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Stable nitrogen isotope ratios in wet and dry nitrate deposition collected with an artificial tree

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ABSTRACT

Amounts of dry NO_3-N deposition and N isotope ratios in wet and dry NO_3-N deposition have been simultaneously determined by examining differences between precipitation collected by open funnels and throughfall collected beneath an artificial Christmas tree. Samples were collected in a forest clearing on Walker Branch Watershed, near Oak Ridge, Tennessee. From mid-summer to early autumn, NO_3-N fluxes beneath the artificial tree were always greater than those measured in precipitation indicating the tree's effectiveness as a passive collector of dry NO_3-N deposition. Dry NO_3-N deposition averaged 60 ± 9 % of total (wet and dry) deposition. The mean ($\pm$SD) calculated $\delta^{15}N$ value for NO_3-N in dry deposition was $+5.6 \pm 2.1$ ‰ ($n = 6$ sampling periods ranging from 4 to 15 days). On averge, this was ≈ 6 ‰ heavier than measured $\delta^{15}N$ values for NO_3-N in precipitation. The calculated $\delta^{15}N$ value for NO_3-N in dry deposition was consistent with that expected if NO_x precursors to HNO_3 vapor (the major constituent of dry deposition at this site) originated principally from coal combustion.

1. Introduction

Dry deposition is a significant nitrogen (N) input to many forest ecosystems (Lovett and Lindberg, 1993). The two major components of dry nitrate-N (NO_3-N) deposition to forests are nitric acid vapor (HNO_3) and NO_3-N associated with coarse particles. Although HNO_3 vapor and aerosol nitrate have multiple pathways of formation, both largely originate from the oxidation of tropospheric nitrogen oxides ($NO_x = NO + NO_2$) (Warneck, 1988). Some data indicate that NO_x emitted from coal combustion has a markedly different N isotope ratio than NO_x emitted from automobiles (Heaton, 1990). Such differences could be useful in determining the sources of atmospheric N deposition to forest ecosystems. The use of N isotopes in studies of atmospheric N deposition depends upon (1) methods for successfully isolating and measuring isotopic ratios of NO_3-N in wet and dry deposition and (2) a knowledge of the isotopic fractionations that accompany the transformations of NO_x in the atmosphere. A variety of techniques have been used in the past to collect dry deposition of NO_3-N for isotope studies including high volume impactors (Freyer, 1991), low volume air samplers (Moore, 1977; Freyer, 1991), and exposure of flat plastic sheets during dry weather (Heaton, 1987). The objectives of this research were: (1) describe the results of a passive sampling method for the simultaneous determination of N isotope ratios in wet and dry NO_3-N deposition, and (2) estimate the N isotope composition of HNO_3 vapor which is an important component of dry N deposition to many forest ecosystems (Lovett and Lindberg, 1993).

2. Methods

2.1. Sampling

The study site was located on Walker Branch Watershed near Oak Ridge, Tennessee (35°58′ N; 84°17′ W). During the summer of 1993 an artificial Christmas tree was set on a 1 m high table in a

forest clearing. The tree was 1.5 m tall, had a base diameter of 1.1 m, and was similar to artificial, plastic, "spruce-like" trees used by Joslin et al. (1990). Three polyethylene funnels (each 20 cm in diameter) were placed equidistant around the center pole beneath the lower branches of each tree. The funnels drained through a glass wool filter into a single polyethylene carboy (11.5 litres). The artificial tree provided an inert surface for the interception of dry N deposition (both HNO_3 vapor and particulate NO_3-N). Approximately 2 m away from the tree, 3 polyethylene funnels (each also 20 cm in diameter) were placed in the open to collect wet deposition. These funnels also drained through a glass wool filter into a polyethylene carboy. The contribution of dry deposition to precipitation samples was minimized by cleaning funnels prior to periods of expected precipitation. At the time of each collection, the volume of deposition was measured and samples were returned to the laboratory where they were frozen prior to analysis. Nitrate concentrations in deposition samples were measured at Oak Ridge National Laboratory (ORNL) by Cd-Cu reduction followed by automated colorimetry (US EPA, 1983).

2.2. *Isotope analysis*

Samples were prepared for analysis of N isotopes by previously described methods (Garten, 1992). Briefly NO_3-N was captured by passing aqueous samples (4 litres) through a column containing Dowex® 1 anion exchange resin (which traps nitrate but not ammonium). Nitrate was eluted from the resin column with 2 M KCl followed by 10 ml of deionized water. The elute was steam distilled in the presence of MgO and Devarda's alloy to reduce NO_3^- to NH_3 and the NH_3 was captured from the distillate in 2% boric acid. Ammonium ions were scavenged from the boric acid solution with a small (50 mg) amount of Dowex® 50 ion exchange resin that was recovered from solution, dried, and combusted at 875°C in the presence of CuO and elemental Cu (Minagawa et al., 1984). Nitrogen gas produced by combustion was cryogenically separated from CO_2 and H_2O under vacuum, trapped on molecular sieve, and thermally desorbed from the molecular sieve for measurement of $^{15}N/^{14}N$ ratios (R) using a VG SIRA II dual inlet isotope ratio mass spectrometer. Analytical results are expressed in units of per mil ($^{o}/_{oo}$) following the classical delta notation (δ) where, $\delta^{15}N = (R_{sample}/R_{reference} - 1) \times 1000$. The reference gas was atmospheric N_2.

2.3. *Calculations*

With this method, it was assumed that NO_3-N deposition to the open funnels was equivalent to the flux of NO_3-N in precipitation (P). The NO_3-N flux beneath the artificial tree (TF) was comprised of two fluxes: (1) NO_3-N in precipitation (P) and (2) NO_3-N in dry deposition (D) that was washed from the tree by precipitation. The flux of NO_3-N (mg/m^2) in P and that in TF was calculated as the product of NO_3-N concentration (mg/l) and the respective deposition volume (L) normalized for the total area of the collecting funnels (0.094 m^2). The flux of NO_3-N in dry deposition (D) was then calculated from:

$$D = \mathrm{TF} - P. \tag{1}$$

The isotopic mass balance for NO_3-N in total deposition beneath the artificial tree is:

$$\mathrm{TF}(\delta_t) = P(\delta_p) + D(\delta_d), \tag{2}$$

where,

δ_t = the measured $\delta^{15}N$ value for NO_3-N in total deposition,

δ_p = the measured $\delta^{15}N$ value for NO_3-N in precipitation,

δ_d = the calculated $\delta^{15}N$ value for NO_3-N in dry deposition.

The isotopic composition of dry deposition (δ_d) can be solved from (1) and (2):

$$\delta_d = [\mathrm{TF}(\delta_t) - P(\delta_p)]/(\mathrm{TF} - P). \tag{3}$$

Concentrations (mg/l) of NO_3-N in TF and precipitation can be substituted for fluxes in eqs. (2) and (3) if the respective volumes are equal.

This calculation assumes that interception and washoff of dry deposition from the artificial tree results in no isotopic fractionation, even though the residence time of dry material may be several days and precipitation is known to contain bacteria. If kinetic isotope fractionation does occur during contact with the artificial tree, it would probably decrease the $\delta^{15}N$ value of NO_3-N in TF

Table 1. *Precipitation amounts (PPTN) and $\delta^{15}N$ values in total NO_3-N deposition beneath the artificial tree (δ_t), wet NO_3-N deposition (δ_p), and dry NO_3-N deposition (δ_d) on different days in 1993*

Julian day	Sampling time (d)	PPTN (mm)	Total (δ_t) $\delta^{15}N$ (‰)	Wet (δ_p) $\delta^{15}N$ (‰)	Dry NO_3-N deposition (mg/m^2)	Dry (δ_d) $\delta^{15}N$ (‰)
209	8	28	+1.5	−1.9	30.8	+2.9
218	9	50	+1.9	−1.3	19.6	+4.2
250	15	40	+4.3	+1.9	19.4	+5.2
267	7	25	+2.6	−2.4	11.4	+6.4
271	4	37	+2.6	−0.4	9.6	+5.8
299	15	24	+5.4	+0.4	12.8	+9.0

The $\delta^{15}N$ value in total and wet deposition was measured while that in dry NO_3-N deposition was calculated from mass balance. Sampling time is the number of days without measurable precipitation prior to a sample collection.

and result in an underestimation of the $\delta^{15}N$ value in dry deposition.

3. Results

3.1. Quality assurance measurements

Previous analyses of standard solutions containing NO_3-N with a known $\delta^{15}N$ value indicated that the accuracy of analysis was within 0.5‰ (Garten, 1992). Two additional NO_3-N standard solutions ($\delta^{14}N = +6.5 \pm 0.3$‰) were analyzed as part of this study and also indicated an analytical error of ±0.5‰. The results of ^{15}N analyses of split samples after elution from the Dowex® 1 ion exchange resin were similar. The mean absolute difference between 7 paired replicate samples was 0.4‰. The methods used appear to be accurate to within 0.5‰.

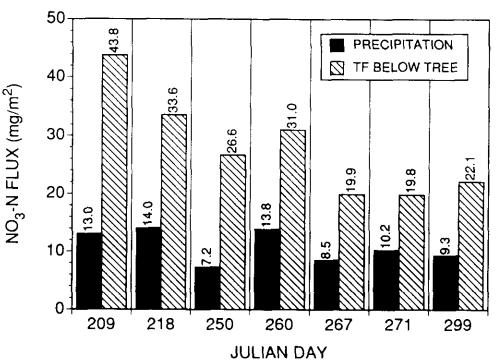

Fig. 1. Fluxes of NO_3-N measured in wet deposition (i.e., precipitation) and in total deposition (i.e., throughfall beneath an artificial Christmas tree) during 1993 at Walker Branch Watershed, Tennessee. Dry NO_3-N deposition (Table 1) was estimated by subtracting the precipitation flux (P) from the throughfall flux (TF).

3.2. Comparative fluxes and N isotope ratios in deposition

Nitrate fluxes beneath the artificial tree were always greater than those in precipitation (Fig. 1). Over 7 different sampling periods, dry deposition was 60 ± 9% of total NO_3-N deposition to the artificial tree. The calculated $\delta^{15}N$ value for NO_3-N in dry deposition ranged from +2.9 to +9.0‰ (mean ±SD = 5.6 ± 2.1‰) for 6 of the sampling periods (Table 1). Samples collected on Julian day 260 (Fig. 1) were lost prior to analysis. A paired t-test indicated that $\delta^{15}N$ values for NO_3-N were significantly greater in dry deposition than in precipitation (mean difference = 6.2‰; $t = 7.02$, df = 5, $p < 0.001$). No correlation between NO_3-N flux and sampling time was evident from the data.

4. Discussion

The use of artificial Christmas trees is an experimental and largely untested method for passively sampling total N deposition. Precipitation, cloudwater, and the washoff of dry deposition from plastic needles all contribute to N in throughfall beneath artificial trees. The efficiency of interception and removal by rainfall into the sample collection and the accuracy of total N flux

derived from this method are unknown. Because of these limitations, N fluxes from this technique should be interpreted with caution.

Previous studies have demonstrated that total atmospheric deposition of sulfate can be estimated from measurements of sulfate fluxes in throughfall beneath forest canopies (Lindberg and Garten, 1988). Application of the throughfall flux method for estimation of total NO_3-N fluxes is more complicated because of potential interactions between the forest canopy and atmospheric NO_3-N deposition. Data from numerous sites indicate that forest canopies take up atmospherically deposited NO_3-N (Lovett and Lindberg, 1993). An artificial tree is a biologically inert collection surface, which is morphologically similar to a live tree, and can provide a means for realistically estimating dry N deposition. Higher NO_3-N fluxes beneath the artificial tree indicated its effectiveness as a passive collector of dry NO_3-N deposition (Fig. 1).

The method described here, which involves subtracting the NO_3-N flux in precipitation from that beneath an artificial tree, may be useful for estimating dry NO_3-N deposition in remote forests where electric power is not available for the operation of air samplers. This method might also be effective for estimating total wet, dry, and cloud deposition of NO_3-N at high elevations. Cloud water deposition in the present study was negligible. Joslin et al. (1990) concluded that artificial trees were good surrogate collectors of cloud water at high elevation spruce forests.

Prior research on Walker Branch Watershed revealed that $\delta^{15}N$ values for NO_3-N in bulk deposition and forest throughfall averaged $+2.3‰$, but the contribution of wet and dry deposition to this composite signature was not determined (Garten, 1992). It appears from the current study that NO_3-N in dry deposition to Walker Branch Watershed is more enriched in ^{15}N than NO_3-N in precipitation (Table 1). Other studies indicate that the components of dry NO_3-N deposition (HNO_3 vapor and particulate NO_3-N) also appear to have different N isotope ratios. Freyer (1991) found that HNO_3 vapor in Germany was isotopically lighter ($\delta^{15}N = -2$ to $-3‰$) than particulate NO_3-N. Several studies indicate that $\delta^{15}N$ values for particulate NO_3-N range from 0 to $+12‰$ (Moore, 1977; Heaton, 1987; Freyer, 1991). The method described here will result in a biased estimate for the $\delta^{15}N$ value of dry N deposition if precipitation samples contain appreciable amounts of dry deposition. Therefore, it is important to use sampling methods with this technique that minimize the contribution of dry deposition to precipitation samples (e.g., "wet only" samplers).

Studies at Walker Branch Watershed (Lindberg et al., 1986; Lovett and Lindberg, 1986) and at a nearby loblolly pine forest (Lovett and Lindberg, 1993) indicate that most (75 to 90%) of the NO_3-N in dry deposition to the artificial tree is HNO_3 vapor with the balance arising from dry deposition of particulate NO_3-N. Given certain assumptions, it is possible to estimate the isotopic composition of N in HNO_3 vapor on Walker Branch Watershed. Assuming that dry NO_3-N deposition to the site is comprised entirely of HNO_3 vapor and particle NO_3-N, a range in $\delta^{15}N$ values for HNO_3 vapor can be constrained through the following mass balance equation:

$$\delta_d = f_1(\delta_v) + f_2(\delta_c), \tag{4}$$

where

$$f_2 = 1 - f_1, \tag{5}$$

and

δ_d = the calculated $\delta^{15}N$ value for NO_3-N in dry deposition (HNO_3 vapor + particle NO_3-N),

δ_v = the $\delta^{15}N$ value for HNO_3 vapor,

δ_c = the $\delta^{15}N$ value for particulate NO_3-N,

f_1 = the fractional contribution of HNO_3 vapor to dry NO_3-N deposition,

f_2 = the fractional contribution of particle NO_3-N to dry NO_3-N deposition.

The $\delta^{15}N$ value for HNO_3 vapor, δ_v, can be calculated from equations 4 and 5 assuming that δ_d, f_1, and δ_c are within the ranges $+2.9$ to $+9.0‰$, 0.75 to 0.9, and 0 to $+12‰$, respectively. If the mean values are taken to be the middle of these ranges, then the mean $\delta^{15}N$ value for HNO_3 would be approximately $+6.0‰$; and if the values are randomly distributed within these ranges then the 1 SD variation would be approximately $\pm 2.3‰$. This estimate of the stable N isotope composition of HNO_3 vapor in east Tennessee differs significantly from that pre-

viously measured in Germany (Freyer, 1991). The latter difference could indicate that contributing sources to tropospheric NO_x vary between the two locations.

Nitric acid vapour, which is a product of the oxidation of tropospheric NO_x, appears to be isotopically heavy relative to atmospheric N_2 ($0‰$) at our study site. More than 90% of the NO_x emitted in the southeastern United States originates from coal fired power plants, industrial combustors, and vehicle emissions (Irving, 1991). Although more research is needed on the isotopic signatures of NO_x emitted from different anthropogenic sources, available data indicate that NO_x emitted from coal fired power plants ($\delta^{15}N = +6$ to $+13‰$) is isotopically distinct from that emitted by automobiles ($\delta^{15}N = -13$ to $-2‰$) (Heaton, 1990). Walker Branch Watershed is within 20 km of two large coal fired power plants (Kingston Steam Plant and Bull Run Steam Plant). The calculated isotopic composition of HNO_3 vapor on the watershed is consistent with that expected if the NO_x precursors to HNO_3 at this site originated principally from coal combustion. We might expect the isotopic composition of HNO_3 vapor to exhibit regional variations depending in part upon the strength of different anthropogenic sources contributing to tropospheric NO_x.

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REFERENCES

Freyer, H. D. 1991. Seasonal variation of $^{15}N/^{14}N$ ratios in atmospheric nitrate species. *Tellus* **43B**, 30–44.

Garten, C. T., Jr. 1992. Nitrogen isotope composition of ammonium and nitrate in bulk precipitation and forest throughfall. *International Journal of Environmental Analytical Chemistry* **47**, 33–45.

Heaton, T. H. E. 1987. $^{15}N/^{14}N$ ratios of nitrate and ammonium in rain at Pretoria, South Africa. *Atmospheric Environment* **21**, 843–852.

Heaton, T. H. E. 1990. $^{15}N/^{14}N$ ratios of NO_x from vehicle engines and coal-fired power stations. *Tellus* **42B**, 304–307.

Irving, P. M. (ed.). 1991. *Acidic deposition: state of the science and technology.* Vol. I. *Emissions, atmospheric processes and deposition.* The US National Acid Precipitation Assessment Program.

Joslin, J. D., Mueller, S. F. and Wolfe, M. H. 1990. Tests of models of cloudwater deposition to forest canopies using artificial and living collectors. *Atmospheric Environment* **24A**, 3007–3019.

Lindberg, S. E. and Garten, C. T., Jr. 1988. Sources of sulphur in forest canopy throughfall. *Nature* **336**, 148–151.

Lindberg, S. E., Lovett, G. M., Richter, D. D. and Johnson, D. W. 1986. Atmospheric deposition and canopy interactions of major ions in a forest. *Science* **231**, 141–145.

Lovett, G. M. and Lindberg, S. E. 1986. Dry deposition of nitrate to a deciduous forest. *Biogeochemistry* **2**, 137–148.

Lovett, G. M. and Lindberg, S. E. 1993. Atmospheric deposition and canopy interactions of nitrogen in forests. *Canadian Journal of Forest Research* **23**, 1603–1616.

Minagawa, M., Winter, D. A. and Kaplan, I. R. 1984. Comparison of Kjeldahl and combustion methods for measurements of nitrogen isotope ratios in organic matter. *Analytical Chemistry* **56**, 1859–1861.

Moore, H. 1977. The isotopic composition of ammonia, nitrogen dioxide and nitrate in the atmosphere. *Atmospheric Environment* **11**, 1239–1243.

U. S. Environmental Protection Agency. 1983. *Methods for chemical analysis of water and wastes.* EPA-600/4-79-020 (350.1-1 to 350.1-6). Environmental Monitoring and Support Laboratory, Cincinnati, OH.

Warneck, P. 1988. *Chemistry of the natural atmosphere.* Academic Press, Inc. San Diego, California.