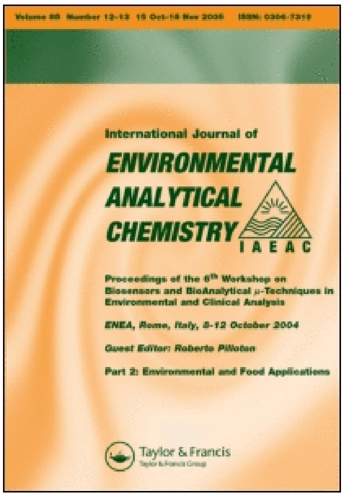

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# Nitrogen Isotope Composition of Ammonium and Nitrate in Bulk Precipitation and Forest Throughfall

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# NITROGEN ISOTOPE COMPOSITION OF AMMONIUM AND NITRATE IN BULK PRECIPITATION AND FOREST THROUGHFALL

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The stable nitrogen isotope composition of ammonium ($NH_4^+$) and nitrate ($NO_3^-$) ions in bulk precipitation and forest throughfall was determined at Walker Branch watershed, a low elevation site (340 m) in northeastern Tennessee, and in cloud water from Whitetop Mountain, a high elevation site (1680 m) in southwestern Virginia. Tests of the method used indicated that sample processing did not introduce significant isotopic fractionation in measurements of nitrogen isotope composition. Mean $\delta^{15}N$ values for $NH_4^+$ and $NO_3^-$ in solutions of artificial rain were within 0.3‰ of the mean $\delta^{15}N$ values of nitrogen compounds used to make the solutions. Over a one-year period on Walker Branch watershed, the measured mean ($\pm$SD) $\delta^{15}N$ value for $NH_4^+$ in bulk precipitation and throughfall ($-3.4 \pm 2.1$‰) was significantly less than that for $NO_3^-$($+2.3 \pm 2.4$‰). The same relative pattern was observed in cloud water from Whitetop Mountain: mean ($\pm$SD) $\delta^{15}N$ in cloud water $NH_4^+$ was $-5.5 \pm 3.2$‰; i.e., isotopically lighter than $NO_3^-$($+1.4 \pm 4.8$‰). The isotopic composition of $NH_4^+$ in bulk precipitation and throughfall on Walker Branch watershed and in cloud water at Whitetop Mountain was consistent with origination through the washout of atmospheric $NH_3$. However, the origins of $NO_3^-$ (gaseous versus aerosol precursors) could not be clearly established from $\delta^{15}N$ measurements.

KEY WORDS: Stable nitrogen isotopes, nitrogen-15, bulk precipitation, throughfall, cloud water, ion exchange.

## INTRODUCTION

High rates of atmospheric deposition of nitrogen (N) currently occur over large regions of Europe and the United States as a result of increased anthropogenic sources[1]. While atmospheric deposition of N is recognized as an important component of acidic deposition, numerous questions remain about its role in forest ecosystems, including the processes of its interactions with the forest canopy and its fate in forest N cycles. Heaton[2] has recently reviewed how studies of stable N isotope ratios ($^{15}N/^{14}N$) in the hydrosphere and the atmosphere might be used to investigate sources and ecosystem processing of atmospheric N deposition. However, there are few studies of stable N isotope ratios in precipitation and N compounds in the atmosphere[3–6].

Hoering[3] first described the use of ion exchange for the quantitative separation of $NH_4^+$ and $NO_3^-$ ions from rain for stable N isotope analysis. Moore[4] also later successfully used ion exchange for this same purpose. Such isotopic data are potentially useful for the identification of precursors to inorganic N in precipitation and for tracing the fate of pollutant N inputs to forest ecosystems. In the present work, Hoering's method[3] has been modified and tested to examine differences in the stable N isotope composition of $NH_4^+$ and $NO_3^-$ in bulk precipitation and forest throughfall at Walker Branch watershed, a low elevation site (340 m) near Oak Ridge, Tennessee, and the isotopic composition of inorganic N in cloud water from Whitetop Mountain, a high elevation site (1680 m) in southwestern Virginia. Modifications to Hoering's methods were made to minimize the generation of hazardous wastes in the laboratory.

## METHODS

### *Sample collections*

Collectors were placed in a ridgetop clearing (Rain Gauge #2) on Walker Branch watershed adjacent to a precipitation chemistry collection site that is part of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) and beneath deciduous (mixed hardwood) and coniferous (loblolly pine) canopies within 400 m of the NADP/NTN station. Bulk precipitation (ie., rainfall collected in a sampler that was continuously exposed to the atmosphere) and throughfall (ie., precipitation collected beneath the forest canopy) was sampled over a period of one year. The rate of sample collection was varied by using one or two polyethylene funnels to direct wet deposition into ion exchange columns. Each funnel (0.03 $m^2$) was covered with an 8 mm mesh polyethylene screen to exclude falling leaves or other large debris. Water exiting each funnel passed a washed glass wool plug to remove fine debris before entering the ion exchangers. During warm weather, the exchange columns were set up in a reverse flow arrangement which kept the exchange resins from drying out. During cold weather, the columns were set up in a direct flow arrangement which allowed excess water to drain from the columns and helped to prevent freezing (Figure 1). Effluent from the exchange columns drained into a vented 7 l plastic carboy. Samples were taken from carboys to determine the efficiency of removal of $NH_4^+$ and $NO_3^-$ from bulk precipitation and throughfall by ion exchange.

Collectors were checked weekly; glass wool plugs were changed and any debris was removed from the funnels. Ion exchange columns were changed when effluent volumes were between 4 and 7 l. Fluxes of $NH_4^+$ and $NO_3^-$ in bulk precipitation and throughfall were calculated based on measured volumes, the amount of $NH_4^+$ or $NO_3^-$ resident on the exchange columns, and the area of the funnel(s). When the sample collection periods were of comparable duration, total $NH_4^+$ and $NO_3^-$ fluxes ($mg\,m^{-2}$) derived from the ion exchange columns for 9 sampling periods between September 5, 1989, and August 14, 1990, were compared with fluxes of $NH_4^+$ and $NO_3^-$ in wet deposition reported by NADP/NTN for Walker Branch watershed. Collection periods ranged from 1 to 6 weeks, depending on the frequency and intensity of rainfall.

Samples of cloud water from Whitetop Mountain, Virginia, were provided for analysis by Dev Joslin (Tennessee Valley Authority). Methods of cloud water

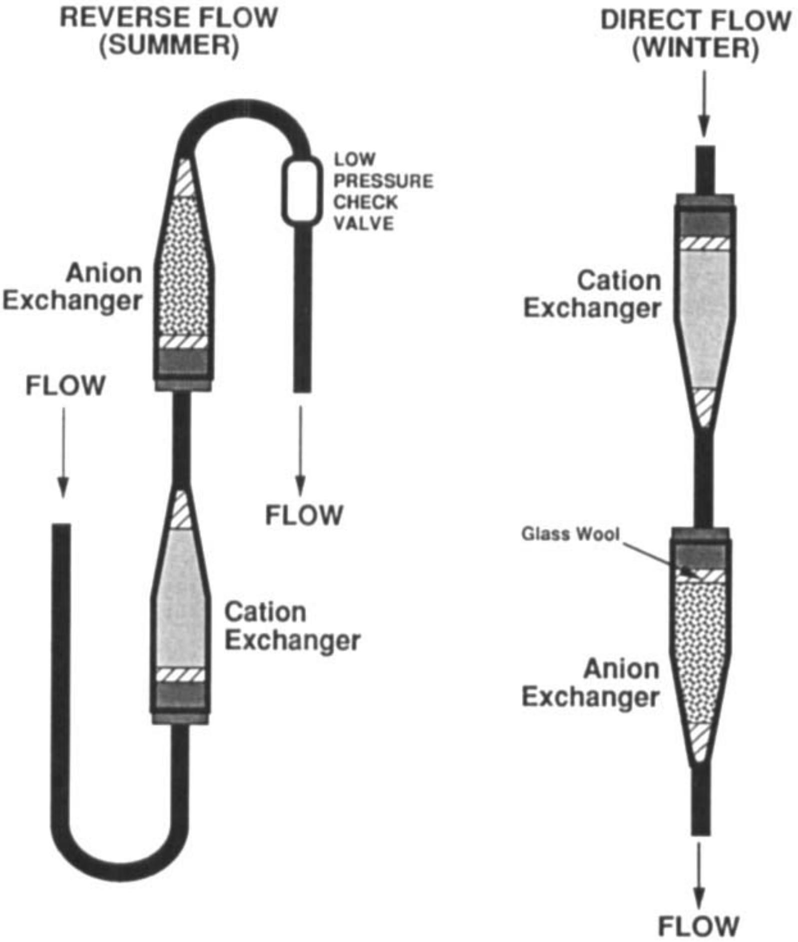

**Figure 1** Arrangement of ion exchange columns during summer and winter collection periods.

collection and preservation are described by Joslin *et al.*[7] The samples were frozen prior to isolation of $NH_4^+$ and $NO_3^-$ by ion exchange methods in the laboratory and subsequent analysis of stable nitrogen isotope composition.

### *Preparation of ion exchangers*

Ion exchange resins ($\approx$2.5 g fresh weight) were loaded into tapered plastic columns (15 mm diameter × 75 mm long) that contained glass wool plugs (previously washed with deionized water) at the bottom and top of the resin column. The cation exchanger (Dowex® 50W-X8, 50 to 100 mesh, $\approx$54% moisture by weight) for collecting $NH_4^+$ was prepared for use in the $H^+$ form and was placed before the anion exchange column (Dowex® 1-X8, 50 to 100 mesh, $\approx$45% moisture by weight) that was converted from a $Cl^-$ to the $OH^-$ form prior to use. The Dowex® 50W-X8 resin is a strongly acidic cation exchanger with sulfonic acid groups attached to a styrene and divinylbenzene copolymer, and does not include N as part of its chemical structure. Dowex® 1-X8 is a strongly basic anion exchange resin with quaternary ammonium groups attached to a styrene and divinylbenzene copolymer.

The amount of resin needed in each column to adsorb $NH_4^+$ or $NO_3^-$ from bulk precipitation or throughfall was based on the total nominal exchange capacity (5.1 meq $g^{-1}$ for the cation exchanger and 3.2 meq $g^{-1}$ for the anion exchanger) and the expected total cation or anion content of rain or throughfall. The weighted average annual concentration of total cations in bulk precipitation (97 $\mu$eq $l^{-1}$) and throughfall (203 $\mu$eq $l^{-1}$) and that for total anions in bulk precipitation (81 $\mu$eq $l^{-1}$) and throughfall (220 $\mu$eq $l^{-1}$) was previously reported from studies on Walker Branch Watershed[8]. In practice, a sample of 4 to 7 liters provided a sufficient amount of N ($>10$ $\mu$mol) for analysis of nitrogen isotope ratios without saturating resin exchange sites.

### *Recovery and isotope analysis*

Isolation and recovery of $NH_4$-N and $NO_3$-N from bulk precipitation or throughfall for isotopic analysis involved four steps: (1) elution of N from the ion exchanger after collection from the field, (2) steam distillation to separate N from the eluate and trap $NH_4$-N in a 2% boric acid solution, (3) sorption of $NH_4^+$ from the boric acid trapping solution onto a small amount of cation exchanger, and (4) conversion to $N_2$ gas (by combustion methods) for isotopic analysis in a mass spectrometer.

*Ammonium-N* In the laboratory, $NH_4^+$ was eluted from the cation exchanger with 40 ml of saturated $K_2SO_4$. Immediately after the addition of MgO (200 mg), the eluate was steam distilled in a Kjeldahl distillation unit and $NH_4^+$ was trapped in 10 ml of a 2% boric acid solution[9,10]. After distillation, a small amount of cation exchanger (50 mg fresh weight) was added to the boric acid distillate to adsorb $NH_4^+$ in solution. After mixing for 3 hours on a rotary shaker, the resin was recovered, washed with 5 ml deionized water, dried at 70°C, and stored in a tightly capped glass vial. Subsamples of the eluate, and distillate before and after shaking with the cation exchanger were analyzed for $NH_4^+$ by automated phenate colorimetry[11] to test recoveries at each step of the analysis.

*Nitrate-N* Nitrate was eluted from the anion exchanger with 40 ml of 2 M KCl followed by 10 ml of deionized water. The method for isolation of $NO_3^-$ was identical to that described above for $NH_4^+$ except that finely ground Devarda's alloy (200 mg) plus MgO (200 mg) was added to the eluate immediately prior to steam distillation to reduce $NO_3^-$ to $NH_4^+$. Subsamples of the eluate were analyzed for nitrate (+ nitrite) by Cd-Cu reduction followed by automated colorimetry[11]. Subsamples of the distillate before and after shaking with 50 mg fresh weight of cation exchanger were analyzed for $NH_4^+$ by automated phenate colorimetry[11].

*Isotopic analysis* Following sorption of $NH_4^+$ from the 2% boric acid solution onto the cation exchanger, an aliquot of the cation exchanger was combusted to yield $N_2$ gas for analysis by mass spectrometry. The combustion method, which is described elsewhere[12], involved mixing a 10 to 12 mg (dry weight) portion of the cation exchanger with 1 gram of cupric oxide powder and overlaying the mixture in a VYCOR® brand glass tube with 1 gram of copper metal granules. The tube was evacuated to <1 mTorr and sealed. The sealed combustion tube was then heated to 850°C (for 3 hours) in a programmable furnace and allowed to cool for 18 h. The combustion gases were released by breaking the tube in a vacuum manifold (<1 mTorr), and $N_2$ was isolated onto 5Å molecular sieve (Alltech Associates, Applied Science Labs, Deerfield, Illinois) cooled by liquid nitrogen after trapping other combustion products. Gas samples were analyzed for $^{15}N/^{14}N$ ratios (R) using a VG Isotech SIRA Series II dual inlet isotope ratio mass spectrometer. Results were expressed in units of per mil (‰) following the classical delta notation ($\delta$) where, $\delta^{15}N = (R_{sample}/R_{reference} - 1) \times 1000$. External precision of the $\delta^{15}N$ measurements was approximately ±0.2‰. The reference gas, which came from a compressed $N_2$ cylinder, was calibrated relative to tropospheric $N_2$ (0.0‰). Analysis of ammonium sulfate standards N-1 and N-2 provided by the National Institute of Standards and Technology, Gaithersburg, Maryland, gave mean (±SD) $\delta^{15}N_{air}$ values of $+0.5 \pm 0.2$‰ (n = 4) and $+20.5 \pm 0.2$‰ (n = 4), respectively.

### *Quality assurance tests*

The sorption efficiency of $NH_4^+$ and $NO_3^-$ from solution by ion exchange and the efficiency of elution from the columns using saturated $K_2SO_4$ or 2 M KCl, respectively, was evaluated by passing freshly collected rain, throughfall, or standard solutions containing known amounts of $NH_4^+$ and $NO_3^-$ through the exchange columns. Each solution was analyzed for $NH_4^+$ and $NO_3^-$ prior to ion exchange to determine the total loading of these ions onto the columns. The eluate from the cation exchanger was analyzed for $NH_4^+$ and the eluate from the anion exchanger was analyzed for $NO_3^-$. The recovery of $NH_4^+$ and $NO_3^-$ by ion exchange from the test solutions was determined based on eluate volume and concentration data, and known inputs to the columns.

Two artificial rain solutions were prepared to test for fractionation effects during the separation, recovery, and preparation of $NH_4$-N and $NO_3$-N by ion exchange methods. Solution A (pH 4.1) contained the following $\mu mol\,l^{-1}$ concentrations of ions: $Mg^{2+}$, 15; $Ca^{2+}$, 64; $Na^+$, 68; $NH_4^+$, 132; $K^+$, 153; $PO_4^-$, 0.6; $NO_3^-$, 59; $Cl^-$, 98; $SO_4^{2-}$, 219. Nitrate and ammonium were supplied to solution A by $KNO_3$ and $(NH_4)_2SO_4$ salts, respectively. Solution B (pH 4.1) contained the following $\mu mol/l^{-1}$ concentrations of ions: $Mg^{2+}$, 54; $Ca^{2+}$, 64; $Na^+$, 34; $NH_4^+$, 128; $K^+$, 93; $PO_4^-$, 0.6; $NO_3^-$, 55; $Cl^-$, 161; $SO_4^{2-}$, 152. Nitrate and ammonium were supplied to solution B by $Mg(NO_3)_2$ and $NH_4Cl$ salts, respectively. Nitrogen-15 abundance in the compounds used to make the artificial rain solutions was determined by mass spectrometry.

Recovery of $NH_4^+$ from solution was tested by shaking the cation exchanger (50 mg fresh weight) with solutions (water or 2% boric acid) containing varying amounts of $NH_4^+$ ion ($NH_4Cl$ form). Solutions were analyzed before and after shaking with the ion exchanger to determine percent recovery. The $NH_4Cl$ used to make the standard solution was analyzed to determine its isotopic composition. The $NH_4^+$ sorbed from each of the solutions onto the ion exchanger was analyzed for its isotopic composition to test for fractionation effects during ion exchange as a function of percent removal of $NH_4^+$ from solution.

## RESULTS

### *Efficiency of field collectors*

Analysis of the effluent from ion exchange columns placed in the field revealed that the ion exchangers had a high efficiency for recovery of both $NH_4^+$ and $NO_3^-$ from bulk precipitation and throughfall. During a six week sampling period (3 October 1989 to 16 November 1989), the input of $NH_4$-N to columns located at rain gauge #2, beneath the deciduous canopy, and beneath the pine canopy was 1420, 1080, and

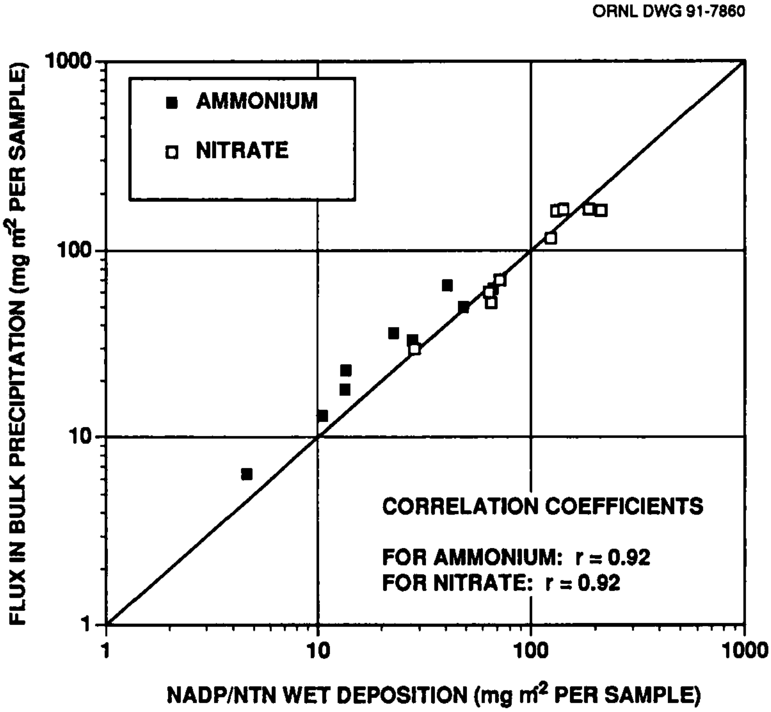

**Figure 2** Correlation between $NH_4^+$ or $NO_3^-$ fluxes in bulk precipitation, as estimated from collections using ion exchange columns, and the respective fluxes in wet deposition only, as measured at the NADP/NTN sampling station on Walker Branch watershed. A reference line of 1:1 correspondence is shown.

1050 µg, respectively. Based on $NH_4^+$ concentrations in the column effluent and effluent volume (7.7 to 9.5 l), less than 5% of the $NH_4^+$ entering the columns passed the cation exchanger. A similar analysis for $NO_3^-$ showed that the calculated input of $NO_3$-N to the columns at the rain gauge, beneath the deciduous, and pine canopies was 1580, 2150, and 3270 µg, respectively. In each case, less than 35 µg $NO_3$-N was found in the column effluent, therefore the anion exchange columns were more than 97% efficient at retaining $NO_3$-N entering the columns.

Ammonium and $NO_3^-$ fluxes in bulk precipitation samples as estimated from the ion exchange columns were highly correlated with fluxes of $NH_4^+$ and $NO_3^-$ in wet deposition reported for the NADP/NTN station on Walker Branch watershed (Figure 2). A paired t-test indicated that $NH_4^+$ fluxes as estimated from the ion exchange columns were approximately 25% higher than those estimated for wet deposition only from the NADP/NTN samplers ($t = -2.30$, $df = 8$; $P < 0.05$). For the sampling periods that were compared, the total $NH_4^+$ flux in wet deposition (NADP/NTN sampler) and that in bulk precipitation (collected by ion exchange) was 248 and 307 mg $m^{-2}$, respectively. A similar test indicated that $NO_3^-$ fluxes estimated by ion exchange and NADP/NTN sampling methods were not significantly different ($t = 0.59$, $df = 8$). For the sampling periods that were compared, the total $NO_3^-$ flux in wet deposition only and that in bulk precipitation was 1026 and 985 mg $m^{-2}$, respectively.

### *Efficiency of recovery through elution, steam distillation, and sorption*

*Elution* Analysis of samples prior to ion exchange and analysis of eluates from the ion exchange columns confirmed observations from field trials that this method had a high efficiency for removal of $NH_4^+$ and $NO_3^-$ from bulk precipitation and throughfall. Table 1 shows the recovery of $NH_4^+$ and $NO_3^-$ from rain, throughfall, and standard solutions that were passed through ion exchange columns in the laboratory. Recovery of $NH_4^+$ and $NO_3^-$ by ion exchange through the elution step was ≈100%.

**Table 1** Recovery of known amounts of $NH_4^+$ and $NO_3^-$ ions from solutions passed through ion exchange columns, followed by elution with saturated $K_2SO_4$ or 2 M KCl, respectively. CV is the coefficient of variation and n is the number of trials.

| *Recovery from* | *Recovery of $NH_4^+$* | | | *Recovery of $NO_3^-$* | | |
|---|---|---|---|---|---|---|
| | *n* | *Mean %* | *CV* | *n* | *Mean %* | *CV* |
| Rainfall | 5 | 111 | 0.05 | 7 | 100 | 0.10 |
| Throughfall | 4 | 97 | 0.16 | 6 | 99 | 0.10 |
| Standard Solution[a] | 4 | 105 | 0.07 | 4 | 95 | 0.11 |

[a] Deionized water with a known addition of $NH_4^+$ or $NO_3^-$.

*Steam distillation* Mean ($\pm$SD) recovery of $NH_4^+$ from saturated $K_2SO_4$ by steam distillation, as determined by analysis of 37 eluates was 90 ±9%. Mean ($\pm$SD) recovery of $NO_3^-$ from 2 M KCl by steam distillation following reduction to $NH_4^+$ with Devarda's alloy, determined by analysis of 34 eluates, was 116 ± 15%.

*Sorption from the distillate* Shaking the distillate (boric acid trapping solution) with 50 mg of cation exchanger quantitatively removed $NH_4^+$ ions from solution. Analysis of 38 trapping solutions before and after shaking with the cation exchanger showed an average 97% (S.D. = 5%) recovery of $NH_4^+$ from solution onto the cation exchange resin.

### *Isotopic fractionation effects during ion exchange*

Values for the nitrogen isotope composition of $NH_4^+$ partially exchanged for $H^+$ on the cation exchanger were in good agreement with the isotopic composition of the original $NH_4$-N added to solution (+0.4 ± 0.3‰, n = 4). The $\delta^{15}N$ value of $NH_4$-N when 35 and 68% of the $NH_4^+$ was adsorbed by the ion exchanger from 2% boric acid solution was +0.3 and +0.2‰, respectively. The $\delta^{15}N$ value of $NH_4$-N when 27, 39, 69, and 70% of the $NH_4^+$ was adsorbed by the ion exchanger from aqueous solution was +0.1, +0.1, +0.2, and +0.1‰, respectively. No significant fractionation effects were introduced by the partial sorption of $NH_4^+$ from water or 2% boric acid solutions by the cation exchanger. The variation observed was within the analytical error of the method.

### *Measurements of $^{15}N$-abundance in artificial rain solutions*

Significant isotopic fractionation of $NH_4$-N and $NO_3$-N by the methods described here was also not apparent in determinations of the isotopic composition of $NH_4$-N and $NO_3$-N in artificial rain solutions. The mean $\delta^{15}N$ values for stock N compounds, which were measured directly, and the means based on the analysis of the solutions

**Table 2** Comparison of $\delta^{15}N$ values in stock N compounds with $\delta^{15}N$ values in artificial rain solutions made from the stock N compounds. Nitrate and ammonium were separated and isolated from artificial rain solutions for isotopic analysis by ion exchange, steam distillation, and sorption onto a cation exchanger (see Methods section)

| *Stock* | *$\delta^{15}N$ in compound* | | | *$\delta^{15}N$ in artificial rain* | | |
|---|---|---|---|---|---|---|
| | *n* | *Mean* | *SE* | *n* | *Mean* | *SE* |
| Solution A | | | | | | |
| $KNO_3$ | 3 | +1.2‰ | ±0.1 | 4 | +0.9‰ | ±0.2 |
| $(NH_4)_2SO_4$ | 4 | −0.3‰ | ±0.2 | 4 | −0.1‰ | ±0.1 |
| Solution B | | | | | | |
| $Mg(NO_3)_2$ | 3 | +6.5‰ | ±0.3 | 4 | +6.2‰ | ±0.3 |
| $NH_4Cl$ | 4 | +0.4‰ | ±0.2 | 4 | +0.6‰ | ±0.2 |

made from those compounds are shown in Table 2. Differences between the $\delta^{15}N$ value in the compound and the $\delta^{15}N$ value in artificial rain reflected the fractionation associated with the entire method of analysis (including capture of $NH_4$-N and $NO_3$-N from artificial rain solutions onto the ion exchange columns, elution from

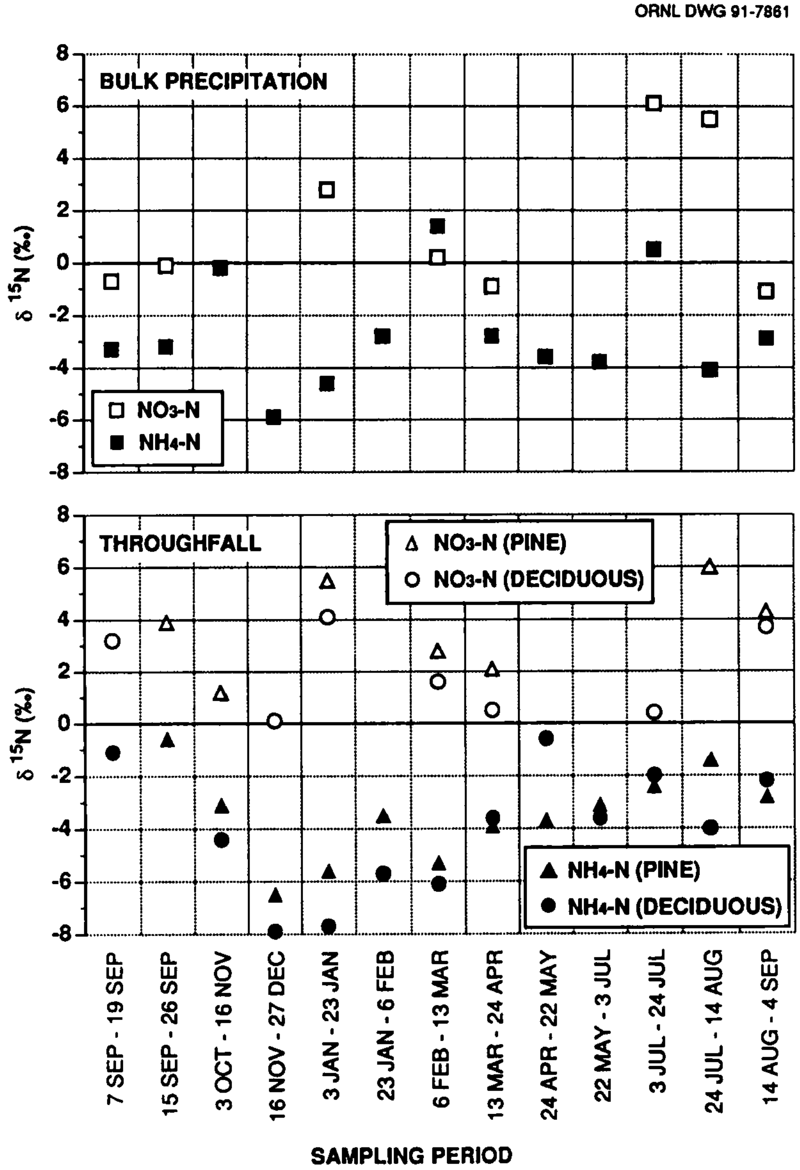

**Figure 3** Measurements of $\delta^{15}N$ for $NH_4$-N and $NO_3$-N in bulk precipitation (above) and in throughfall collected beneath pine and deciduous forest stands (below) on Walker Branch watershed. Some $NO_3$-N samples were lost due to technical difficulties with steam distillation. Bud break on deciduous trees occurs in early April and autumn leaf fall occurs in early November.

the columns, steam distillation, recovery of $NH_4^+$ from the distillate onto the cation exchanger, and combustion to convert $NH_4^+$ to $N_2$ gas). Mean $\delta^{15}N$ values for $NH_4^+$ and $NO_3^-$ in artificial rain were within 0.3‰ of the mean $\delta^{15}N$ in stock N compounds used to make the solutions (Table 2).

### *Measurements of $^{15}N$-abundance in bulk precipitation and throughfall*

Figure 3 shows measurements of $\delta^{15}N$ in $NH_4^+$ and $NO_3^-$ in bulk precipitation and throughfall beneath forest stands on Walker Branch watershed for different sampling periods over one-year. Nitrate-N was generally enriched in $^{15}N$ relative to $NH_4$-N in both bulk precipitation and forest throughfall. A one-way analysis of variance indicated a statistically significant difference in $\delta^{15}N$ values between the following six groups: (1) $NH_4^+$ in bulk precipitation, (2) $NO_3^-$ in bulk precipitation, (3) $NH_4^+$ in pine throughfall, (4) $NO_3^-$ in pine throughfall, (5) $NH_4^+$ in deciduous throughfall, and (6) $NO_3^-$ in deciduous throughfall ($F = 21.11$, df = 5, 53; $P < 0.01$). Multiple comparisons between group means, made using Tukey's honest significant difference, indicated that the $\delta^{15}N$ of $NO_3^-$(+1.5‰) in bulk precipitation was not statistically different from that of throughfall $NO_3^-$ beneath pine (+3.7‰) and deciduous (+1.9‰) stands. Similarly, the $\delta^{15}N$ of $NH_4^+$ (−2.7‰) in bulk precipitation was not statistically different from that of throughfall $NH_4^+$ beneath pine (−3.5‰) and deciduous (−4.1‰) stands. However, in bulk precipitation and both types of throughfall samples, $NO_3^-$ always had significantly higher $\delta^{15}N$ values than those for $NH_4^+$. The frequency distributions for $\delta^{15}N$ in $NO_3^-$ and $NH_4^+$ in combined bulk precipitation and throughfall are shown in Figure 4.

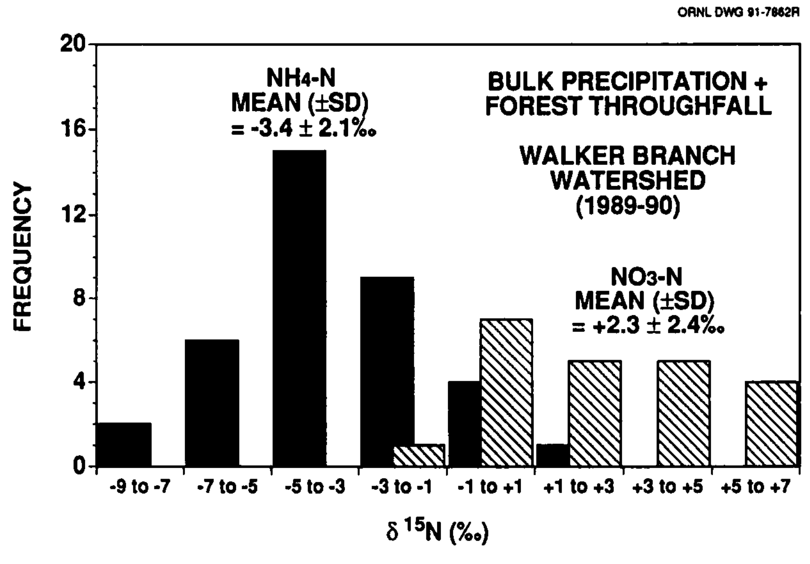

**Figure 4** Frequency distribution of $\delta^{15}N$ for $NH_4$-N and $NO_3$-N in combined collections of bulk precipitation and throughfall on Walker Branch watershed.

**Table 3** Cloud water sampling period, concentration of $NH_4^+$ or $NO_3^-$, and $\delta^{15}N$ in cloud water collected at the summit of Whitetop Mountain, Virginia

| *Sampling period* | *$NH_4^+$* | | *$NO_3^-$* | |
|---|---|---|---|---|
| | *μg N ml$^{-1}$* | *$\delta^{15}N$* | *μg N ml$^{-1}$* | *$\delta^{15}N$* |
| 17 July–28 July, 1987 | 5.3 | −3.4‰ | 2.5 | −3.5‰ |
| 5 August 1987 | 4.5 | −3.5‰ | 5.5 | +7.4‰ |
| 11 August–13 August, 1987 | 3.7 | −5.1‰ | 3.9 | −1.5‰ |
| 4 May–6 May, 1988 | 2.0 | −10.1‰ | 2.3 | +3.1‰ |

### *Measurement of $^{15}N$-abundance in high elevation cloud water*

Although, there was considerable variation between samples (Table 3), relative trends in the $\delta^{15}N$ of cloud water $NH_4^+$ and $NO_3^-$ from Whitetop Mountain were similar to those observed for $NH_4^+$ and $NO_3^-$ in bulk precipitation on Walker Branch watershed. Mean (±SD) $\delta^{15}N$ in cloud water $NH_4^+$ was −5.5 ± 3.2‰; i.e., isotopically depleted in $^{15}N$ relative to the mean $\delta^{15}N$ in cloud water $NO_3^-$ (+ 1.4 ± 4.8‰). Concentrations of $NH_4$-N and $NO_3$-N in cloud water from each sampling period ranged between 2 and 5.5 μg N ml$^{-1}$ cloud water (Table 3). These concentrations are considerably higher than average concentrations for $NH_4$-N and $NO_3$-N in rainfall on Walker Branch watershed (0.16 μg N ml$^{-1}$ and 0.29 μg N ml$^{-1}$, respectively).

## DISCUSSION

In his study of stable N isotopes in rainfall, Hoering[3] originally used a saturated barium chloride solution to elute $NH_4^+$ ions from a cation exchanger. Under some circumstances, laboratory wastes containing barium compounds may now be classified as "hazardous" because barium has toxic properties. As a step toward waste minimization in this work, potassium sulfate (a less hazardous compound to health) was substituted for barium chloride to elute $NH_4^+$ ions from the cation exchanger. This substitution was made without any apparent adverse effect on the method.

In most cases $NH_4$-N in bulk precipitation and throughfall on Walker Branch watershed and in cloud water from Whitetop Mountain, Virginia, contained less $^{15}N$ (relative to $^{14}N$) than did $NO_3$-N. Freyer[5] reported the same trend for rainfall in the vicinity of Julich, Germany, where, during 2 years of sampling, rainfall $NO_3^-$ ($\delta^{15}N$ = −3.1‰) was consistently enriched in $^{15}N$ relative to rainfall $NH_4^+$ ($\delta^{15}N$ = −12.1‰). Freyer attributed the different isotopic composition of $NH_4$-N and $NO_3$-N in rain to different gaseous precursors in the atmosphere: $NH_4^+$ originating from the washout of atmospheric $NH_3$, a strongly depleted source[2], and $NO_3^-$ originating from the washout of atmospheric nitric oxides (NO and $NO_2$). The equilibrium exchange reactions between NO and $NO_3^-$ or $NO_2$ and $NO_3^-$ are both accompanied by large isotopic fractionations[13] (≈50 to 100‰) that result in the isotopic enrichment of the product, $NO_3^-$. However, different patterns have been reported by other authors. Heaton[6] observed a similarity in the isotopic composition of rainfall $NH_4$-N ($\delta^{15}N = -3.8‰$) and $NO_3$-N ($\delta^{15}N = -3.5‰$) over a one-year period of collections in Pretoria, South Africa. Heaton concluded that the isotope data from Pretoria were consistent with the formation of these ions in rain from gaseous atmospheric precursors ($NH_3$ and $NO_x$, respectively) assuming little overall isotopic fractionation. Moore[4] reported an opposite pattern for $NH_4$-N ($\delta^{15}N = -1.4‰$) and $NO_3$-N ($\delta^{15}N = -6.6‰$) in rain collected near Boulder, Colorado. Differences between these studies may be caused by differences in the isotopic composition of gaseous precursors, or different mechanisms (kinetic versus equilibrium exchange) by which gaseous precursors are dissolved in precipitation, or methodological artifacts.

The isotopic composition of $NH_4$-N in bulk precipitation and throughfall on Walker Branch watershed is more consistent with the washout of $NH_3$ from the atmosphere than the solution of aerosol and particulate $NH_4^+$ by precipitation. Ammonium in dry deposition (aerosols and particulates) tends to be isotopically enriched in $^{15}N$ relative to atmospheric nitrogen[2,4]. Ammonium-N in bulk precipitation and throughfall on Walker Branch watershed was depleted in $^{15}N$ relative to atmospheric $N_2$ and was similar isotopically to values previously reported for $NH_4$-N in rain from Colorado[4]. Hoering[3] measured $\delta^{15}N$ values ranging from $-0.1$ to $+9.0‰$ for rainfall $NH_4^+$ in Arkansas, and concluded that his data were in agreement with the hypothesis that $NO_3^-$ in precipitation arose from the oxidation of atmospheric $NH_3$. In the present study, there was no significant correlation between the isotopic composition of $NH_4$-N and $NO_3$-N in bulk precipitation and throughfall which is consistent with independent origins for these two different chemical forms.

The mean $\delta^{15}N$ value for $NO_3^-$ in bulk deposition and throughfall on Walker Branch watershed was higher than values from previous studies of stable N isotopes in rainfall[2]. One possible cause may be the importance of dry N deposition at this site[14]. The watershed is located within 25 km of two coal-fired power stations. Dry deposition of nitric acid vapor contributes $\approx 50‰$ of the total annual atmospheric flux of $NO_3^-$ to the watershed[14]. Nitrogen dioxide deposition may constitute as much as 40% of dry N deposition during the growing season[15]. The isotopic composition of $NO_3$-N in dry deposition (aerosols and particulates) tends to be enriched in $^{15}N$ relative to wet deposition[2,4]. For example, Moore[4] reported that $NO_3$-N in dry deposition had a mean $\delta^{15}N$ value of $+5.0‰$ near Boulder, Colorado. In addition, $NO_x$ from coal-fired power plants, a potential source of $NO_3$-N in rainfall, is reported to have $\delta^{15}N$ values in the range of $+6$ to $+13‰$[16]. The higher $\delta^{15}N$ value for $NO_3$-N in bulk precipitation and throughfall on Walker Branch watershed is consistent with the washout of particulate $NO_3^-$ from the atmosphere as well as $NO_3^-$ formation from anthropogenic $NO_x$. Therefore, unlike $NH_4^+$ in rain, the origins of $NO_3^-$ in bulk deposition and throughfall on Walker Branch watershed (ie. gaseous versus aerosol precursors) are not clear from $\delta^{15}N$ measurements, but the higher $\delta^{15}N$ values for $NO_3$-N are probably related to dry deposition.

Data on the isotopic composition of inorganic N in precipitation and throughfall has potential for tracing the fate of pollutant N inputs to forest ecosystems. For example, on N-deficient ridges and slopes on Walker Branch watershed, the mean ($\pm$SD) $\delta^{15}N$ value of leaf N in red maple (*Acer rubrum*) trees is $-3.2 \pm 1.2‰$ (n = 36, unpublished data); similar to that of $NH_4$-N in bulk precipitation and throughfall and different from that of $NO_3$-N (Figure 4). This comparison suggests (but does not prove) that foliar N in *Acer rubrum* is partly derived from $NH_4$-N in precipitation inputs to the forest canopy or throughfall inputs to shallow roots in the forest floor. Tracer studies with enriched $^{15}N$ under laboratory conditions have shown that $NH_4^+$ applied to *Acer rubrum* and *Quercus alba* (white oak) leaves in simulated rainfall is preferentially retained relative to $NO_3^-$.[17] This finding is also consistent with field observations of flux or concentration differences between rain and throughfall that indicate the uptake of ammonium deposition by the forest canopy[14,17]. Together our studies indicate a potential importance of $NH_4$-N inputs to forest N cycling on Walker Branch watershed. Future studies of stable N isotopes in wet and dry deposition may help improve our understanding of forest N cycling and changes in N cycling as a result of increasing or decreasing anthropogenic N emissions to the atmosphere.

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