA), snow (SN), thunderstorm (TS), vicinity thunderstorm (VCTS), and unknown or mixed precipitation (UP).

Storm track data determined using the NOAA HYSPLIT model showed that air masses approached Frederick, Maryland from several different directions (Table 1). The three-dimensional model results for storms are included in Appendix E. For some of the storms, air masses at 500m, 1000m, and 1500m above ground level moved towards Frederick in the same direction. For other storms, air masses at different elevations entered the region from different directions.

The storm track data did not exhibit a strong seasonal pattern. For each season, air masses moved into the area from several different directions. For example, for the storms sampled in Spring 2003, dominant directions of air mass movement included from the west (W), south (S), east (E), northeast (NE), west northwest (WNW), and southwest (SW).
### Table 1: Precipitation collection, meteorological, and storm track data.

Meteorological data was obtained from the National Climate Data Center. Abbreviations for precipitation types are rain (RA), snow (SN), thunderstorm (TS), vicinity thunderstorm (VCTS), and unknown or mixed precipitation (UP). Storm track data was determined using the NOAA HYSPLIT model. Abbreviations for directions of air mass movement include from the west (W), East (E), North (N), South (S). In some cases, these letters are combined to give more detailed information. For example, NW indicates from the northwest, and WNW indicates from the west northwest (more from the west than from the north). The table is continued on the following two pages.

<table>
<thead>
<tr>
<th>Sample # by date</th>
<th>Precip Start Time (Eastern US)</th>
<th>Precip End Time (Eastern US)</th>
<th>Precip Types</th>
<th>Portion of the storm collected</th>
<th>Back Trajectory Start Time (UTC)</th>
<th>Direction of Air Mass Movement</th>
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<tr>
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<td>W</td>
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<td>W</td>
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<td>E (500m), SE (1000m), and W (1500m)</td>
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<td>3/13/03 17:00</td>
<td>WSW</td>
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<td>from 4-7-03 11:15 to end</td>
<td>4/7/03 2:00</td>
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<tr>
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</tr>
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<td>entire</td>
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Table 1 (continued)

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<th>Sample # by date</th>
<th>Precip Start Time (Eastern US)</th>
<th>Precip End Time (Eastern US)</th>
<th>Precip Types</th>
<th>Portion of the storm collected</th>
<th>Back Trajectory Start Time (UTC)</th>
<th>Direction of Air Mass Movement</th>
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<tr>
<td>24</td>
<td>9/18/03 9:22</td>
<td>9/19/03 15:41</td>
<td>RA</td>
<td>from 9-18-03 at 18:00 to 9-18-03 at 22:00</td>
<td>9/18/03 16:00</td>
<td>E</td>
</tr>
<tr>
<td>25</td>
<td>9/18/03 9:22</td>
<td>9/19/03 15:41</td>
<td>RA</td>
<td>from 9-18-03 22:00 to end</td>
<td>9/18/03 20:00</td>
<td>E</td>
</tr>
<tr>
<td>26</td>
<td>9/22/03 15:21</td>
<td>9/23/03 6:25</td>
<td>RA, TS, VCTS</td>
<td>entire</td>
<td>9/22/03 13:00</td>
<td>SE</td>
</tr>
<tr>
<td>27</td>
<td>9/25/03 17:21</td>
<td>9/25/03 20:23</td>
<td>RA, TS, VCTS</td>
<td>entire</td>
<td>9/25/03 15:00</td>
<td>WSW</td>
</tr>
<tr>
<td>28</td>
<td>9/27/03 21:44</td>
<td>9/28/03 6:42</td>
<td>RA, TS, VCTS</td>
<td>entire</td>
<td>9/27/03 20:00</td>
<td>S</td>
</tr>
<tr>
<td>29</td>
<td>11/5/03 5:41</td>
<td>11/5/03 21:41</td>
<td>RA</td>
<td>entire</td>
<td>11/5/03 5:00</td>
<td>S</td>
</tr>
<tr>
<td>30</td>
<td>11/6/03 6:21</td>
<td>11/6/03 18:40</td>
<td>RA</td>
<td>entire</td>
<td>11/6/03 5:00</td>
<td>WSW</td>
</tr>
<tr>
<td>Sample # by date</td>
<td>Precip Start Time (Eastern US)</td>
<td>Precip End Time (Eastern US)</td>
<td>Precip Types</td>
<td>Portion of the storm collected</td>
<td>Back Trajectory Start Time (UTC)</td>
<td>Direction of Air Mass Movement</td>
</tr>
<tr>
<td>-----------------</td>
<td>-------------------------------</td>
<td>-------------------------------</td>
<td>--------------</td>
<td>--------------------------------</td>
<td>---------------------------------</td>
<td>--------------------------------</td>
</tr>
<tr>
<td>31</td>
<td>11/11/03 10:01</td>
<td>11/12/03 20:41</td>
<td>RA</td>
<td>entire</td>
<td>11/11/03 9:00</td>
<td>W</td>
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<tr>
<td>32</td>
<td>11/24/03 16:01</td>
<td>11/24/03 21:41</td>
<td>RA</td>
<td>entire</td>
<td>11/24/03 15:00</td>
<td>S</td>
</tr>
<tr>
<td>33</td>
<td>11/28/03 5:01</td>
<td>11/28/03 19:40</td>
<td>RA</td>
<td>entire</td>
<td>11/28/03 4:00</td>
<td>SSW</td>
</tr>
<tr>
<td>34</td>
<td>12/4/03 21:40</td>
<td>12/6/05 10:01</td>
<td>RA, SN, UP</td>
<td>entire</td>
<td>12/4/03 21:00</td>
<td>S (500m), SW (100m, 1500m)</td>
</tr>
<tr>
<td>35</td>
<td>12/10/03 13:21</td>
<td>12/11/03 8:19</td>
<td>RA, UP</td>
<td>entire</td>
<td>12/10/03 12:00</td>
<td>S</td>
</tr>
<tr>
<td>36</td>
<td>12/14/03 3:20</td>
<td>12/24/03 13:39</td>
<td>RA, SN, UP</td>
<td>entire (First storm 12-14-03 from 3:20 to 19:20, second storm 12-17-03 from 4:19 to 14:02, and third storm 12-24-03 from 00:20 to 13:39)</td>
<td>12/14/03 2:00</td>
<td>NW</td>
</tr>
<tr>
<td>37</td>
<td>1/5/04 7:40</td>
<td>1/5/04 14:02</td>
<td>RA</td>
<td>entire</td>
<td>1/5/04 6:00</td>
<td>SW</td>
</tr>
<tr>
<td>38</td>
<td>1/23/04 21:02</td>
<td>1/26/04 22:40</td>
<td>SN</td>
<td>entire</td>
<td>1/23/04 20:00</td>
<td>NW</td>
</tr>
<tr>
<td>39</td>
<td>2/3/04 6:40</td>
<td>2/3/04 14:20</td>
<td>RA, SN, UP</td>
<td>entire</td>
<td>2/3/04 6:00</td>
<td>E,S</td>
</tr>
<tr>
<td>40</td>
<td>2/5/04 20:40</td>
<td>2/6/04 19:20</td>
<td>RA, SN, UP</td>
<td>entire</td>
<td>2/5/04 19:00</td>
<td>NW</td>
</tr>
<tr>
<td>41</td>
<td>3/5/04 21:40</td>
<td>3/6/04 15:42</td>
<td>RA, TS, VCTS</td>
<td>entire</td>
<td>3/5/04 20:00</td>
<td>SW</td>
</tr>
<tr>
<td>42</td>
<td>3/18/04 18:20</td>
<td>3/19/04 9:40</td>
<td>RA, SN, VCTS</td>
<td>entire</td>
<td>3/18/04 17:00</td>
<td>W</td>
</tr>
<tr>
<td>43</td>
<td>3/31/04 21:42</td>
<td>4/3/04 12:41</td>
<td>RA, VCTS</td>
<td>entire</td>
<td>3/31/04 21:00</td>
<td>NE (500m), SW (1000m, 1500m)</td>
</tr>
<tr>
<td>44</td>
<td>4/12/04 5:20</td>
<td>4/13/04 18:40</td>
<td>RA, VCTS</td>
<td>entire</td>
<td>4/12/04 4:00</td>
<td>local NE</td>
</tr>
<tr>
<td>46</td>
<td>5/1/04 20:20</td>
<td>5/3/04 19:40</td>
<td>RA</td>
<td>entire</td>
<td>5/1/04 18:00</td>
<td>SSW</td>
</tr>
</tbody>
</table>
5.2. AgNO₃/decomposition method data

5.2.1. Standards analyzed by AgNO₃/decomposition methods

The results of the experiments of dissolved standards taken through the wet chemical procedure showed that $\delta^{15}$N values were not affected by the wet chemical procedure, while $\delta^{18}$O values of the processed standards were significantly lower than the standards taken directly from their vials (Table 2). The results of the blank experiment produced 0.6mg of a dark brown solid. Analyses of %C content using the elemental analyzer revealed the presence of carbon. The dissolved standards had been contaminated by an oxygen containing compound during the analytical procedure.

Table 2: Data obtained for the standard solutions put through the wet chemical procedure. The standard USGS-34 has published values of $\delta^{18}$O = -27.5‰ and $\delta^{15}$N = -1.87‰. USGS-35 has published values of $\delta^{18}$O = +57.5‰ and $\delta^{15}$N = +2.86‰.

<table>
<thead>
<tr>
<th>Standard</th>
<th>Freeze-Dried Sample Description</th>
<th>mmol NO₃ used</th>
<th>mmol NO₃ recov.</th>
<th>% yield mmol NO₃</th>
<th>$\delta^{15}$N AIR (%o) ±0.5 (1σ)</th>
<th>$\delta^{18}$O VSMOW (%o) ±0.5 (1σ)</th>
<th>$\Delta^{17}$O (%o) ±0.05 (1σ)</th>
<th>% C ±0.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>USGS-34 (KNO₃) white</td>
<td>0.251</td>
<td>0.233</td>
<td>92.8%</td>
<td>-1.5</td>
<td>-26.1</td>
<td>0.86</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>USGS-34 (KNO₃) white, grayish brown tinge</td>
<td>0.049</td>
<td>0.052</td>
<td>104.7%</td>
<td>-1.8</td>
<td>-21.6</td>
<td>0.55</td>
<td>1.82</td>
<td></td>
</tr>
<tr>
<td>USGS-35 (NaNO₃) white, slightly tan</td>
<td>0.249</td>
<td>0.221</td>
<td>88.7%</td>
<td>2.9</td>
<td>56.7</td>
<td>21.60</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>USGS-35 (NaNO₃) white, slightly tan</td>
<td>0.055</td>
<td>0.052</td>
<td>93.7%</td>
<td>2.5</td>
<td>55.3</td>
<td>21.23</td>
<td>1.45</td>
<td></td>
</tr>
</tbody>
</table>
The measured $\delta^{18}O$ values represented the precipitation samples plus the analytical blank. The following mass-balance calculation was used to determine the magnitude and isotopic composition of the analytical blank (HAYES, 2004). ($N$ terms represent molar quantities, $\delta$ represents $\delta^{18}O$, $\Sigma$ represents the sample prepared for analysis, $s$ represents the sample, and $b$ represents the blank.)

$$N_\Sigma \delta_\Sigma = N_s \delta_s + N_b \delta_b$$

The substitution of $N_\Sigma - N_b$ for $N_s$ and the rearrangement of the equation gave the following equation in the form of $y = mx + b$.

$$\delta_\Sigma = \delta_s - N_b(\delta_s - \delta_b)/N_\Sigma$$

If the results of multiple analyses were plotted for $\delta_\Sigma$ vs. $1/N_\Sigma$, the intercept would be $\delta_s$. In the case of the standard experiments, the values of $\delta_s$ were known. Therefore, for both the USGS-34 and USGS-35 experiments, it was possible to plot the measured $\delta^{18}O$ values for each prepared aliquot versus the inverse values of the molar quantities obtained with the published values of the standards as the intercepts. The molar quantities of oxygen were calculated by dividing the masses of the prepared samples by the molar mass of AgNO$_3$ 169.91g/mol and multiplying by three moles oxygen for every one mole of AgNO$_3$. Since the samples were not pure silver nitrate, this calculation introduces some uncertainty. A linear regression was performed on the data for each standard, and the intersection of the two lines yielded the $\delta^{18}O$ of the blank and molar quantity of oxygen from the blank. The blank consisted of 0.015mmol oxygen and had a $\delta^{18}O$ of 34.6‰.
5.2.2. Observations on prepared silver nitrates

Three observations provided evidence that the prepared silver nitrates were impure. First, whereas silver nitrate crystals should be colorless, the prepared silver nitrates exhibited colors ranging from white to very dark brown (Table 3). Second, whereas pure silver nitrate should have a molar ratio of nitrogen to oxygen of 0.33, the N/O of the prepared silver nitrates ranged from 0.16 to 0.31 (Table 3). Molar ratios were calculated from the weight percent nitrogen and oxygen data obtained using the thermal conversion elemental analyzer and continuous flow mass spectrometer. Third, whereas pure silver nitrate does not contain carbon, the prepared silver nitrates contained 0.97 to 3.03%C (Table 3). Since organic matter typically contains approximately 40% oxygen, the presence of carbon provides evidence for the presence of an oxygen-containing contaminant in the prepared silver nitrates.

The silver nitrates prepared from precipitation samples contained more carbon than could be attributed to the analytical blank. In addition to the organic compounds added during the wet chemical procedure, there was likely a second source of carbon (and oxygen) in the prepared silver nitrates. The %C results for the standard experiments (Table 2) showed that carbon content is roughly proportion to the moles of sample. In the experiments in which more than 0.2mmoles of nitrate salts were dissolved, the prepared silver nitrates had approximately 0.25% carbon. In the experiments in which only approximately 0.05mmoles of nitrate salts were dissolved, the prepared silver nitrates still had less than 2% carbon. For several of the precipitation nitrate samples that yielded more than 0.2mmoles, the %C values were significantly larger than 0.25% (Table 3), providing evidence of a second oxygen-containing contaminant, which is described in more detail in section 6.1.
Table 3: Observations on the silver nitrates prepared from precipitation samples. Weight percent nitrogen and oxygen data was determined during separate runs using the thermal conversion elemental analyzer and continuous flow mass spectrometry. Molar N/O values were calculated using the weight percent data with an overall uncertainty of 0.08.

<table>
<thead>
<tr>
<th>Sample # by date</th>
<th>Precip Start Date</th>
<th>AgNO₃ (mmol)</th>
<th>Freeze-Dried Sample Description</th>
<th>Wt% N (TC/EA)</th>
<th>Wt% O (TC/EA)</th>
<th>N/O ±0.08</th>
<th>Wt% C (EA) ±0.05%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2/06/03</td>
<td>0.036</td>
<td>dark brown, sticky</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2/15/03</td>
<td>0.177</td>
<td>med-dark brown granular</td>
<td>8.33</td>
<td>29.67</td>
<td>0.25</td>
<td>2.93</td>
</tr>
<tr>
<td>4</td>
<td>3/13/03</td>
<td>0.190</td>
<td>med-dark brown</td>
<td>9.07</td>
<td>26.10</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4/07/03</td>
<td>0.163</td>
<td>med-dark brown</td>
<td>9.51</td>
<td>27.19</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>5/15/03</td>
<td>0.523</td>
<td>med-dark brown granular</td>
<td>6.09</td>
<td>27.11</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>5/15/03</td>
<td>0.357</td>
<td>med-dark brown, fluffy</td>
<td>8.77</td>
<td>29.87</td>
<td>0.26</td>
<td>2.32</td>
</tr>
<tr>
<td>9</td>
<td>5/16/03</td>
<td>0.164</td>
<td>dark brown</td>
<td>9.24</td>
<td>27.60</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>5/23/03</td>
<td>0.385</td>
<td>med-dark brown, fluffy</td>
<td>8.92</td>
<td>29.17</td>
<td>0.27</td>
<td>1.70</td>
</tr>
<tr>
<td>14</td>
<td>6/13/03</td>
<td>0.077</td>
<td>medium brown</td>
<td>8.21</td>
<td>28.46</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>7/03/03</td>
<td>0.298</td>
<td>golden tan</td>
<td>4.80</td>
<td>25.47</td>
<td>0.16</td>
<td>2.22</td>
</tr>
<tr>
<td>18</td>
<td>7/22/03</td>
<td>0.058</td>
<td>dark brown</td>
<td>6.09</td>
<td>31.22</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>8/12/03</td>
<td>0.039</td>
<td>dark brown, sticky</td>
<td>7.18</td>
<td>27.66</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>9/01/03</td>
<td>0.037</td>
<td>dark brown, sticky</td>
<td>5.99</td>
<td>29.36</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>9/15/03</td>
<td>0.076</td>
<td>slightly tan, fluffy</td>
<td>5.26</td>
<td>23.25</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>9/18/03</td>
<td>0.034</td>
<td>tan, fluffy</td>
<td>7.65</td>
<td>27.80</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>9/22/03</td>
<td>0.046</td>
<td>vanilla tan</td>
<td></td>
<td>29.88</td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>11/24/03</td>
<td>0.042</td>
<td>grayish tan</td>
<td>7.95</td>
<td>27.95</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>12/04/03</td>
<td>0.130</td>
<td>white</td>
<td>8.74</td>
<td>26.97</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>12/10/03</td>
<td>0.062</td>
<td>dark</td>
<td>7.30</td>
<td>25.59</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>1/05/04</td>
<td>0.105</td>
<td>white, powdery</td>
<td>9.08</td>
<td>26.23</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>1/23/04</td>
<td>0.245</td>
<td>white, fluffy</td>
<td>8.96</td>
<td>26.84</td>
<td>0.29</td>
<td>0.97</td>
</tr>
<tr>
<td>40</td>
<td>2/05/04</td>
<td>0.067</td>
<td>white</td>
<td>7.84</td>
<td>26.63</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>3/05/04</td>
<td>0.132</td>
<td>caramel, granular</td>
<td>7.79</td>
<td>26.29</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>3/18/04</td>
<td>0.164</td>
<td>white, fluffy</td>
<td>8.49</td>
<td>25.45</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>3/31/04</td>
<td>0.498</td>
<td>grayish tan</td>
<td>6.94</td>
<td>24.77</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>4/12/04</td>
<td>0.147</td>
<td>caramel</td>
<td>6.67</td>
<td>23.95</td>
<td>0.24</td>
<td>3.03</td>
</tr>
</tbody>
</table>
5.2.3. Samples analyzed by AgNO₃/decomposition methods

The δ¹⁵N values for Frederick, Maryland precipitation nitrate obtained using the AgNO₃/decomposition method ranged from -5.1±0.5‰ to +5.9±0.5‰ (Table 4). Contributions of nitrogen from the analytical blank were negligible, and therefore no blank correction was necessary. The highest δ¹⁵N values occurred in the winter and the lowest δ¹⁵N values occurred in the summer.

Table 4: Precipitation nitrate isotope ratios obtained using the AgNO₃/decomposition method. It was unnecessary to apply a blank correction to the δ¹⁵N data. There was an analytical blank correction applied to δ¹⁸O and Δ¹⁷O to account for oxygen-containing contaminants in the prepared silver nitrates.

<table>
<thead>
<tr>
<th>Sample # by date</th>
<th>Precipitation Start Date</th>
<th>δ¹⁵N_AIR (%)</th>
<th>δ¹⁸O_VSMOW (%)</th>
<th>&quot;Analytical Blank Corrected&quot; δ¹⁸O_VSMOW (%)</th>
<th>Δ¹⁷O (%)</th>
<th>&quot;Analytical Blank Corrected&quot; Δ¹⁷O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2/06/03</td>
<td>-5.1</td>
<td>74.5</td>
<td>-5.1 (1σ)</td>
<td>30.12</td>
<td>30.98</td>
</tr>
<tr>
<td>2</td>
<td>2/15/03</td>
<td>-3.3</td>
<td>80.2</td>
<td>81.5 (1σ)</td>
<td>30.10</td>
<td>31.71</td>
</tr>
<tr>
<td>4</td>
<td>3/13/03</td>
<td>-2.3</td>
<td>79.5</td>
<td>81.9 (1σ)</td>
<td>30.10</td>
<td>31.71</td>
</tr>
<tr>
<td>5</td>
<td>4/07/03</td>
<td>-1.2</td>
<td>74.2</td>
<td>77.1 (1σ)</td>
<td>26.47</td>
<td>28.37</td>
</tr>
<tr>
<td>7</td>
<td>5/15/03</td>
<td>-3.0</td>
<td>53.1</td>
<td>53.3 (1σ)</td>
<td>16.59</td>
<td>16.75</td>
</tr>
<tr>
<td>8</td>
<td>5/15/03</td>
<td>-3.9</td>
<td>67.1</td>
<td>68.2 (1σ)</td>
<td>23.00</td>
<td>23.77</td>
</tr>
<tr>
<td>9</td>
<td>5/16/03</td>
<td>-0.9</td>
<td>64.5</td>
<td>66.8 (1σ)</td>
<td>23.54</td>
<td>25.36</td>
</tr>
<tr>
<td>11</td>
<td>5/23/03</td>
<td>-1.7</td>
<td>74.4</td>
<td>75.5 (1σ)</td>
<td>21.93</td>
<td>22.54</td>
</tr>
<tr>
<td>14</td>
<td>6/13/03</td>
<td>-2.9</td>
<td>55.5</td>
<td>57.0 (1σ)</td>
<td>17.81</td>
<td>19.02</td>
</tr>
<tr>
<td>15</td>
<td>7/03/03</td>
<td>-3.5</td>
<td>42.5</td>
<td>42.6 (1σ)</td>
<td>15.08</td>
<td>15.33</td>
</tr>
<tr>
<td>18</td>
<td>7/22/03</td>
<td>-5.1</td>
<td>50.6</td>
<td>52.1 (1σ)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
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<td>62.6</td>
<td>67.4 (1σ)</td>
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<tr>
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<td>61.9</td>
<td>65.2</td>
<td>20.96 (1σ)</td>
<td>23.47</td>
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<td>73.8</td>
<td>79.0 (1σ)</td>
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<td>12/04/03</td>
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<td>79.4 (1σ)</td>
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<tr>
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<td>57.9 (1σ)</td>
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<td>65.1 (1σ)</td>
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</tbody>
</table>
The oxygen isotope data from the AgNO₃/decomposition method required an analytical blank correction. As described in section 5.2.1., there was approximately 0.015 moles of an oxygen-containing contaminant added during the wet chemical procedure. The δ¹⁸O of the contaminant was determined to be 34.6‰, and the Δ¹⁷O was assumed to be zero. Table 4 shows the δ¹⁸O and Δ¹⁷O of precipitation nitrate obtained using the AgNO₃/decomposition method before and after the analytical blank correction. The δ¹⁸O of precipitation nitrate ranged from +42.6±0.5‰ to +81.9±0.5‰ and the Δ¹⁷O of precipitation nitrate ranged from +15.33±0.05‰ to +31.71±0.05‰ using the AgNO₃/decomposition method. The highest δ¹⁸O and Δ¹⁷O values occurred in the winter and the lowest δ¹⁸O and Δ¹⁷O occurred in the summer, but there was significant within-season variation.

5.3. Denitrifier method data

Analysis of precipitation nitrate samples using the denitrifier method yielded results of 3.6±0.2‰ to +7.1±0.2‰ for δ¹⁵N (Table 5). The δ¹⁸O of precipitation nitrate obtained using the denitrifier method ranged from +61.6±0.3‰ to +86.8±0.3‰ (Table 5). Both δ¹⁵N and δ¹⁸O exhibited a strong seasonal pattern with the highest values in the winter and the lowest values in the summer, and intermediate values in the spring and autumn. There was minimal within-season variation in the δ¹⁵N and δ¹⁸O data from the denitrifier method.
Table 5: Precipitation nitrate isotope ratios obtained using the denitrifier method.

<table>
<thead>
<tr>
<th>Sample # by date</th>
<th>Precipitation Start Date</th>
<th>$\delta^{15}$N_AIR (‰) ±0.2</th>
<th>$\delta^{18}$O_VSMOW (‰) ±0.3</th>
</tr>
</thead>
<tbody>
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<td>86.81</td>
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<td>85.55</td>
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<td>05/15/03</td>
<td>-3.63</td>
<td>69.98</td>
</tr>
<tr>
<td>10</td>
<td>05/20/03</td>
<td>-1.82</td>
<td>77.63</td>
</tr>
<tr>
<td>12</td>
<td>06/08/03</td>
<td>-3.02</td>
<td>64.58</td>
</tr>
<tr>
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<td>06/12/03</td>
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</tr>
<tr>
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<td>06/13/03</td>
<td>-0.87</td>
<td>61.57</td>
</tr>
<tr>
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<td>07/03/03</td>
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<td>71.14</td>
</tr>
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<td>07/09/03</td>
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</tr>
<tr>
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<td>02/03/04</td>
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<td>80.59</td>
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<tr>
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<td>03/18/04</td>
<td>3.12</td>
<td>81.27</td>
</tr>
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<td>04/12/04</td>
<td>1.50</td>
<td>79.44</td>
</tr>
<tr>
<td>46</td>
<td>05/01/04</td>
<td>1.99</td>
<td>64.63</td>
</tr>
</tbody>
</table>

5.4. Ion concentration data

There were large ranges of ammonium, sulfate, and nitrate+nitrite concentrations for the Frederick precipitation samples (Table 6). Ammonium concentrations ranged from 8±5µM to 205±5µM. Sulfate concentrations ranged from 7±5µM to 75±5µM, and nitrate + nitrite concentrations ranged from 2.1±0.2µM to 173.6±0.2µM. There were no strong linear relationships between ammonium, sulfate, or nitrate+nitrite concentrations and date. Although precipitation samples with high nitrate+nitrite concentrations generally also had high ammonium and sulfate concentrations, there were no significant linear correlations between the different...
concentrations. Furthermore, there was no apparent relationship between concentration data and nitrate isotope ratios.

Table 6: Ion concentration data and the $\delta^{34}$S of precipitation sulfate.

<table>
<thead>
<tr>
<th>Sample # by date</th>
<th>Precipitation Start Date</th>
<th>$[\text{NH}_4^+]$ (µM) ±5 (color)</th>
<th>$[\text{SO}_4^{2-}]$ (µM) ±5 (IC)</th>
<th>$[\text{NO}_3^-]$ (µM) ±5 (IC)</th>
<th>$[\text{NO}_3^-] + [\text{NO}_2^-]$ (µM ±0.2 (NOx box)</th>
<th>$\delta^{34}$S ±0.5 (%)</th>
</tr>
</thead>
<tbody>
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<td>02/07/03</td>
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<td>1 ±5</td>
<td>15.7 ±5</td>
<td>6.6</td>
<td></td>
</tr>
<tr>
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<td>30 ±5</td>
<td>4 ±5</td>
<td>37.4 ±5</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>02/28/03</td>
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<td>6.1</td>
<td></td>
</tr>
<tr>
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<td>67 ±5</td>
<td>5.8</td>
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</tr>
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<td>9 ±5</td>
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</tr>
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<td></td>
</tr>
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76
Table 6 (continued)

<table>
<thead>
<tr>
<th>Sample # by date</th>
<th>Precipitation Start Date</th>
<th>[NH₄⁺] (µM) ±5 (color)</th>
<th>[SO₄²⁻] (µM) ±5 (IC)</th>
<th>[NO₃⁻] (µM) ±5 (IC)</th>
<th>[NO₃⁻] + [NO₃⁻] (µM) ±0.2 (NO₃ box)</th>
<th>δ³⁴S (‰)</th>
<th>1σ for δ³⁴S (‰)</th>
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</tbody>
</table>

5.5. δ³⁴S of precipitation sulfate

With the exception of three samples collected during Hurricane Isabel in September 2003, the δ³⁴S of precipitation sulfate ranged from 4.4±0.3‰ to 7.6±0.4‰ (Table 6). The mean δ³⁴S value for Frederick, Maryland precipitation sulfate during the sampling period was 5.8‰ ± 0.8‰ (1σ for the sample measurements). The δ³⁴S values for the three Isabel samples in order of the storm’s progression were 8.4±0.5‰, 8.5±0.5‰, and 12.3±0.5‰. The higher δ³⁴S values of the hurricane samples could be the result of increased oceanic contributions. Whereas the δ¹⁵N of precipitation nitrate varied seasonally, the δ³⁴S of precipitation sulfate remained relatively constant. There was no correlation between δ³⁴S and sulfate concentrations or δ³⁴S and δ¹⁵N.
6. Discussion

6.1. Comparison of the AgNO₃/decomposition and denitrifier methods

Many authors have discussed the possibility or presence of dissolved organic matter in the nitrate salts used for decomposition analyses (e.g., Kendall, 1998). Recently, Heaton and coworkers (2004) reported that organic contaminants in silver nitrates prepared from arctic snow samples led to decreases in measured $\delta^{18}O$ values and used C/N and N/O data to determine the extent of organic contamination. Here, we present a method assessment based on a comparison of precipitation nitrate isotope measurements obtained by the AgNO₃/decomposition and denitrifier methods.

Previous comparisons of nitrate salt/decomposition and the denitrifier method identified a tendency for the denitrifier method to overestimate $\delta^{15}N$ by as much as 1-2‰ for nitrates with non-zero $\Delta^{17}O$ (Coplen et al., 2004). In this study, we took $\Delta^{17}O$ into consideration in our data reduction and re-evaluated the $\delta^{15}N$ of the denitrifier and AgNO₃/decomposition methods. We also considered whether dissolved organic nitrogen compounds interfered with $\delta^{15}N$ measurements.

There were significant differences between the $\delta^{15}N$ values obtained using the AgNO₃/decomposition and denitrifier methods. In general, measurements of $\delta^{15}N$ using the denitrifier method were higher than those obtained using the AgNO₃/decomposition method. In some cases, the difference between the two methods was greater than -2.5‰. There was a linear relationship between the $\delta^{15}N$
values obtained using the AgNO₃/decomposition and denitrifier methods \( (r^2 \approx 0.9) \) (Figure 8).

Figure 8: \( \delta^{15}N \) versus \( \delta^{15}N \) obtained using the AgNO₃/decomposition and denitrifier techniques. Error bars represent 1σ mass spectrometric reproducibility of nitrate standards. Data from the AgNO₃/decomposition method are averages of duplicate analyses. The solid line is the 1:1 line, and the dashed line shows the linear regression of the data \( (y=0.79x+1.09, r^2=0.89) \).

The \( \delta^{15}N \) of the prepared silver nitrates may have been affected by organic nitrogen. While the organic contaminant from the analytical procedure had negligible amounts of nitrogen, organic nitrogen from the precipitation itself may have affected \( \delta^{15}N \) values. Heaton et al. (2004) reported that increased organic contamination, determined by measured C/N ratios, coincided with slightly higher \( \delta^{15}N \) values. In their study, the \( \delta^{15}N \) values of arctic snow NO₃⁻ exhibited a range from -18 to -7‰, which is significantly lower than the range of \( \delta^{15}N \) values for Maryland precipitation nitrate. Thus, the magnitude and direction of the effect of organic contaminants on
the $\delta^{15}N$ of Maryland precipitation NO$_3^-$ would not necessarily be the same. In order for organic contaminants to cause $\delta^{15}N$ measurements to be lower than the actual $\delta^{15}N$ of Maryland precipitation NO$_3^-$, the $\delta^{15}N$ of the organic contaminant would have to be lower than -4‰. The observed differences in $\delta^{15}N$ may also be the result of a scale contraction in the denitrifier method results.

Although both the AgNO$_3$/decomposition and denitrifier methods measure the $\delta^{18}O$ of nitrate standards accurately and precisely (CascioTTI et al., 2002), previous studies reveal there may be differences between atmospheric nitrate measurements obtained by these techniques. The $\delta^{18}O$ of atmospheric nitrate measured by nitrate salt/ decomposition methods ranges from +17 to +77‰, whereas the $\delta^{18}O$ of atmospheric nitrate measured by denitrifier ranges from +57 to +90‰. The lower and mid-range values of the nitrate salt/decomposition methods may be the result of organic compounds with lower $\delta^{18}O$ values contaminating prepared nitrate salts (KENDALL, 1998). To date, there have been no published comparisons of the isotope ratios of atmospheric nitrate measured by the AgNO$_3$/decomposition and the denitrifier methods. Analyzing precipitation nitrate from Frederick, Maryland by both methods provided a unique test for the effect of organic contaminants on isotope ratio measurements.

There were large and inconsistent differences between the $\delta^{18}O$ measurements obtained using the AgNO$_3$/ decomposition and denitrifier methods. In general, the $\delta^{18}O$ values from the denitrifier method were significantly higher than from the AgNO$_3$/decomposition method. The differences between the two methods were inconsistent, and some of the differences between measurements were nearly 30‰.
There was not a strong linear correlation (0.41) between the δ^{18}O values measured by the two methods (Figure 9).

![Graph showing δ^{18}O versus δ^{18}O obtained using the AgNO₃/decomposition and denitrifier techniques. Error bars represent 1σ mass spectrometric reproducibility of nitrate standards. The data obtained using the AgNO₃/decomposition method are averages of duplicate analyses. The solid line is the 1:1 line, and the dashed line shows the linear regression of the data (y=0.37x+49.63, r^2=0.41).]

The most plausible explanation for the differences between the δ^{18}O obtained using the two techniques is the effect of organic contamination on the δ^{18}O results from the AgNO₃/decomposition method. “On-line” combustion methods accurately measured the δ^{18}O of the total oxygen in the samples introduced to the TC/EA. When impure samples were analyzed, the results were actually the weighted sums of the contaminants and the precipitation NO₃⁻.

Heaton and coworkers (2004) considered the deviation of N/O of the prepared silver nitrates from the N/O of pure silver nitrate (0.33) in order to correct δ^{18}O
values. The prepared silver nitrates were a mix of snow nitrate and an organic contaminant. Heaton and coworkers used $+25\%$ as the value for the organic end-member, which was the $\delta^{18}O$ of “brown organic particles” present in their prepared silver nitrates. On a plot of $\delta^{18}O$ of silver nitrates versus measured N/O, they extrapolated from an organic end-member through sample measurements to N/O of 0.33 to determine the $\delta^{18}O$ of uncontaminated arctic snow nitrate. Uncorrected $\delta^{18}O$ values ranged from $+42.1$ to $+70.8\%$, while the corrected $\delta^{18}O$ values ranged from approximately $+60$ to $+85\%$ (Heaton et al., 2004). The correction method of Heaton and others (2004) was applied to the data set for Frederick precipitation NO$_3^-$ samples (Figure 10).

Figure 10: Data correction method used by Heaton et al. (2004) applied to Frederick, Maryland precipitation samples. Error bars for N/O are 0.08 (1$\sigma$) and were calculated as described in the text. Error bars for $\delta^{18}O$, which represent the 1$\sigma$ reproducibility of standards, are smaller than the data symbols.
The corrected range of $\delta^{18}$O values was $+52\%$ to $+101\%$ with uncertainties related to the precision of N/O. Heaton and coworkers (2004) did not include error bars on their N/O or describe ways to address uncertainties associated with their correction method. In our study, N and O were measured during separate runs using the TC/EA and continuous flow mass spectrometry. We determined the uncertainty of N/O by dividing randomly selected mole% N values of nitrate standards (calculated from measured wt% O values) by randomly selected mole% O values of nitrate standards (calculated from measured wt % O values). One standard deviation of the calculated N/O values was 0.08. The uncertainty on the “corrected range” of $\delta^{18}$O values was determined by extrapolating through the error bars to N/O of 0.33. Considering the uncertainties of N/O, the range of $\delta^{18}$O values is from +50 to $+113\%$. This calculated range is significantly wider than the range measured for $\delta^{18}$O using the denitrifier method.

6.2. Negligible effect of scavenging processes on isotope ratios

When considering the isotopic composition of precipitation NO$_3^-$, which is only a portion of the total NO$_3^-$ deposited from the atmosphere, there are additional variables to consider. Reactive nitrogen compounds are constantly being removed from air masses via dry deposition. Recent studies on the $\delta^{15}$N of size-segregated aerosol NO$_3^-$ (YEATMAN et al., 2001; YEATMAN et al., 2001; YEATMAN et al., 2001) have also taken into consideration the report by Spokes and coworkers (2000) that dry deposition and precipitation selectively removes coarse-mode aerosol NO$_3^-$. Furthermore, as Eriksson (1959) first emphasized, precipitation does not
quantitatively remove NO$_x$ from the atmosphere, and isotope fractionation likely occurs during scavenging. Heaton (1987) showed that the amount of recent rainfall had an effect on the $\delta^{15}$N of precipitation NO$_3^-$. Precipitation NO$_3^-$ from storms that followed periods of heavy precipitation exhibited lower $\delta^{15}$N values than precipitation NO$_3^-$ from events that occurred after periods of lighter precipitation. Within storm variations in the $\delta^{15}$N of precipitation NO$_3^-$ have also been reported (Heaton, 1987; Moore, 1974). While the results of Moore (1974) were not straightforward, Heaton (1987) found that during the course of a rain event, there was an increase in the $\delta^{15}$N of precipitation NO$_3^-$. In addition, a study in Guiyang, China (Xiao and Liu, 2002) showed that mean $\delta^{15}$N values for light rainfalls were significantly lower than the mean $\delta^{15}$N for heavy rainfalls, although the causes for this difference were unclear.

If in- and below-cloud scavenging processes have a major effect on isotope ratios, then there may be a relationship between the amounts of precipitation and the $\delta^{15}$N, $\delta^{18}$O, and $\Delta^{17}$O values. There may also be a relationship between the amounts of precipitation recently fallen and the isotope ratios. Concentration data may also provide information useful for assessing the role of scavenging processes. Scavenging processes may contribute to a relationship between ion concentrations, but there are numerous factors that influence concentrations that likely affect different ions in variable ways. Heavy precipitation events may yield lower ion concentrations than light precipitation. The time between precipitation events may also influence ion concentrations because wet periods minimize the build up of trace gases and aerosols and because less frequent washout during dry periods leads to higher ion concentrations in individual precipitation events. Rates of dry deposition, which are
influenced by many factors, may also affect ion concentrations in precipitation because they control the background atmospheric NO\textsubscript{y} levels.

Although the role of below cloud scavenging processes is difficult to assess, there is no evidence that scavenging processes have a major effect on isotope ratios. The lack of correlation between concentration data and between concentration and isotope ratios supports the hypothesis that scavenging processes were unlikely the primary control on isotopic compositions.

Previous studies considered the effect of recent rainfall on nitrogen isotope ratios. Heaton (1987) showed that $\delta^{15}$N values were influenced by the amount of recent rainfall. It was not possible to evaluate our data using amounts of recent rainfall because quantitative rainfall totals were unavailable from nearby weather stations (see section 4.2). For the most part, the sampling period for the Frederick, Maryland study was characterized by frequent rain events. It would be interesting to compare this set of samples to samples collected during drier sampling periods.

There was one instance in which we were able to evaluate isotopic changes during a storm. For the storm collected from 5-15-03 to 5-18-03, there were separate collections of the first part of the storm and the second part of the storm. Precipitation nitrate from the second part of the storm had a higher $\delta^{15}$N value than the first part of the storm. The observation of higher $\delta^{15}$N values as the storm progressed were consistent with the trend observed by Heaton (1987). One explanation for lower $\delta^{15}$N values later in the storm may be that precipitation removes coarse-fraction aerosol NO\textsubscript{3}\textsuperscript{-}, which tend to have lower $\delta^{15}$N values (closer to precipitation NO\textsubscript{3}\textsuperscript{-}), more readily than fine-fraction aerosol NO\textsubscript{3}\textsuperscript{-}, which generally
have higher $\delta^{15}\text{N}$ values (Freyer, 1991). As storms progress, there is less coarse-fraction aerosol NO$_3^-$ remaining in the atmosphere. With less coarse-fraction aerosol NO$_3^-$ contributing to precipitation NO$_3^-$, the $\delta^{15}\text{N}$ values of precipitation NO$_3^-$ decrease. Other causes for this effect may be due to isotope fractionation associated with the dissolution of NO$_y$ species into rain droplets.

6.3. Influences on the $\delta^{15}\text{N}$ of precipitation nitrate

Both the AgNO$_3$/decomposition and denitrifier methods revealed seasonal variation in the $\delta^{15}\text{N}$ of precipitation nitrate from Frederick, Maryland (Figure 11). Values in the winter were significantly higher than values in summer.

![Figure 11: The $\delta^{15}\text{N}$ of precipitation nitrate versus date for the AgNO$_3$/decomposition and denitrifier methods. Error bars represent the $1\sigma$ reproducibility of nitrate standards, and error bars for the denitrifier method are smaller than the data symbols. The data for the AgNO$_3$/ decomposition method are averages of duplicate analyses.](image)
The $\delta^{15}\text{N}$ of precipitation nitrate may reflect the $\delta^{15}\text{N}$ of precursor NO$_x$ and/or nitrogen isotope fractionation processes. If the $\delta^{15}\text{N}$ of precursor NO$_x$ is the major factor determining the $\delta^{15}\text{N}$ of atmospheric NO$_3^-$, then the seasonal variation may be due to changes in the dominant NO$_x$ formation processes. There may also be a relationship between the $\delta^{15}\text{N}$ of precipitation nitrate and storm track data. A seasonal pattern in air mass movements could possibly be the cause for the seasonal variations in $\delta^{15}\text{N}$. In addition, if the precursor NO$_x$ and SO$_x$ come from similar sources and if sources are key in understanding the isotopic compositions of precipitation nitrate and sulfate, then there may also be a relationship between the $\delta^{15}\text{N}$ of nitrate and the $\delta^{34}\text{S}$ of sulfate in the precipitation. On the other hand, if there are no seasonal patterns in NO$_x$ sources or storm track data, then the $\delta^{15}\text{N}$ of NO$_x$ of precipitation nitrate may vary seasonally as a result of seasonal changes in atmospheric chemistry that affect nitrogen isotope fractionation.

6.3.1. Effect of precursor NO$_x$ on the $\delta^{15}\text{N}$ of precipitation nitrate

If the majority of NO$_x$ is deposited in the region where the NO$_x$ was produced, then the $\delta^{15}\text{N}$ of atmospheric nitrate would reflect the $\delta^{15}\text{N}$ of the precursor NO$_x$. Since there is evidence that NO$_x$ produced by different processes have characteristic $\delta^{15}\text{N}$ ranges (HEATON, 1987; 1990), the $\delta^{15}\text{N}$ of atmospheric NO$_3^-$ could provide information about the relative significance of different NO$_x$ sources (HASTINGS et al., 2003; RUSSELL et al., 1998). While NO$_x$ produced by different processes may also have different oxygen isotope ratios (KENDALL, 1998), the $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ of atmospheric NO$_3^-$ most likely do not reveal the signature of the precursor NO$_x$. 
because oxygen atoms are transferred back and forth from O₃ during NOₓ cycling (HASTINGS et al., 2003; MICHALSKI et al., 2003).

The δ¹⁵N of total NOₓ introduced to a particular air mass (δ¹⁵Nₚ) can be represented as the weighted sum of the δ¹⁵N of NOₓ by the major producers, including automobiles (δ¹⁵Nₐ), power plants (δ¹⁵Nₚₚ), non-utility industries (δ¹⁵Nᵢ), biomass burning (δ¹⁵Nᵦᵦ), microbial production (δ¹⁵Nᵦᵦᵦ), and lightning (δ¹⁵Nᵢ), by

\[ \delta^{15}N_T \times N_T \approx \delta^{15}N_a \times N_a + \delta^{15}N_{pp} \times N_{pp} + \delta^{15}N_i \times N_i + \delta^{15}N_{bb} \times N_{bb} + \delta^{15}N_{mp} \times N_{mp} + \delta^{15}N_l \times N_l, \]

where N is the number of moles of NOₓ or the fraction of the total NOₓ.

According to the Maryland Department of the Environment (M.D.E., 2002-2005), approximately 46% of NOₓ in the Baltimore area in the summer of 1990 was produced by internal combustion engines in “off-road” and “on-road” mobile sources, and 38% was generated by power plants. Manufacturing industries accounted for roughly 8% of the NOₓ and the remaining 8% was attributed to unlisted sources. The mass balance calculation for Maryland precipitation nitrate using these estimates can be written as

\[ \delta^{15}N_T \approx \delta^{15}N_a \times 0.46 + \delta^{15}N_{pp} \times 0.38 + \delta^{15}N_i \times 0.08 + \delta^{15}N_{unlisted sources} \times 0.08 \]

Different processes may produce NOₓ with characteristic nitrogen isotope compositions (section 3.3.1). In summary, measurements of automobile exhaust range from −13‰ to +2‰, while data on coal-fired power plant exhaust ranges from +5 to +13‰. Hoering (1957) provided evidence that the δ¹⁵N of electrical discharge and possibly lightning NOₓ is near 0‰, and researchers have speculated that the δ¹⁵N of microbial NOₓ is negative and potentially lower than −15‰ (e.g., Moore, 1977). Assuming that δ¹⁵Nᵢ exhibits the same range as power plants and that the majority of
the uncharacterized 8% exhibits a $\delta^{15}\text{N}$ of 0‰ (e.g., lightning), then roughly half of the NO$_x$ would have the composition of the NO$_x$ of mobile sources and half would have the composition of power plants. The total $\delta^{15}\text{N}$ during the summer would be an average of the $\delta^{15}\text{N}_u$ (-13 to +2) and $\delta^{15}\text{N}_{pp}$ (+6 to +13‰), which would be -3.5‰ using the lowest values in the ranges and +7.5 using the highest values in the ranges.

In Maryland and the surrounding regions, production of NO$_x$ by utilities remains relatively constant throughout the year because residents rely on power plants to generate electricity for heating and air conditioning. In general, NO$_x$ from mobile sources is highest during the summer and lowest during the winter. Typically, increased thunderstorm activity during the summer leads to more NO$_x$ produced by lightning. Microbial NO$_x$ may also be higher in the spring and summer due to increased biological activity. Since the $\delta^{15}\text{N}$ values typical of NO$_x$ from mobile sources, lightning, and biological activity are all lower than the $\delta^{15}\text{N}$ values of power plants, the total $\delta^{15}\text{N}$ of NO$_x$ introduced to air masses may be lower in the summer than the winter due to seasonal changes in NO$_x$ formation processes.

6.3.2. Comparison of the $\delta^{15}\text{N}$ of nitrate and storm track data

The movement of air masses can transport NO$_x$ away from the sites of NO$_x$ generation. Therefore, the $\delta^{15}\text{N}$ of precipitation nitrate may not reflect the $\delta^{15}\text{N}$ of NO$_x$ produced in that region, but rather the NO$_x$ produced in the region where the air mass presided the day before. Using reported ranges for the $\delta^{15}\text{N}$ of NO$_x$ produced by the major formation processes and estimates, previous studies have qualitatively determined the relative contributions of NO$_x$ sources to different regions. In
particular, investigators have hypothesized that if the $\delta^{15}$N of precursor NO$_x$ is the main control on the $\delta^{15}$N of atmospheric NO$_3^-$, there would likely be a relationship between the $\delta^{15}$N of precipitation NO$_3^-$ and the source regions for the storm’s air masses. For individual storm events, the location of the air masses can be traced back to their locations on the previous days using models, such as the NOAA Air Resources Laboratory HYSPLIT model.

An investigation of N deposition to Lewes, Delaware considered the relationship between air source regions and the concentration and $\delta^{15}$N of precipitation NO$_3^-$ (Russell et al., 1998). Of the five dominate directions of air transport to the region, the largest fluxes of NO$_3^-$ were attributed to air masses from the south. These southerly air masses were slow moving and were associated with large amounts of precipitation. The next largest fluxes were from the northwest, followed by the west and then the southwest. The lowest fluxes were from easterly air masses, most likely because of relatively low emissions over the ocean. The median $\delta^{15}$N values for the different clusters were not statistically different and ranged from -1.3 to $+0.5\%$ with an overall range of $\delta^{15}$N values from -4.0 to $+4.4\%$. The authors concluded that fossil fuel combustion represented the greatest source of NO$_x$. Higher NO$_3^-$ concentrations during the spring were attributed to increased inputs from soil emissions, which were possibly related to agricultural activities. Although there was not a statistically significant difference, the median $\delta^{15}$N value was also lower for spring than the other seasons, which could represent a microbial NO$_x$ source characterized by negative $\delta^{15}$N.
Other studies have observed an effect of seasonal patterns in the movement of air masses on the $\delta^{15}N$ of atmospheric $\text{NO}_3^-$. Hastings and coworkers (2003) interpreted their observed seasonal variation in $\delta^{15}N$ of Bermuda rain $\text{NO}_3^-$ using storm track data. In the cool season (mean $\delta^{15}N = -5.9\%$), the majority of air masses that contributed to Bermuda’s storms were transported from the North American continent. The lower $\delta^{15}N$ of cool season precipitation $\text{NO}_3^-$ were explained by higher contributions of NO$_x$ from anthropogenic emissions, particularly automobiles with negative $\delta^{15}N$ values. During the warm season (mean $\delta^{15}N = -2.1\%$), many of Bermuda’s air masses originated over the oceans. The mean $\delta^{15}N$ value closer to $0\%$ was attributed to higher contributions of lightning-derived NO$_x$. Yeatman and colleagues (2001) also showed that there was a difference between the mean $\delta^{15}N$ of aerosol $\text{NO}_3^-$ at a coastal site in Weybourne, England depending on whether the air masses originated in northern UK ($+15\pm3\%$) or southern UK ($10\pm3\%$). Higher $\delta^{15}N$ in air masses from northern UK were attributed to more NO$_x$ from industrial activity.

For Frederick, Maryland samples, the observed variation in the $\delta^{15}N$ of precipitation nitrate could not be explained using storm track data alone. Whereas there was a seasonal pattern in the $\delta^{15}N$ values (Figure 11), there was a significant amount of within-season variation in the storm track data (Table 1).

6.3.3. Comparison of the $\delta^{15}N$ of nitrate to the $\delta^{34}S$ of sulfate

Whereas the $\delta^{15}N$ of precipitation nitrate varied seasonally, the $\delta^{34}S$ of precipitation sulfate remained relatively constant throughout the sampling period (Figure 12). Atmospheric sulfate is the result of the atmospheric oxidation of SO$_2$. 
Similar to the $\delta^{15}$N of atmospheric NO$_3^-$, the $\delta^{34}$S of SO$_2$ may reflect the isotopic composition of the gaseous precursor or atmospheric fractionation processes. The $\delta^{34}$S of sulfate may reflect the relative contributions of atmospheric sulfur compounds from coal combustion, biogenic emissions, and ocean sources (Xiao and Liu 2002).

Figure 12: The $\delta^{34}$S of Frederick, MD precipitation sulfate versus time obtained using an elemental analyzer coupled to a continuous flow isotope ratio mass spectrometer. Error bars represent 1σ mass spectrometric reproducibility of NBS-127 sulfate standard. Typically, two standards were measured before and after every set of six samples. The $\delta^{34}$S data are averages of duplicate analyses.

The three samples that had $\delta^{34}$S values higher than 8‰ were from Hurricane Isabel in September 2003 and were collected in a time series. The higher $\delta^{34}$S values could be associated with the hurricane samples containing more sulfur derived from ocean sources, which may have higher $\delta^{34}$S values than coal combustion or biogenic emissions (Xiao and Liu 2002). As the storm progressed the $\delta^{34}$S of precipitation
sulfate increased. The direction of the isotope effect observed in sulfur isotope ratios as the storm progressed was the same as the isotope effect in the nitrogen isotope ratios of nitrate during the May 15-18th storm described previously.

There was no correlation between the $\delta^{15}$N of nitrate and the $\delta^{34}$S of sulfate in Frederick precipitation. If the processes that produced NO$_x$ and SO$_x$ varied seasonally and if their isotopic compositions were determined by formation processes, there would likely have been a relationship between nitrate and sulfate isotope ratios. Lack of correlation between the $\delta^{15}$N of nitrate and storm track and the $\delta^{15}$N of nitrate and the $\delta^{34}$S of sulfate provides evidence that precursor NO$_x$ is not the only relevant parameter influencing $\delta^{15}$N values.

6.3.4. Influence of isotope fractionation on the $\delta^{15}$N of nitrate

Although the observed seasonal variation in Frederick, Maryland precipitation nitrate may be the result of changes in the contributions from different NO$_x$ producers, such as automobiles, power plants, and lightning channels, there is evidence that the seasonal changes in NO$_x$ chemistry affect atmospheric nitrogen isotope fractionation. The seasonal variation observed in the $\delta^{15}$N was similar to the patterns shown in previous investigations. Figure 13 shows mean seasonal $\delta^{15}$N values plotted along with data taken from the literature. With the exceptions of the data reported by Hastings et al. (2003) and Russell et al. (1998), the highest $\delta^{15}$N values were measured in winter atmospheric nitrate and the lowest $\delta^{15}$N values were measured in summer atmospheric nitrate at all of the locations.
Figure 13: Comparison of seasonal $\delta^{15}N$ variation in Frederick precipitation nitrate to observations of previous studies. Unless indicated as “AEROSOL,” the measurements are of precipitation nitrate. Data on Weybourne, England (Yeatman et al. 2001), Frederick, MD (this study) Pretoria, South Africa (Heaton, 1987), and Julich, Deuselbach, and Ahrensburg, Germany, and Le Conquet, France (Freyer, 1991) are mean seasonal values. Data on Lewes, DE (Russell et. al 1998) are median seasonal values. Bermuda rain data (Hastings et al. 1003) are mean values for the warm and cool seasons.

The seasonal pattern observed in Frederick, Maryland has also been identified at number of international locations, including Ahrensburg and Deuselbach, Germany and Le Conquet, France in the northern hemisphere (Freyer, 1991) and Pretoria, South Africa in the southern hemisphere (Heaton, 1987). At the time of the studies, Pretoria had significantly less industry and more lightning than Jülich. The finding that both regions exhibited the same seasonal signature despite largely different NO$_x$ sources provides support for an explanation related to seasonal changes in atmospheric chemistry. The seasonal pattern of the highest $\delta^{15}N$ values in the winter
and the lowest $\delta^{15}\text{N}$ values in the summer was also observed in aerosol NO$_3^-$ from the coastal site of Weybourne, England (Yeatsman et al., 2001).

Freyer and others (1993) postulated that seasonal changes in the photochemical steady-state conditions of NO and NO$_2$ or NO$_x$ oxidation pathways were responsible for the variation in the $\delta^{15}\text{N}$ of aerosol and precipitation NO$_3^-$. Within minutes of entering the atmosphere during the day, NO reaches chemical equilibrium with NO$_2$ due to rapid NO$_2$ photolysis and reaction of NO with O$_3$ to regenerate NO$_2$. There are seasonal changes in atmospheric chemistry that affect the NO$_x$ photochemical stationary state. During the summer, higher O$_3$/NO$_x$ ratios cause the majority of NO$_x$ to be in the form of NO$_2$, while lower O$_3$/NO$_x$ ratios in the summer result in higher concentrations of atmospheric NO.

Freyer and coworkers (1993) measured NO$_x$ (NO+NO$_2$), NO$_2$, and O$_3$ concentrations and the $\delta^{15}\text{N}$ of NO$_x$ and NO$_2$ in Jülich, Germany during 1988-1991. The absolute values for the $\delta^{15}\text{N}$ of NO$_2$ were 4-6‰ lower than aerosol NO$_3^-$ and 2-4‰ higher than precipitation NO$_3^-$ determined in Jülich during earlier sampling periods (1975/1976 and 1979/1984) (Freyer, 1991). There was a linear relationship between daily NO$_2$/NO$_x$ and $\delta^{15}\text{N}$ ($r^2=0.94$) with lower NO$_2$/NO$_x$ and higher $\delta^{15}\text{N}$ in the winter and higher NO$_2$/NO$_x$ and lower $\delta^{15}\text{N}$ in the summer. The hypothesis offered by Freyer and others (1993) involved the exchange reactions between NO and NO$_2$ shown below, where $k+$ and $k-$ are rate constants.

\[ \text{Since only one } N \text{ atom is} \]

\[ ^{15}\text{NO} + ^{14}\text{NO}_2 \xrightleftharpoons{k+} ^{14}\text{NO} + ^{15}\text{NO}_2 \]

\[ ^{14}\text{NO} + ^{15}\text{NO}_2 \xrightleftharpoons{k-} ^{15}\text{NO} + ^{14}\text{NO}_2 \]
being exchanged the equilibrium constant, $K_{eq}$, and equilibrium fractionation factor $\alpha_{eq}$ are the same for this reaction.

$$K_{eq} = \frac{k + [^{14}NO][^{15}NO_2]}{k - [^{13}NO][^{14}NO_2]} = \alpha_{eq} = \frac{\beta(NO_2)}{\beta(NO)}$$

Using the $\beta$-factors tabulated by Richet et al. (1977), the $\alpha_{eq}$ for this exchange reaction is 1.044 at 0°C. Freyer and coworkers (1993) assumed that oxidation of NO to NO$_2$ by HO$_2$ and RO$_x$ is minor relative to oxidation by O$_3$. During the summer, most NO is oxidized to NO$_2$ by O$_3$ due to high O$_3$ concentrations and the $\delta^{15}$N of NO$_2$ reflects the $\delta^{15}$N of NO$_x$. During the winter, NO and NO$_2$ coexist because O$_3$ concentrations are insufficient to completely oxidize NO to NO$_2$. As a result of equilibrium isotope exchange, the $\delta^{15}$N of NO$_2$ increases as the $\delta^{15}$N of NO decreases. Then, NO$_2$ with higher $\delta^{15}$N values undergoes further transformations that result in aerosol and precipitation NO$_3^-$ with higher $\delta^{15}$N values than the precursor pool of NO$_x$. The remaining NO may get transported away from the region of NO$_x$ formation.

### 6.4. Influences on the $\delta^{18}$O and $\Delta^{17}$O of precipitation nitrate

While there are differences between the AgNO$_3$/decomposition and denitrifier methods, the $\delta^{18}$O of precipitation nitrate obtained using both methods exhibited seasonal variation with higher $\delta^{18}$O in the winter and lower $\delta^{18}$O in the summer (Figure 14). There is more within-season variation in the AgNO$_3$/decomposition results, most likely as a result of the inconsistent effects of organic contamination.
The seasonal variation observed in the δ¹⁸O of Frederick precipitation nitrate samples was consistent with the results of previous investigations. Analyses of throughfall NO₃⁻ in Bavaria Germany showed that the lowest δ¹⁸O values occur in the summer (DURKA et al., 1994; VOERKELIUS, 1990). Data on throughfall and precipitation NO₃⁻ in Leading Ridge, Pennsylvania and Fernow, West Virginia also varied seasonally with the highest δ¹⁸O values in winter samples and the lowest values in summer samples. (WILLIARD et al., 2001). Slightly different ranges for rain NO₃⁻ (+40 to +65‰) and snow NO₃⁻ (+50 to +70) appeared in data from Loch Vale, Colorado (CAMPBELL et al., 2002), and the mean δ¹⁸O for rain NO₃⁻ (+58‰) was
significantly different than the mean δ¹⁸O for snow NO₃⁻ (+67‰) in New Hampshire (PARDO et al., 2004). Bermuda rain NO₃⁻ also showed seasonal variation with warm season samples averaging +68.6‰ and cool season samples averaging +79.6‰ (HASTINGS et al., 2003). At Summit Greenland, the mean δ¹⁸O of summer samples was +69.8‰, while the mean δ¹⁸O of winter samples was +77.5‰ (HASTINGS et al., 2004).

The Δ¹⁷O of precipitation nitrate in Frederick, Maryland also revealed a trend of higher values in the winter and lower values in the summer (Figure 15), which is the seasonal pattern reported by Michalski and coworkers (2003) for aerosol nitrate from La Jolla, CA. The range of Δ¹⁷O values for this study (+15.3±0.05‰ to +31.7±0.05‰) is wider than the range reported by Michalski et al. (2003) of +15.3 to +30.1‰, which may be the result of the effect organic contamination on Δ¹⁷O.

Figure 15: Δ¹⁷O of Frederick, MD precipitation NO₃⁻ versus time. Error bars representing 1σ reproducibility of standards are smaller than the data symbols.
Michalski and others (2003) successfully reproduced their $\Delta^{17}O$ measurements of aerosol nitrate using a $\Delta^{17}O$ isotope fractionation model that was coupled to a photochemical box model for the polluted marine boundary layer (PMBL). They showed that atmospheric $NO_3^-$ exhibited positive $\Delta^{17}O$ values because of the transfer of oxygen atoms from ozone ($O_3$). The $\Delta^{17}O$ of atmospheric $NO_3^-$ depends on the number of oxygen atoms derived from tropospheric $O_3$, which has $\Delta^{17}O$ as high as 35‰ (Krankowsky et al. 1995), compared to the $\Delta^{17}O$ of other atmospheric oxidants, such as the peroxy radical ($HO_2$), organic peroxy radicals ($RO_x$), hydroxyl radical ($OH$), and $H_2O$, which are close to zero. The qualitative observations made for Frederick, MD precipitation oxygen isotopes were consistent with their model.

Seasonal variations in the $\delta^{18}O$ and $\Delta^{17}O$ of atmospheric $NO_3^-$ were likely the result of different proportions of the three major nitrate production pathways (Figure 16). The pathways with greater contributions of oxygen atoms from ozone result in atmospheric nitrate with higher $\delta^{18}O$ and $\Delta^{17}O$ values. While some NO gets oxidized to NO$_2$ by the oxidants the peroxy radical ($HO_2$) or organic peroxy radicals ($RO_x$), generally the oxygen atoms in NO$_2$ are from $O_3$. In pathway #1, the third oxygen atom is derived from the hydroxyl radical ($OH$), which has a $\Delta^{17}O$ close to zero. Therefore, only 2/3 of the oxygen atoms in nitrate are derived from ozone. In the case of pathway #2, all six of the oxygen atoms can possibly be from $O_3$. In the case of pathway #3, as much as 5/6 of the oxygen atoms in atmospheric nitrate can be derived from $O_3$, with only 1/6 derived from $H_2O$. 


Figure 16: Atmospheric reaction pathway with estimates of the maximum number of oxygen atoms transferred from ozone to atmospheric nitrate. Pathway #1, which dominates daylight (and summer) chemistry results in nitrate with a maximum of $2/3$ oxygen atoms from ozone (lower $\delta^{18}O$ and $\Delta^{17}O$ values). Pathways #2 and #3 become more important during nighttime (and winter) chemistry and produce nitrate with a maximum of $3/3$ and $5/6$ oxygen atoms from ozone, respectively (higher lower $\delta^{18}O$ and $\Delta^{17}O$ values).

The oxygen isotope observations made for Frederick precipitation nitrate can be explained by seasonal changes in NO$_x$ oxidation chemistry. Since the majority of nitric acid forms by pathway #1 in the summer, the $\delta^{18}O$ and $\Delta^{17}O$ of precipitation nitrate are lower. In the winter, higher contributions of nitric acid formation by pathways #2 and #3 lead to increased $\delta^{18}O$ and $\Delta^{17}O$ values.
7. Conclusions

The comparison of the AgNO₃/decomposition and denitrifier methods showed that the results of the decomposition method were affected by the presence of organic contaminants in the prepared silver nitrates. Some of the organic contaminants were added during the analytical procedure. Contamination likely occurred as a result of sulfonic acid leaching from the silver resin used to remove chloride and produce AgNO₃. Incomplete removal of organic compounds from the precipitation itself added to the contamination issues. Researchers using the AgNO₃/decomposition method in the future should develop a method of removing organic contaminants prior to freeze-drying the prepared AgNO₃ solutions or devise an approach to correct measurements for organic contamination. Some of the advantages to using the denitrifier method in future studies include smaller sample size requirements and the absence of issues associated with organic contamination.

Precipitation nitrate exhibited the highest $\delta^{15}$N, $\delta^{18}$O, and $\Delta^{17}$O values in the winter and the lowest values in the summer. Source regions of air masses were not primarily responsible for the observed isotope variations. While $\delta^{15}$N, $\delta^{18}$O, and $\Delta^{17}$O varied seasonally, storm track data for the Frederick storm events showed that the geographical origins of the air masses varied within seasons. Below cloud scavenging processes were also unlikely the major determinants of isotope ratios. There were no observable relationships between isotope ratios and concentration data as there would be if isotope ratios were primarily determined by nitrate removal rates via dry or wet deposition.
Whereas the δ^{34}S of precipitation sulfate remained constant with the exception of hurricane samples, the δ^{15}N of precipitation nitrate varied seasonally, and there was no relationship between the δ^{15}N of precipitation nitrate and the δ^{34}S of precipitation sulfate. If the isotopic composition of precursor NOₓ and SO₂ were the major determinants of the δ^{15}N of precipitation nitrate and the δ^{34}S of precipitation sulfate, and if processes contributed similar proportions of the total atmospheric NOₓ and SO₂, then there would be a relationship between these parameters.

The most likely causes for the observed variations in δ^{15}N, δ^{18}O, and Δ^{17}O were seasonal variations in atmospheric chemistry that influenced nitrogen isotope fractionation processes and the dominant oxidation pathways of nitrate formation. The nitrogen isotope ratios of precipitation nitrate from Frederick, Maryland exhibited the same seasonal pattern as precipitation nitrate from Jülich, Germany (Freyer, 1978; Freyer, 1991) and Pretoria, South Africa (Heaton, 1987) and aerosol nitrate from Weybourne, England (Yeatman et al. 2001). Nitrate in snow and winter rain samples had the highest δ^{15}N values, while summer rain samples had the lowest δ^{15}N values. These observations were consistent with the model of Freyer and coworkers (1993), which showed that the δ^{15}N of NO₂ increased with decreasing atmospheric NO₂/NOₓ ratios. Equilibrium isotope exchange between NO and NO₂ during the winter resulted in higher δ^{18}O values in NO₂ and thus precipitation NO₃⁻. Rapid conversion of NO to NO₂ during the summer minimized the effect of equilibrium isotope exchange.

The δ^{18}O and Δ^{17}O of Maryland precipitation nitrate showed the same pattern as previous studies (Hastings et al., 2003, Michalski et al., 2003). Oxygen isotope
ratios were primarily affected by seasonal changes in the predominant pathways of nitrate formation. The $\delta^{18}O$ and $\Delta^{17}O$ of atmospheric nitrate depends on the proportion of oxygen atoms from O$_3$, which has significantly higher $\delta^{18}O$ and $\Delta^{17}O$ values than other atmospheric oxidants.

This study provides evidence that atmospheric fractionation processes are relevant in understanding atmospheric NO$_3^-$ isotope ratios. Atmospheric fractionation networks can increase our understanding of atmospheric chemistry in addition to mechanisms of isotope exchange. Increased knowledge about variations in atmospheric NO$_3^-$ as a result of these fractionation networks can also improve our ability to trace atmospheric NO$_3^-$ through watersheds.
Appendix A

The following procedure was used to treat the anion exchange resin AG2X-8 (Cl⁻ form, 100-200 mesh), purchased from Biorad, prior to use. These methods were adopted from the procedure used by J. Hannon’s at the USGS, Reston for anion exchange resin AG1X-8).

1. Weigh out 150g of AG2X-8 into a clean 600mL beaker.

2. Rinse the resin using Millipore water.
   a. Add Millipore water to the resin (150g of AG2X-8 occupies approximately 200mL).
   b. Add approximately 250mL additional Millipore water.
   c. Stir the resin/water mixture.
   d. After allowing the resin to settle for five minutes, pour off the Millipore water and any resin still suspended.
   e. Repeat steps b-e six times.

3. Transfer the resin to a 2.5cm diameter by 50cm column with a clean stop cock attached to the end of the column.

4. Gravity drip 2000mL 1.0 M NaOH through the column (the resin turns a darker orange color as it converts from the Cl⁻ form to the OH⁻ form).

5. Gravity drip 1000mL Millipore water through the column.

6. Gravity drip 1000mL 2.0 M HCl (e.g., 168mL concentrated HCl diluted to one liter using Millipore water) through the column to convert the resin back to the Cl⁻ form. During this step, heat is released and air bubbles form.
7. Shake column gently to release the air bubbles formed during step 6.
8. Gravity drip 2000mL Millipore water through the column.
9. Gravity drip 450mL methanol through the column.
10. Transfer the resin from the column to a clean beaker and allow the resin to air dry at room temperature for approximately one week.
11. Transfer the resin to a clean bottle and store dry.
12. When ready to extract ions from a sample, fill a 1.0cm diameter glass column with a clean stop cock attached to the end of the column with an appropriate amount of AG2X-8 resin:
   a. Estimate the amount of resin needed to accommodate the anions in the sample using concentration data (if available) and the volume of sample being passed through the column (AG2X-8 can accommodate 1200meq per mL resin). Use approximately twice the amount of resin calculated. If no concentration data is available, assume maximum concentration values.
   b. Pipette 1mL of water into a 1.0cm diameter glass column, and mark the outside of the column to indicate the resin bed height that corresponds to 1mL. Continue pipetting particular volumes of water into the column and marking the outside of the column with the corresponding resin bed heights until the column is marked up to 6mL
   c. Use a metal spatula (cleaned with ethanol) to transfer several milliliters of the dry resin to a small clean bottle.
   d. Add Millipore water to the bottle with the dry resin.
e. Fill the marked column halfway with Millipore water.

f. Use a 1-5mL pipette to transfer the appropriate amount of AG2X-8 resin from the bottle to the column. (Pipetting the resin into a column filled with water will decrease the formation of gas bubbles in the resin bed.)
Appendix B

The following procedure was used to treat the cation exchange resin AG50WX-8 (H⁺ form, 100-200 mesh), purchased from Biorad, prior to use.

1. Weigh out 150g of AG50WX-8 into a clean 600mL beaker.
2. Rinse the resin using Millipore water.
   a. Add Millipore water to the resin.
   b. Add approximately 250mL additional Millipore water.
   c. Stir the resin/water mixture.
   d. After allowing the resin to settle for one minute, pour off the Millipore water and any resin still suspended.
   e. Repeat steps b-e three times.
3. Transfer the resin to a 2.5cm diameter by 50cm column with a clean stop cock attached to the end of the column.
4. Gravity drip 4L of 4M HCl through the resin packed column at a rate of 50-100 drips per minute.
5. Gravity drip 1L of 1M HCl through the column.
6. Transfer the resin from the column to a clean bottle, storing the resin in 1M HCl.
7. When ready to run the sample through a cation exchange column, fill a 1.5cm diameter glass column with a clean stop cock attached to the end of the column with an appropriate amount of AG50WX-8 resin:
a. Pipette 1mL of water into a 1.5cm diameter glass column with a clean stop cock attached to the end of the column, and mark the outside of the column to indicate the resin bed height that corresponds to 1mL. Continue pipetting particular volumes of water into the column and marking the outside of the column with the corresponding resin bed heights until the column is marked up to 5mL.

b. Fill the marked column halfway with Millipore water.

c. Use a 1-5mL pipette to transfer 5mL AG50WX-8 resin from the storage bottle to the column. (Pipetting the resin into a column filled with water will decrease the formation of gas bubbles in the resin bed.)

d. Gravity drip approximately 250mL Millipore water through the packed column until the pH of the solution coming through the column is 6.0.
Appendix C

The following procedures were used to prepare colorimetric test solutions and to identify the presence of nitrate/nitrite.

1. Prepare the nitrate reducing solution:
   a. Prepare hydrazine sulfate solution:
      i. Dissolve 13.75 g hydrazine sulfate in Millipore water.
      ii. Dilute solution to 500mL using Millipore water.
   b. Prepare CuSO\(_4\) solution:
      i. Dissolve 4.00 g CuSO\(_4\) in Millipore water.
      ii. Dilute solution to 1000mL using Millipore water.
   c. Prepare the final solution:
      i. Combine 1.35mL hydrazine sulfate solution and 0.80mL CuSO\(_4\) solution.
      ii. Dilute solution to 100mL with Millipore water.
   d. The hydrazine sulfate solution and CuSO\(_4\) solutions can be used for up to one year, while a new batch of the final solution should be prepared every month.

2. Prepare 0.3M NaOH solution.

3. Prepare the nitrite coloring solution:
   a. Dissolve 1.0 g sulfanilamide in 10mL concentrated HCl.
   b. Carefully add the sulfanilamide in HCl solution to 75mL Millipore water.
c. Add 50 mg N-(1-naphthyl) ethylenediamine dihydrochloride to the solution.

d. Dilute the solution to 100mL with Millipore water.

4. Test for the Presence of nitrate/nitrite.

   a. To one of the slots in a porcelain plate, add two drops of Millipore water.

   b. To another slot in the porcelain plate, add two drops of a sample solution.

   c. Add one drop of nitrate reducing solution and one drop of 0.3M NaOH solution to the Millipore water and sample solution in the porcelain plate.

   d. After waiting for 20 minutes, add two drops of nitrite coloring solution to the Millipore water and sample solution.

   e. After waiting for two minutes, compare the colors of the Millipore water and the sample solution.

      i. If both solutions are a very pale pink, the concentration of nitrate/nitrite in the sample solution is below detection.

      ii. If the Millipore water is very pale pink and the sample solution is significantly darker pink, nitrate/nitrite is present in the sample solution.

      iii. Sample solutions will vary in shades of pink with solutions of higher nitrate/nitrite concentration being darker.
Appendix D

The following procedure was used to convert the AG MP-50 (H⁺) resin, purchased from Biorad, to the Ag⁺ form (modified from a personal communication with J. Hannon). Although the resin was prepared in batches as described below, the various batches were homogenized and stored in a single amber colored bottle.

1. Weigh out approximately 60g AG MP-50 (H⁺) and add to a clean 600-mL beaker.

2. Add approximately 250mL of Millipore water to the resin and stir for two minutes.

3. After allowing three minutes for the resin to settle to the bottom of the beaker, pour out the rinse water and the resin that remains suspended.

4. Repeat steps 2-3 ten times, or until the rinse water appears clear.

5. Transfer the resin using Millipore water to a 2.5 cm diameter glass column.

6. Prepare 0.44M AgNO₃(aq) (e.g., 15g AgNO₃(s) for every 200mL Millipore water).

7. Gravity drip 0.44M AgNO₃(aq) through the packed column and observe changes (e.g., color) as Ag⁺ replaces H⁺ on the exchange sites of the resin.

8. Verify the conversion of the resin from the H⁺ form to the Ag⁺ form:
   a. At first, the solution passing through the column will have a pH of 0-1 (verify using pH paper), and will not contain silver ions (verify by collecting several milliliters of the solution in a clean test tube and
adding a few drops of HCl; AgCl precipitate will form in the presence of Ag⁺ ions).

b. As the exchange sites fill with Ag⁺ ions, the pH of the solution coming through the column will increase and silver ions will become present.

c. When the pH of the solution coming through the column is greater than 4, conversion to the Ag⁺ form is complete. (On average, 550mL 0.44M AgNO₃(aq) is required to convert 60g AG MP-50 from the H⁺ form to the Ag⁺ form.)

9. Rinse the resin thoroughly using several liters of Millipore water. (On average, 6L of Millipore water is rinsed through the column.)

   a. Mix the resin periodically.

   b. Check for the presence of nitrate using colorimetric test solutions (for more details, see Appendix C).

   c. Verify that there is no nitrate present in the water coming through the column and transfer the prepared resin to an amber colored bottle.
Appendix E

Strom track data for sample 1

NOAA HYSPLIT MODEL
Backward trajectories ending at 19 UTC 06 Feb 03
EDAS Meteorological Data

Source ★ at 39.34N 77.34W

Meters AGL

1500 ★ ★
1000 ★ ★
500 ★ ★

16 12 06 00 02/06

Job ID: 35895   Job Start: Tue Jul 19 19:38:55 GMT 2005
lat: 39.342   lon: -77.337   hghts: 500, 1000, 1500 m AGL

Trajectory Direction: Backward   Duration: 24 hrs   Meteor Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 2

NOAA HYSPLIT MODEL
Backward trajectories ending at 14 UTC 15 Feb 03
EDAS Meteorological Data
Strom track data for sample 3

NOAA HYSPLIT MODEL
Backward trajectories ending at 06 UTC 27 Feb 03
EDAS Meteorological Data

Source ★ at 39.34 N 77.34 W

Meters AGL

Job ID: 35913   Job Start: Tue Jul 19 19:44:13 GMT 2005
lat: 39.342  lon: -77.337  hghts: 500, 1000, 1500 m AGL

Trajectory Direction: Backward  Duration: 24 hrs  Metec Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)

115
Strom track data for sample 4

NOAA HYSPLIT MODEL
Backward trajectories ending at 17 UTC 13 Mar 03
EDAS Meteorological Data

Source ★ at 39.34 N 77.34 W

Meters AGL

Job ID: 35929   Job Start: Tue Jul 19 19:46:41 GMT 2005
lat: 39.342  lon: -77.337  hghts: 500, 1000, 1500 m AGL
Trajectory Direction: Backward   Duration: 24 hrs   Meteo Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 5

NOAA HYSPLIT MODEL
Backward trajectories ending at 02 UTC 07 Apr 03
EDAS Meteorological Data

Job ID: 35944
Job Start: Tue Jul 19 19:48:17 GMT 2005
lat: 39.342 lon: -77.337 hgt: 500, 1000, 1500 m AGL

Trajectory Direction: Backward
Duration: 24 hrs
Metec Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 6

NOAA HYSPLIT MODEL
Backward trajectories ending at 07 UTC 08 May 03
EDAS Meteorological Data
Strom track data for samples 7 and 8

NOAA HYSPLIT MODEL
Backward trajectories ending at 14 UTC 15 May 03
EDAS Meteorological Data
Strom track data for sample 9

NOAA HYSPLIT MODEL
Backward trajectories ending at 07 UTC 16 May 03
EDAS Meteorological Data
Strom track data for sample 10

NOAA HYSPLIT MODEL
Backward trajectories ending at 19 UTC 20 May 03
EDAS Meteorological Data

Source ★ at 39.34 N 77.34 W

Meters AGL

05/20

Job ID: 36099   Job Start: Tue Jul 19 19:57 46 GMT 2005
lat.: 39.342  lon.: -77.337  hghts: 500, 1000, 1500 m AGL

Trajectory Direction: Backward  Duration: 24 hrs  Meteor Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 11

NOAA HYSPLIT MODEL
Backward trajectories ending at 10 UTC 23 May 03
EDAS Meteorological Data

122
Strom track data for sample 12

NOAA HYSPLIT MODEL
Backward trajectories ending at 20 UTC 08 Jun 03
EDAS Meteorological Data

[Map showing backward trajectories with source at 39.34 N, 77.34 W. The map includes data points at different altitudes (500, 1000, 1500, 2000 meters AGL).]

Job ID: 36124  Job Start: Tue Jul 19 20:03:03 GMT 2005
lat: 39.342  lon: -77.337  hgt: 500, 1000, 1500 m AGL

Trajectory Direction: Backward  Duration: 24 hrs  Meteo Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 13

NOAA HYSPLIT MODEL
Backward trajectories ending at 13 UTC 12 Jun 03
EDAS Meteorological Data

Source ★ at 39.34 N 77.34 W

Meters AGL

1500 ★
1000 ★
500 ★
00/12
12 06 18
Job ID: 36197
00 00 12
Job Start: Tue Jul 19 20:07 36 GMT 2005
lat: 39.342 lon: -77.337 hghts: 500, 1000, 1500 m AGL
Trajectory Direction: Backward
Duration: 24 hrs
Meteo Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 14

NOAA HYSPLIT MODEL
Backward trajectories ending at 12 UTC 13 Jun 03
EDAS Meteorological Data

Job ID: 36171  
Job Start: Tue Jul 19 20:06 50 GMT 2005  
lat.: 39.342  lon.: -77.337  hghts: 500, 1000, 1500 m AGL

Trajectory Direction: Backward  
Duration: 24 hrs  
Meta Data: EDAS  
Vertical Motion Calculation Method: Model Vertical Velocity

Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 15

NOAA HYSPLIT MODEL
Backward trajectories ending at 11 UTC 03 Jul 03
EDAS Meteorological Data

Source ★ at 39.34 N 77.34 W

Meters AGL

Trajectory Direction: Backward  Duration: 24 hrs  Meteor Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 16

NOAA HYSPLIT MODEL
Backward trajectories ending at 17 UTC 06 Jul 03
EDAS Meteorological Data

Trajectory Direction: Backward  Duration: 24 hrs  Meteo Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 17

NOAA HYSPLIT MODEL
Backward trajectories ending at 06 UTC 09 Jul 03
EDAS Meteorological Data
Strom track data for sample 18

NOAA HYSPLIT MODEL
Backward trajectories ending at 16 UTC 22 Jul 03
EDAS Meteorological Data

Trajectory Direction: Backward  
Duration: 24 hrs  
Meteo Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity

Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 19

NOAA HYSPLIT MODEL
Backward trajectories ending at 13 UTC 12 Aug 03
EDAS Meteorological Data

Source ★ at 39.34 N 77.34 W

Meters AGL

Job ID: 36281  Job Start: Tue Jul 19 20:16 56 GMT 2005
lat: 39.342  lon: -77.337  hghts: 500, 1000, 1500 m AGL

Trajectory Direction: Backward  Duration: 24 hrs  Meteo Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 20

NOAA HYSPLIT MODEL
Backward trajectories ending at 12 UTC 01 Sep 03
EDAS Meteorological Data

Job ID: 36285   Job Start: Tue Jul 19 20:18:42 GMT 2005
lat.: 39.342  lon.: -77.337  hgt.: 500, 1000, 1500 m AGL

Trajectory Direction: Backward   Duration: 24 hrs   Meteo Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 21

NOAA HYSPLIT MODEL
Backward trajectories ending at 18 UTC 03 Sep 03
EDAS Meteorological Data

[Map showing backward trajectories with sources at 39.34 N 77.34 W, trajectories at 500, 1000, 1500, and 2000 meters AGL over time from 09/03 12 to 09/03 18]
Strom track data for sample 22

NOAA HYSPLIT MODEL
Backward trajectories ending at 15 UTC 15 Sep 03
EDAS Meteorological Data

Source ★ at 39.34 N 77.34 W

Meters AGL

lat.: 39.342  lon.: -77.337  hghts: 500, 1000, 1500 m AGL

Trajectory Direction: Backward  Duration: 24 hrs  Meteo Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 23

NOAA HYSPLIT MODEL
Backward trajectories ending at 07 UTC 18 Sep 03
EDAS Meteorological Data

Source ★ at 39.34 N 77.34 W

Meters AGL

06 00 18 12 09/18

1500 ★ 1000 ★ 500 ★

Job ID: 36325  Job Start: Tue Jul 19 20:24 23 GMT 2005
lat: 39.342  lon: -77.337  hghts: 500, 1000, 1500 m AGL

Trajectory Direction: Backward  Duration: 24 hrs  Meteo Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 24

NOAA HYSPLIT MODEL
Backward trajectories ending at 16 UTC 18 Sep 03
EDAS Meteorological Data

Source ★ at 39.34 N 77.34 W

Meters AGL

Job ID: 36342   Job Start: Tue Jul 19 20:28 24 GMT 2005
lat.: 39.342   lon.: -77.337   hghts: 500, 1000, 1500 m AGL
Trajectory Direction: Backward   Duration: 24 hrs   Meteo Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Storm track data for sample 25

NOAA HYSPLIT MODEL
Backward trajectories ending at 20 UTC 18 Sep 03
EDAS Meteorological Data

Source ★ at 39.34 N 77.34 W

Meters AGL

1500 ★ 1500
1000 ★ 1000
500 ★ 500

Job ID: 36352  Job Start: Tue Jul 19 20:29:08 GMT 2005
lat: 39.342  lon: -77.337  hghts: 500, 1000, 1500 m AGL

Trajectory Direction: Backward  Duration: 24 hrs  Meteo Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 26

NOAA HYSPLIT MODEL
Backward trajectories ending at 13 UTC 22 Sep 03
EDAS Meteorological Data

Job ID: 360865  Job Start: Wed Aug 10 15:59 02 GMT 2005
lat: 39.34  lon: -77.34  hghts: 500, 1000, 1500 m AGL

Trajectory Direction: Backward  Duration: 24 hrs  Meteo Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 27

NOAA HYSPLIT MODEL
Backward trajectories ending at 15 UTC 25 Sep 03
EDAS Meteorological Data

Source ★ at 39.34 N 77.34 W

Meters AGL

03/25

Job ID: 36378   Job Start: Tue Jul 19 20:31 20 GMT 2005
lat: 39.342 lon: -77.337 hghts: 500, 1000, 1500 m AGL

Trajectory Direction: Backward   Duration: 24 hrs   Meteo Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 28

NOAA HYSPLIT MODEL
Backward trajectories ending at 20 UTC 27 Sep 03
EDAS Meteorological Data

Job ID: 36933   Job Start: Tue Jul 19 20:32:43 GMT 2006
lat: 39.342  lon: -77.337  hghts: 500, 1000, 1500 m AGL

Trajectory Direction: Backward   Duration: 24 hrs   Meteor Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 29

NOAA HYSPLIT MODEL

Backward trajectories ending at 05 UTC 05 Nov 03

EDAS Meteorological Data

Source ⭐ at 39.34°N 77.34°W

Meters AGL

Job ID: 36360   Job Start: Tue Jul 19 20:34:38 GMT 2005
lat: 39.342°   lon: -77.337°  hgt: 500, 1000, 1500 m AGL

Trajectory Direction: Backward   Duration: 24 hrs   Meteor Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 30

NOAA HYSPLIT MODEL
Backward trajectories ending at 05 UTC 06 Nov 03
EDAS Meteorological Data

Source ★ at 39.34 N 77.34 W

Meters AGL

00  12  18  06  11:06

1500  1000  500

Job ID: 36405   Job Start: Tue Jul 19 20:35 20 GMT 2005
lat: 39.342  lon: -77.337  hghts: 500, 1000, 1500 m AGL

Trajectory Direction: Backward  Duration: 24 hrs  Meteo Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 31

NOAA HYSPLIT MODEL
Backward trajectories ending at 09 UTC 11 Nov 03
EDAS Meteorological Data

Job ID: 361158  Job Start: Wed Aug 10 16:06:08 GMT 2005
lat.: 39.34  lon.: -77.34  hghts: 500, 1000, 1500 m AGL

Trajectory Direction: Backward  Duration: 24 hrs  Meteo Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 32

NOAA HYSPLIT MODEL
Backward trajectories ending at 15 UTC 24 Nov 03
EDAS Meteorological Data
Strom track data for sample 33

NOAA HYSPLIT MODEL
Backward trajectories ending at 04 UTC 28 Nov 03
EDAS Meteorological Data
Strom track data for sample 34

NOAA HYSPLIT MODEL
Backward trajectories ending at 21 UTC 04 Dec 03
EDAS Meteorological Data

Source ★ at 39.34 N 77.34 W

Meters AGL

Job ID: 36443    Job Start: Tue Jul 19 20:43 08 GMT 2005
lat: 39.342    lon: -77.337    hghts: 500, 1000, 1500 m AGL

Trajectory Direction: Backward    Duration: 24 hrs    Meteo Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)

145
Strom track data for sample 35

NOAA HYSPLIT MODEL
Backward trajectories ending at 12 UTC 10 Dec 03
EDAS Meteorological Data
Strom track data for sample 36

NOAA HYSPLIT MODEL
Backward trajectories ending at 02 UTC 14 Dec 03
EDAS Meteorological Data
Strom track data for sample 37

NOAA HYSPLIT MODEL
Backward trajectories ending at 06 UTC 05 Jan 04
EDAS Meteorological Data

Source ★ at 39.34 N 77.34 W

Trajectory Direction: Backward  Duration: 24 hrs  Meteo Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 38

NOAA HYSPLIT MODEL
Backward trajectories ending at 20 UTC 23 Jan 04
EDAS Meteorological Data

Source ★ at 39.34 N 77.34 W

Meters AGL

lat: 39.34   lon: -77.34   hghts: 500, 1000, 1500 m AGL

Trajectory Direction: Backward   Duration: 24 hrs   Meteo Data: EDAS   Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 39

NOAA HYSPLIT MODEL
Backward trajectories ending at 06 UTC 03 Feb 04
EDAS Meteorological Data

Source ★ at 39.34 N 77.34 W

Trajectory Direction: Backward  Duration: 24 hrs  Meteo Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 40

NOAA HYSPLIT MODEL
Backward trajectories ending at 19 UTC 05 Feb 04
EDAS Meteorological Data

Source ★ at 39.34 N, 77.34 W

Meters AGL

02/05

Job ID: 36531   Job Start: Tue Jul 19 20:56 20 GMT 2005
lat: 39.342  lon.: -77.337  hghts: 500, 1000, 1500 m AGL
Trajectory Direction: Backward  Duration: 24 hrs  Meteo Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 41

NOAA HYSPLIT MODEL
Backward trajectories ending at 20 UTC 05 Mar 04
EDAS Meteorological Data
Strom track data for sample 42

NOAA HYSPLIT MODEL
Backward trajectories ending at 17 UTC 18 Mar 04
EDAS Meteorological Data

Job ID: 36553  Job Start: Tue Jul 19 20:59:39 GMT 2005
lat: 39.342  lon: -77.337  hghts: 500, 1000, 1500 m AGL

Trajectory Direction: Backward  Duration: 24 hrs  Meta Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 43

NOAA HYSPLIT MODEL
Backward trajectories ending at 21 UTC 31 Mar 04
EDAS Meteorological Data

Source ★ at 39.34 N 77.34 W

Meters AGL

Job ID: 36561   Job Start: Tue Jul 19 21:01:18 GMT 2005
lat: 39.342 lon: -77.337 hghts: 500, 1000, 1500 m AGL

Trajectory Direction: Backward   Duration: 24 hrs   Meteor Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 44

NOAA HYSPLIT MODEL
Backward trajectories ending at 04 UTC 12 Apr 04
EDAS Meteorological Data

Source ⋆ at 39.34 N 77.34 W

Meters AGL

04/12
00 12 18 06

1500 ⋆ 1500
1000 ⋆ 1000
500 ⋆ 500

Job ID: 36609  Job Start: Tue Jul 19 21:03:20 GMT 2005
lat.: 39.342 lon.: -77.337 hghts: 500, 1000, 1500 m AGL

Trajectory Direction: Backward  Duration: 24 hrs  Meteor Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 45

NOAA HYSPLIT MODEL
Backward trajectories ending at 16 UTC 23 Apr 04
EDAS Meteorological Data

Job ID: 36621   Job Start: Tue Jul 19 21:05 09 GMT 2005
lat: 39.342 lon: -77.337 htgs: 500, 1000, 1500 m AGL

Trajectory Direction: Backward  Duration: 24 hrs  Meteo Data: EDAS
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Strom track data for sample 46

NOAA HYSPLIT MODEL
Backward trajectories ending at 18 UTC 01 May 04
EDAS Meteorological Data

Source ★ at 39.34 N 77.34 W

Meters AGL

05/01
12 06 00 18
500 ★ 1000 ★ 1500 ★

Job ID: 361232   Job Start: Wed Aug 10 16 07:44 GMT 2005
lat: 39.34   lon: -77.34   hghts: 500, 1000, 1500 m AGL
Trajectory Direction: Backward   Duration: 24 hrs   Meteo Data: EDAS40
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)
Bibliography


