

Analysis of atmospheric inputs of nitrate to a temperate forest ecosystem from $\Delta^{17}\text{O}$ isotope ratio measurements

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[1] Determining the fate of atmospheric N deposited in forest ecosystems is essential to understanding the ecological impact of increased anthropogenic N deposition. We hypothesize that a significant fraction of soil nitrate (dry deposited HNO_3 and wet deposited NO_3^-) in northern Michigan is derived from atmospheric deposition. To test this idea, soil, rainfall, and cloud water were sampled in a temperate forest in northern Lower Michigan. The fraction of the soil solution NO_3^- pool directly from atmospheric deposition was quantified using the natural isotopic tracer, $\Delta^{17}\text{O}$. Our results show that on average 9% of the soil solution NO_3^- is unprocessed (no microbial turnover) N derived directly from the atmosphere. This points to the potential importance of anthropogenic N deposition and contributes to the long-standing need to improve our understanding of the impacts of atmospheric nitrogen processing and deposition on forest ecosystems and forest productivity. **Citation:** Costa, A. W., G. Michalski, A. J. Schauer, B. Alexander, E. J. Steig, and P. B. Shepson (2011), Analysis of atmospheric inputs of nitrate to a temperate forest ecosystem from $\Delta^{17}\text{O}$ isotope ratio measurements, *Geophys. Res. Lett.*, 38, L15805, doi:10.1029/2011GL047539.

1. Introduction

[2] Recent studies have indicated that atmospheric N deposition has an important function in the N cycle of forest ecosystems [Asner *et al.*, 2001; McNeil *et al.*, 2007]. It has been shown that oxidized atmospheric N compounds (e.g. organic nitrates, HNO_3) and N-containing aerosols can be deposited to the biosphere and used as a nutrient source [Sparks *et al.*, 2003; Lockwood *et al.*, 2008]. Because C and N cycles are so intertwined in terrestrial ecosystems, wet and dry deposition of atmospheric N may also have a significant impact on net ecosystem exchange of carbon, particularly in N limited systems. However, there are conflicting reports in the literature regarding the magnitude of this impact [Nadelhoffer *et al.*, 1999; Magnani *et al.*, 2007; Zak *et al.*, 2008]. Nadelhoffer *et al.* [1999] reviewed and conducted

^{15}N tracer studies and concluded that atmospheric N deposition cannot account for the additional C storage in northern temperate and boreal forests. Similarly, Zak *et al.* [2004, 2008] conducted a study in northern Lower Michigan using ^{15}N labeled NO_3^- treatments. After one year, they found that the NO_3^- deposition increased overstory leaf and branch nitrogen concentrations indicating that atmospheric deposition contributed to net ecosystem productivity (NEP) [Zak *et al.*, 2004]. In 2008, Zak *et al.* [2008] determined that N deposition at that site increased C storage though forest floor organic matter accumulation and surface mineral soil. On the extreme end of reports, Magnani *et al.* [2007] concluded that net C sequestration in temperate and boreal forests is primarily driven by atmospheric N deposition.

[3] Resolving the fate and impact of deposited N in forests is crucial for estimating its impacts on forest ecosystems. The amount of atmospheric N deposition is predicted to more than double in the next 40 years due to a global increase in agricultural activities and the combustion of fossil fuels [Galloway *et al.*, 2004]. This increase has the potential to affect net primary productivity (NPP) depending on the current nutrient supply and demand of the ecosystem. Nitrogen limited systems are likely to see an initial increase in NPP due to increased nutrient availability. However, in systems saturated with N, this excess can lead to soil acidification, eutrophication, and the eventual decline in NPP [Fenn *et al.*, 1998; Magnani *et al.*, 2007]. Because our understanding of the fate of atmospheric nitrogen input into forest environments is unresolved, it is unclear what effect an increase in anthropogenic N will have on ecosystem dynamics and C storage. Therefore, we aim to determine what fraction of the soil nitrate (sum of dry deposited $\text{HNO}_{3(\text{g})}$ and wet deposited $\text{NO}_{3(\text{aq})}^-$) pool originates from atmospheric deposition and is un-cycled by bacteria.

[4] New isotope techniques enable quantitative insights into this issue. The mass difference between stable isotopes of the same element impacts the rate of partitioning between phases and products/reactants in chemical reactions [Criss, 1999]. Isotopic fractionation results in a small change in the minor/major isotopic ratio ($R_{\text{ox}} = {}^{18}\text{O}/{}^{16}\text{O}$, ${}^{17}\text{O}/{}^{16}\text{O}$) relative to a standard, typically the standard mean ratio for oxygen in ocean water (SMOW). This fractionation is denoted by δ in parts per thousand (‰) as shown in equation (1):

$$\delta(\text{‰}) = \left(\frac{R_{\text{Sample}}}{R_{\text{Std}}} - 1 \right) \times 1000 \quad (1)$$

For oxygen, which has three stable isotopes, the theoretical mass dependent relationship between the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values is $\delta^{17}\text{O} \approx 0.52 \times \delta^{18}\text{O}$ [Matsuhisa *et al.*, 1978; Miller, 2002; Young *et al.*, 2002]. The notable exception to this rule

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is the observed equal enrichment of ^{17}O and ^{18}O during the formation of ozone [Thiemens, 2001; Michalski and Bhattacharya, 2009]. This excess ^{17}O is defined in “delta notation” as $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$. The origin of positive $\Delta^{17}\text{O}$ values during ozone formation appears to be mainly a result of increased dynamic coupling terms of the asymmetric relative to symmetric ozone isotopologues [Hathorn and Marcus, 2000; Thiemens, 2001; Gao and Marcus, 2002; Michalski and Bhattacharya, 2009]. NO_3^- produced photochemically in the atmosphere has positive $\Delta^{17}\text{O}$ values ($\sim 20\text{--}32\text{‰}$) and is believed to be solely a result of chemical processing by O_3 [Michalski et al., 2003; Alexander et al., 2009]. In contrast, NO_3^- produced by microbial nitrification has $\Delta^{17}\text{O}$ of zero [Michalski et al., 2004]. This makes $\Delta^{17}\text{O}$ a natural isotopic tracer of the fraction of soil nitrate originating from the atmosphere relative to microbial nitrification [Michalski et al., 2004; Tsunogai et al., 2010]. This distinctive isotopic signal was used to test the hypothesis that a significant fraction of available nitrate in soil solution originates from atmospheric deposition. Isotopic analysis ($\Delta^{17}\text{O}$, $\delta^{18}\text{O}$, $\delta^{17}\text{O}$) of extracted nitrate in soil, cloud water, and precipitation was conducted and reported here.

2. Experiment

2.1. Site Description and Sample Collection

[5] From June to August 2009, samples were collected in a temperate forest near the University of Michigan Biological Station (UMBS), located in northern lower Michigan ($45^\circ 35.5'\text{N}$, $84^\circ 43'\text{W}$). The site characteristics are thoroughly described by Gough et al. [2010]. Briefly, the location is a high level outwash plain containing a relatively homogeneous distribution of vegetation. The site is a primary successional mixed northern forest dominated by big tooth aspen (*Populus grandidentata*) with smaller amounts of trembling aspen (*Populus tremuloides*) and paper birch (*Betula papyrifera*). The average tree age is about 90 years old, consistent with the late 19th century clear-cut and burn [Gough et al., 2010]. These forests are currently undergoing a transition from the early successional species that dominate the site to late successional species, most notably northern red oak (*Quercus rubra*) and red maple (*Acer rubrum*), but also including American beech (*Fagus grandifolia*), sugar maple (*Acer saccharum*), and white pine (*Pinus strobus*) [Gough et al., 2010].

[6] Cloud water was collected using the Airborne Laboratory for Atmospheric Research (ALAR; <http://www.chem.purdue.edu/shepson/alar.html>) fitted with a Mohnen slotted rod cloud water collector [Hill et al., 2007]. Rain water samples were collected on an event-basis for the duration of the study following the technique detailed by Hill et al. [2005]. Soil samples were obtained using a stainless steel soil corer to a depth of 30 cm, transferred to pre-labeled, clean, polyethylene bags and homogenized by hand. Forest floor samples were collected by removing the surface litter and cutting 25×25 cm squares down to the base of the organic horizon, approximately 5 to 8 cm in depth. Both forest floor samples and soil cores were collected a minimum of 48 hours after rain events. To investigate the impact of rain water on soil NO_3^- fractionation, 30 cm soil cores were collected both immediately and 20 hrs after the com-

pletion of a rain event. All samples collected were frozen at -4°C until extracted for analysis.

2.2. Sample Preparation and Analysis

[7] Prior to extraction, all soil samples were sieved and any visible roots, rocks, and insects were removed. Homogenized soil cores were sub-sampled in 50 g aliquots, extracted with 60 mL nano-pure water (to remove the nitrate in soil solution), and underwent $0.22\ \mu\text{m}$ filtration. Rain and cloud water samples were weighed and filtered using the same system. Samples were analyzed with an analytical ion chromatograph (Dionex Corporation, Sunnyvale, CA), using an AS-11 Ion-Pac column and an ED40 electrochemical detector, to determine nitrate concentrations. All samples that had NO_3^- concentrations below the minimum size required for isotope ratio mass spectrometry (IRMS, 100 nmols in 10 mL) analysis were pre-concentrated using a technique detailed in the auxiliary material.¹ Once at the desired concentration, samples were analyzed with a Finnigan Delta Plus Advantage isotope ratio mass spectrometer (Thermo Fischer Scientific, Waltham, MA) using the bacterial reduction and thermal decomposition method described by Casciotti et al. [2002] and Kaiser et al. [2007]. Briefly, aqueous samples undergo bacterial reduction using a strain of *Pseudomonas aur-eofaciens* to convert aqueous phase NO_3^- to gas phase nitrous oxide (N_2O). The N_2O is thermally converted to O_2 and N_2 by reduction over a Au surface at 800°C . The O_2 and N_2 were separated using a 5A molecular sieve gas chromatograph and analyzed by continuous flow isotope ratio mass spectrometry.

2.3. Calculation of the Atmospheric Contribution

[8] The atmospheric contribution (Avg. $\%_{\text{atm}}$) was calculated using a two-source mixing model [Michalski et al., 2004] shown in equations (2)–(4):

$$\Delta^{17}\text{O}_{\text{sample}} = x \cdot \Delta^{17}\text{O}_{\text{atm}} + (1 - x) \cdot \Delta^{17}\text{O}_{\text{bio}} \quad (2)$$

Since the $\Delta^{17}\text{O}_{\text{bio}} = 0\text{‰}$, and the $\Delta^{17}\text{O}_{\text{atm}}$ value is derived from our cloud water samples ($\Delta^{17}\text{O}_{\text{atm}} = 23.4 \pm 1.0\ \text{‰}$), Equation (2) can be simplified to

$$\Delta^{17}\text{O}_{\text{sample}} = x \cdot 23.4\text{‰} \quad (3)$$

Here x is the mole fraction of the atmospheric contribution. The $\Delta^{17}\text{O}$ values yield both the percentage of the atmospheric (equation (4)) and the biological derived nitrate.

$$\% \text{NO}_3^-_{\text{atm}} = (\Delta^{17}\text{O}_{\text{sample}} / 23.4\text{‰}) \cdot 100 \quad (4)$$

Uncertainties were calculated for $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ using the water exchange model described below.

[9] Oxygen isotope data were corrected for exchange with water during the sample processing denitrification of nitrate to nitrous oxide. We used NO_3^- reference materials USGS35, USGS34, and three mixtures of USGS35 and USGS34 (25:75, 50:50, and 75:25) with nitrate quantities ranging from 10 to 250 nmols to quantify the exchange. A description of the characterization and application of this correction is available in the auxiliary material. The long-term precision for analysis of two nitrate reference materials (USGS35 and a 50:50

¹Auxiliary materials are available in the HTML. doi:10.1029/2011GL047539.

Table 1. Summary of the Collected Data Separated by Sample Type^a

Sample Type	<i>n</i>	$\Delta^{17}\text{O}(\text{‰}) \pm \text{Sample SD}$	Average (‰_{atm})
Cloud Water	2	$23.4 \pm 1.0^*$	100
Rain Water	17	23.1 ± 1.8	100
Soil Extracts			
Soil Cores (0 – 30 cm)	16	2.0 ± 1.1	8.6 ± 4.7
Forest Floor Samples (0 – 8 cm)	4	3.6 ± 2.4	15.4 ± 10.3
Post Rain Event (0 – 30 cm core)	6	1.6 ± 0.3	6.8 ± 1.3
20 hrs Post Rain Event (0 – 30 cm core)	4	0.6 ± 0.2	2.6 ± 0.9

^aThe $\Delta^{17}\text{O}$ values are the averages reported with \pm one standard deviation in units of per mil (‰). *n* is the number of samples. *Standard deviation for this sample range is not rigorous as only two data points were collected.

mixture of USGS35:USGS34) at 100–300 nmols of nitrate is 0.6 ‰ (1σ). For smaller sample quantities (<50 nmols) the precision degrades to 1.6 ‰ (1σ).

[10] Exchange processes occurring in the soil solution do not affect the $\Delta^{17}\text{O}$ calculation. $\delta^{18}\text{O}$ alterations do occur, but $\Delta^{17}\text{O}$ values are unaffected because they are independent of the absolute $\delta^{18}\text{O}$ values [Michalski *et al.*, 2004]. Additionally the equilibrium exchange of oxygen between nitric acid and water is too slow to be measurable at low concentrations. This only changes in the presence of nitrite or lower oxidation state species, which are not in significant concentrations at the field site [Bunton *et al.*, 1953]. Therefore it is assumed that atmospheric $\Delta^{17}\text{O}$ values from nitrate are robust and un-impacted by soil reactions prior to biological processing.

3. Results and Discussion

[11] Table 1 shows a summary of the analyzed data by sample type. The oxygen isotope data for all nitrate samples analyzed for calculation of the atmospheric contribution are shown in Figure 1. This 2-D plot shows the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values for all soil samples plotted in three isotope space

along with the mass dependent ($\delta^{17}\text{O} = 0.52 \times \delta^{18}\text{O}$) and independent ($\delta^{17}\text{O} = \delta^{18}\text{O}$) fractionation lines. The error bars are the calculated uncertainties for $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$. The $\Delta^{17}\text{O}$ uncertainty is significantly lower (avg of 0.6 ‰ for 100–300 nmols) as determined by deviation from known nitrate standards.

[12] The $\Delta^{17}\text{O}$ data indicates that nitrate in UMBS soil contains a significant atmospheric component ($\Delta^{17}\text{O} = 2.0 \pm 1.1$ ‰; $\text{‰NO}_3^-_{\text{atm}} = 9\%$ on average), with a greater fraction in the forest floor ($\Delta^{17}\text{O} = 3.6 \pm 2.4$ ‰; $\text{‰NO}_3^-_{\text{atm}} =$ approximately 15%). All uncertainties are expressed as ± 1 standard deviation unless stated otherwise. To determine that the averages reported in Table 1 are statistically different, we applied an unbalanced one-way analysis of variance (ANOVA). In addition, two outliers underwent a cubic regression analysis (q-test) described by Rorabacker [1991] and were determined to fall outside the 99% confidence limits. These two data points were eliminated from the reported averages in Table 1. For the comparison of the forest floor and soil core samples we reject the null hypothesis at the $\alpha = 0.1$ confidence level and conclude statistically different sample means. The larger $\text{‰NO}_3^-_{\text{atm}}$ in the top layer

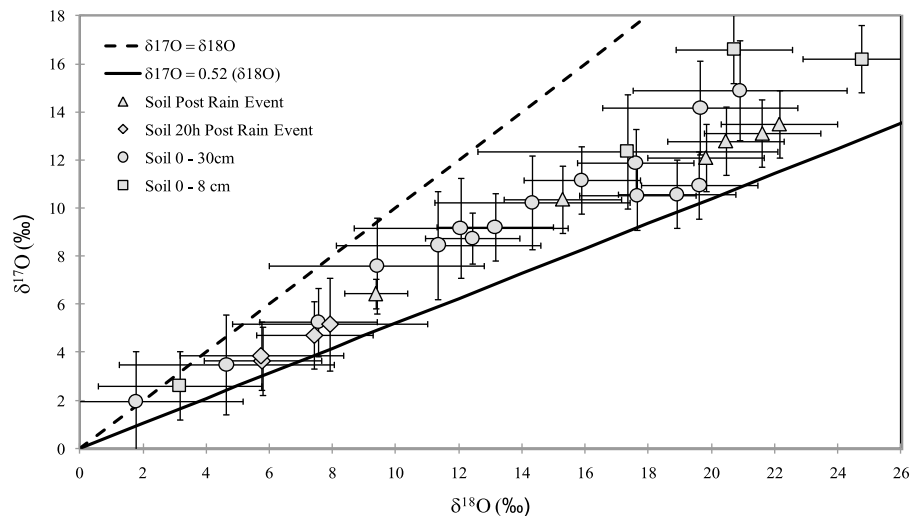


Figure 1. Plot of all soil samples in three isotope space, specifically the major ($\delta^{18}\text{O}$) and minor ratios ($\delta^{17}\text{O}$) of oxygen. The solid line is the Standard Mean for Ocean Water (SMOW), indicating the mass dependent fractionation line ($\delta^{17}\text{O} = 0.52 \times \delta^{18}\text{O}$). The mass independent fractionation line indicating 100% atmospheric processing ($\delta^{17}\text{O} = \delta^{18}\text{O}$) is illustrated by the dashed line. The uncertainty for all samples was dependent on sample quantity (nmols) and exchange with water. Each sample has error bars consistent with the calculated uncertainty (1σ) from the nitrate standards analyzed and integrated into the exchange mixing model described in the auxiliary material. Note that these are the uncertainties for $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$; for $\Delta^{17}\text{O}$ the average uncertainty was 0.6‰.

(~15%) is consistent with the evolution of nitrate in the ecosystem. As soil depth increases, time since deposition also increases, increasing the fraction of the deposited nitrogen that is processed by bacteria. Thus it is likely that 9% is a lower limit to the atmospheric nitrate impact.

[13] For the rain and cloud water $\Delta^{17}\text{O}$ averages, $23.1 \pm 1.8\%$ and $23.4 \pm 1.0\%$, respectively, the null hypothesis is accepted at the $\alpha = 0.05$ confidence level. Therefore, the samples have statistically indistinguishable means. These values are slightly lower than the *Alexander et al.* [2009] model of atmospheric nitrate that calculated monthly-mean $\Delta^{17}\text{O}$ values for $\text{NO}_3^-_{\text{atm}}$ of 26.0–27.7‰ in Michigan during June through August. Our rain and cloud water $\Delta^{17}\text{O}$ data are slightly lower, but within the spread of aerosol samples ($26 \pm 3\%$) collected by *Michalski et al.* [2004] in southern California. Furthermore, since it is known that metabolically active bacteria exist in cloud water [*Hill et al.*, 2007], it is possible that in-cloud bacterial processing decreased the $\Delta^{17}\text{O}$ for cloud and rain water NO_3^- prior to sampling. This does not affect the analysis conducted in this study as only a baseline $\Delta^{17}\text{O}$ from the local atmosphere was needed.

[14] The nitrate $\Delta^{17}\text{O}$ values from soil cores collected immediately after precipitation ($1.6 \pm 0.3\%$) are not significantly different from the pre-event 0–30 cm values ($2.0 \pm 1.1\%$). This result was unexpected. Due to an increase in atmospheric nitrate deposition (wet deposition and canopy wash down of dry deposited nitrogen) we anticipated an increase in $\Delta^{17}\text{O}$ values immediately after precipitation. However, at the UMBS site the soil pore space is approximately 50% of the bulk volume, and the average precipitation nitrate concentrations are $1.7 \mu\text{gNO}_3^-/\text{mL}$ [*Hill et al.*, 2005]. Thus, if the pore space was saturated by rain we would expect an increase of $0.85 \mu\text{gNO}_3^-/\text{cm}^3$ of bulk soil volume ($0.19 \mu\text{gN}/\text{cm}^3$), assuming no soil nitrate is displaced by the rain. *Zogg et al.* [2000] determined that dried UMBS soil has a nitrate concentration of $1.3 \mu\text{g N}/\text{g}$ soil and a soil density of $0.82 \text{ g soil}/\text{cm}^3$, giving an average concentration of nitrate nitrogen of $1.1 \mu\text{gN}/\text{cm}^3$. This means that the rain would contribute 14.7% of the total nitrate present in the soil after rainfall, and a calculated $\Delta^{17}\text{O}$ of ~4‰ (assuming no leaching or nitrification), which is well within the detection capabilities of the IRMS, stated above. Based on the *Zogg et al.* [2000] average soil concentrations a minimum change of $0.03 \mu\text{gN}/\text{cm}^3$ (0.6‰) would be required to register the impact of atmospheric deposition. That would correspond to filling 15% of the pore space volume with water at the average rainfall nitrate concentration.

[15] Additionally, while it appeared that there was no statistically significant change in the total extractable nitrate concentration after rain events (pre rain $[\text{NO}_3^-] = 41 \pm 79 \mu\text{M}$ (for extraction of 50g samples into 60 mLs water); post rain $[\text{NO}_3^-] = 25 \pm 22 \mu\text{M}$), this cannot be conclusively stated, because soil moisture was not measured during sample collection nor were the soil samples dried prior to being weighed (to minimize the possibility of transformations of nitrate during processing). Rainfall could have effectively diluted the soil mass due to the presence of water, and given an artificially low soil nitrate concentration for the post rain samples. Therefore, it is possible that the N pool size had increased and only the isotopic ratios remained constant. Soil cores (0 to 30 cm) collected 20 hours after the completion of a rain event ($0.6 \pm 0.2\%$) were determined to be significantly different from the pre rain and immediate post

rain soil cores at the same depths. This decrease in atmospheric contribution to the nitrate pool can be attributed to two possible sources; a) a change in net nitrification due to the increased biological activity stimulated by the rain, and/or b) rapid uptake, immobilization, mineralization, and denitrification/re-nitrification of the incoming atmospheric nitrate. Both sources are likely, as a study by *Stark and Firestone* [1993] found that the highest nitrification rates occurred during increased water potential. Additionally, as the water potential decreased from evaporative drying, they found an exponential decline in nitrification rates. This is consistent with our data that indicates a ‘pulse’ of biologically processed (decrease of atmospheric contribution from ~9% to ~3%) nitrate 20 hours after rain events followed by the return to pre-rain contributions within 48 hours. For all the soil samples, the large sample standard deviation can be attributed to the significant spatial heterogeneity of soil at the collection site. Factors such as vegetation cover, root density, and localized microbial communities can affect nitrate concentration and isotopic fractionation within several meters. However, these data clearly show the value of $\Delta^{17}\text{O}$ as a measurement of the activity of biological processing, and the distribution of processed versus deposited nitrate.

[16] Because these results represent only the atmospheric nitrate component of nitrogen fractionation at the time of sampling, and a snapshot in the soil nitrogen cycling process, they should be considered in the context of the complete cycle of nitrogen. Previously it was believed that plant nutrients originated as soil organic matter or nitrate and were cycled by microbes to generate ammonium (NH_4^+), which was subsequently taken up by roots after microbial assimilation. This paradigm has been expanded in recent years [*Schimmel and Bennett*, 2004]. Recent studies have shown that plants obtain their nutrients from a variety of sources including direct root uptake of nitrate [*Min et al.*, 1998] and organic nitrogen [*Näsholm et al.*, 2009], in addition to canopy uptake through leaves [*Lockwood et al.*, 2008; *Sparks et al.*, 2003]. However, at this site, the extractable ammonium and organic nitrogen in soil solution (which have similar concentrations) can be twice the total extractable nitrate [*Zak et al.*, 2004]. Thus, although direct root uptake of nitrate is an important pathway, it is a significantly smaller source of N for plants due to a smaller concentration in soil solution. Figure 2 shows a simplified pictorial representation of the forest nitrogen cycle for a temperate (nitrogen-limited) forest, where the arrow width represents relative fluxes. As shown, most plant species preferentially uptake ammonium followed by either nitrate or organic nitrogen [*Schimmel and Bennett*, 2004]. However, this preference is greatly dependent on tree species, soil solution concentrations, and local temperature and hydration [*Min et al.*, 1998, 1999; *Templer and Dawson*, 2004]. A study by *Min et al.* [1998] determined that at low nitrogen concentrations, trembling aspen showed high rates of nitrate uptake and a 2–3 fold preference for ammonium over nitrate [*Min et al.*, 1999]. This preference is significantly smaller than for many other tree species. These results indicate that direct root uptake of nitrate from soil solution may be significant at our field site. However, plants are not the only sink for ammonium and nitrate in soil solution. It has previously been suggested that microbes out-compete plants for the uptake of inorganic nitrogen [*Zak and Pregitzer*, 1990].

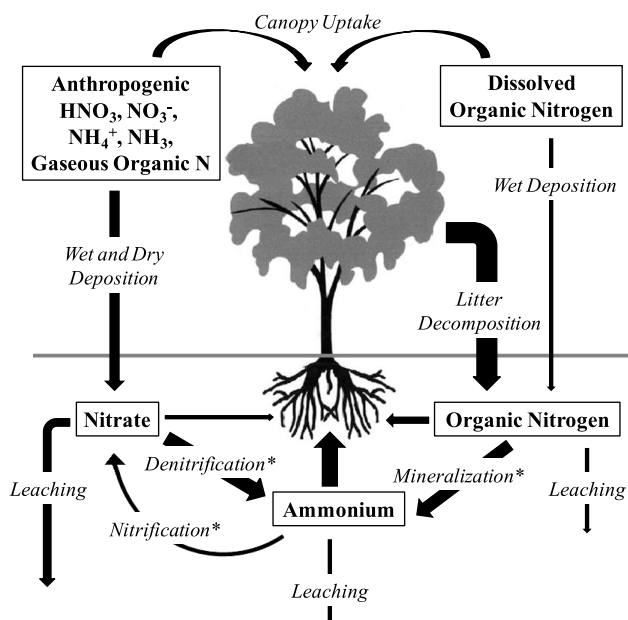


Figure 2. Simplified schematic of nitrogen cycling in temperate, nitrogen limited forests. The width of the arrows denotes the relative magnitude of the flows. Asterisk indicates microbial processing.

In recent studies by Zogg *et al.* [2000] and Zak *et al.* [2004], it was concluded that microbes were a significant short-term sink for nitrate. Additionally, several studies in areas of low nitrogen have found microbial growth to be limited due to uptake of nitrogen by roots [Jingguo and Bakken, 1997]. Although this evidence is indirect, it appears that in some cases plants can successfully compete with microbes for incoming inorganic nitrogen and limit bacterial nitrogen immobilization. This competition is important for understanding how atmospheric nitrate deposition impacts N cycling and the potential sources of N for plant nutrients.

[17] Evaluating our results in this context, the observation that 9 to 15% of water-extractable soil NO_3^- is derived from the atmosphere suggests that atmospheric processes have a direct impact on soil N cycling. Previous studies have determined that the relative concentrations of nitrate and ammonium are within a factor of two, and that the tree species present at UMBS can effectively uptake NO_3^- as a source of nutrients. Therefore, it can be concluded that while microbial nitrogen cycling is the principal source of nutrients for the ecosystem, atmospheric deposition significantly contributes to the N pool, and thus has the potential to contribute to net primary productivity in this forest.

4. Conclusions

[18] An analysis of the atmospheric contribution to the nitrate pool has been performed utilizing measurements of the $\Delta^{17}\text{O}$ nitrate composition and the results discussed in the context of forest nitrogen cycling. Previously no direct measurement of the contribution of atmospheric nitrate to the soil solution nitrogen pool has been conducted for this type of forest. It has been thought that (for this site) atmospheric nitrogen played an insignificant part in nutrient uptake and carbon storage [Nadelhoffer *et al.*, 1999]. This

study determined that approximately 9% of the nitrate pool is un-cycled nitrate directly from atmospheric deposition. This is a significant potential source for uptake by the plant stand. Furthermore, due to the link between nitrogen availability and biomass accumulation, it is possible that such un-cycled nitrate contributes significantly to net primary production and carbon storage. From this work it is clear that atmospheric nitrate deposition is an important component of nutrient cycling in nitrogen-limited forests and, for this type of forest, atmospheric inputs are likely to increase in importance. The atmospheric component of the total nitrogen pool is very likely to be even larger than was found in the current study due to atmospheric deposition of $\text{NH}_3/\text{NH}_4^+$. Hill *et al.* [2005] found that 61% of the nitrogen deposited from the atmosphere at the UMBS site was from $\text{NH}_3/\text{NH}_4^+$ (compared to 31% for $\text{HNO}_3/\text{NO}_3^-$). It is clear that measurements of the mass independent fraction of oxygen ($\Delta^{17}\text{O}$) in nitrate are a useful complement to other measurements of soil nitrogen processing.

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