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# Monitoring Deposition of Nitrogen-Containing Compounds in a High-Elevation Forest Canopy

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Measurements of airborne (gaseous and aerosol), cloud water, and precipitation concentrations of nitrogen compounds were made at Mt. Mitchell State Park (Mt. Gibbs, ~2006 m MSL), North Carolina, during May through September of 1988 and 1989. An annular denuder system was used to ascertain gaseous (nitric acid, nitrous acid, and ammonia) and particulate (nitrate and ammonium) nitrogen species, and a chemiluminescence nitrogen oxides analyzer was used to measure nitric oxide and nitrogen dioxide. Measurements of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  ions in cloud and rain water samples were made during the same time period. Mean concentrations of gaseous nitric acid, nitrous acid, and ammonia were  $1.14 \mu\text{g}/\text{m}^3$ ,  $0.3 \mu\text{g}/\text{m}^3$ , and  $0.62 \mu\text{g}/\text{m}^3$  for 1988, and  $1.40 \mu\text{g}/\text{m}^3$ ,  $0.3 \mu\text{g}/\text{m}^3$ , and  $1.47 \mu\text{g}/\text{m}^3$  for 1989, respectively. Fine particulate nitrate and ammonium ranged from  $0.02$  to  $0.21 \mu\text{g}/\text{m}^3$  and  $0.01$  to  $4.72 \mu\text{g}/\text{m}^3$  for 1988, and  $0.1$  to  $0.78 \mu\text{g}/\text{m}^3$  and  $0.24$  to  $2.32 \mu\text{g}/\text{m}^3$  for 1989, respectively. The fine aerosol fraction was dominated by ammonium sulfate particles. Mean concentrations of nitrate and ammonium ions in cloud water samples were  $238$  and  $214 \mu\text{mol}/\text{l}$  in 1988, and  $135$  and  $147 \mu\text{mol}/\text{l}$  in 1989, respectively. Similarly, the concentrations of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in precipitation were  $26.4$  and  $14.0 \mu\text{mol}/\text{l}$  in 1988, and  $16.6$  and  $15.2 \mu\text{mol}/\text{l}$  in 1989, respectively. The mean total nitrogen deposition due to wet, dry, and cloud deposition processes was estimated as  $\sim 30$  and  $\sim 40 \text{ kg N}/\text{ha}/\text{year}$  (i.e.,  $\sim 10$  and  $\sim 13 \text{ kg N}/\text{ha}/\text{growing season}$ ) for 1988 and 1989. Based on an analytical analysis, deposition to the forest canopy due to cloud interception, precipitation, and dry deposition processes was found to contribute  $\sim 60$ ,  $\sim 20$ , and  $\sim 20$  percent, respectively, of the total nitrogen deposition.

## Introduction

Air pollution is suspected of being one of the stress factors that may contribute to the forest decline in the eastern United States and Europe.<sup>1-5</sup> High-elevation red spruce (*Picea rubens* Sarg.) and Fraser fir (*Abies fraseri* (Pursh.) Poir.) forests from Maine to North Carolina in the eastern United States have shown visible symptoms of injury, decreased radial growth, and increased mortality.<sup>6</sup> At Mt. Mitchell State Park in North Carolina (elevation  $\sim 2038 \text{ m}$ ), the spruce-fir ecosystem is exhibiting considerable deterioration. This decline could be caused by the combination of several stress factors, namely, physical climate, biological stress, air pollution, availability of nutrient elements, increased competition from other trees, and human activities.<sup>7</sup>

Atmospheric nitrogen deposition (wet and dry deposition of  $\text{NH}_3/\text{NH}_4^+$ , nitrogen oxides, ammonia, and nitrate) has been suggested as one of the key factors that may have triggered the forest dieback in Europe.<sup>8,9</sup> The deposition of nitrogen-containing pol-

lutants on foliage and soils may inhibit the hardening-off processes by which needles protect themselves from frost injury during severe winter weather.<sup>10</sup> Therefore, it is important to establish the extent to which nitrogen is supplied by atmospheric deposition throughout the growing season.<sup>11-13</sup> Characterization of the atmosphere with regard to nitrogen species (such as oxides of nitrogen, nitric acid, ammonia, particulate ammonium, and nitrate) and their deposition therefore becomes an important factor in exploring the forest decline research at Mt. Mitchell, North Carolina.

The specific sources of pollutants deposited at any site are largely unknown but are generally acknowledged to result from the widespread use of coal, natural gas, oil, and motor fuels in North America. Under a national program entitled Mountain Cloud Chemistry/Forest Exposure Study (MCCP) and funded by the U.S. Environmental Protection Agency (EPA), the chemical and physical climates in five high-elevation sites in the eastern United States were monitored.<sup>14,15</sup> Mt. Mitchell is the southernmost site of this network and has the distinction of being the highest point east of the Mississippi River in the United States.

In this paper we present measurements of nitrogen-containing pollutants (gaseous and aerosol pollutants, cloud water, and precipitation) and their canopy deposition. We compare and

## Implications

Deposition of atmospheric pollutants to the canopy of the high-elevation spruce-fir forests in the southern Appalachian Mountains occurs via cloud interception, precipitation, and dry deposition. Excess deposition (i.e., in excess of the critical load) of nitrogen compounds is one of the most likely mechanisms by which airborne pollutants can have a negative impact on these forest ecosystems.

contrast the relative contribution to the total deposition budget by these three mechanisms at a high-elevation site (Mt. Gibbs, ~2006 m MSL) located in Mt. Mitchell State Park in North Carolina (35°44'05"N, 82°17'15"W) during the summer and autumn (May through September) of 1988 and 1989.

**Experimental**

A 16.5 m meteorological tower was installed at Mt. Gibbs (~2006 m MSL), just outside the Mt. Mitchell State Park, about two kilometers southwest of Mt. Mitchell (Figure 1). The aluminum walk-up tower was equipped with an electronic weather station, capable of measuring temperature, relative humidity, wind speed and direction, solar radiation, and barometric pressure, and having a cloud detector. Meteorological measurements were stored as 15-minute and one-hour averaged values in an on-site datalogger. A precipitation sampler was positioned in a clearing near the tower. Meteorological sensors were placed at least 10 m above the forest canopy, which consisted mostly of six- to seven-m Fraser fir trees.<sup>16-18</sup>

The tower also was equipped with an elevator assembly with an attached instrument carriage on the north face of the tower. The instrument carriage was equipped with two cloud collectors, one passive (ASRC-type)<sup>19</sup> and one active (Caltech-type),<sup>20</sup> as well as a Forward Scattering Spectrometer Probe (FSSP). The cloud water collectors were used to collect bulk hourly samples of cloud water during a cloud event. The immersion of the top of the tower in a cloud for more than 15 minutes, as noted by an observer and an optical cloud detector,<sup>21</sup> was defined as the start of a cloud event. Manual cloud water collection then commenced at the top of the tower, and the liquid water content (LWC) of the cloud was measured hourly by a gravimetric technique.<sup>22</sup> Cloud collection was almost continuous from May to September in 1988, while samples were collected only during two intensive periods (May 15 to June 15, and July 15 to August 15) during 1989.

Chemical analyses consisted of pH; soluble Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>; and total dissolved Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, and NH<sub>4</sub><sup>+</sup>. The pH of the cloud water samples was measured in the field within 15 minutes of collection and again in the laboratory. Internal and external audits were conducted during the sampling period at each field location and at the analytical laboratory. Chemical analyses were monitored by using external quality control samples and by submitting separate cloud water subsamples to the Central Analytical Laboratory of the National Atmospheric Deposition Program in Urbana, Illinois. In addition, internal and external EPA audits were performed by EPA personnel at the

field site and in the chemical laboratory throughout each sampling season.

Continuous gas-phase measurements of ozone, sulfur dioxide, and nitrogen oxides were made above the canopy near the base of the tower.<sup>23,24</sup> Ozone measurements were made with a Thermo Electron Company analyzer, Model 49, based on ultraviolet absorption. The level of detection for the ozone analyzer was 2 ppbv. For ozone concentrations greater than 20 ppbv, the accuracy objective was ±20 percent; for values in the range of 0 to 20 ppbv, the accuracy was ±4 ppbv. Oxides of nitrogen were measured with a Monitor Lab Model 8440 analyzer, based on chemiluminescence; however, levels were generally lower than the detection limit of the analyzer (~2 ppbv). Sulfur dioxide was measured with a Thermo Electron Company analyzer, Model 43. The level of detection for the sulfur dioxide analyzer was 0.6 ppbv, the accuracy objective was ±20 percent for SO<sub>2</sub> levels in the range of 18 to 22 ppbv, and the precision was ±5 ppbv in the range of 10 to 22 ppbv. The quality assurance protocols for ozone, oxides of nitrogen, and sulfur dioxide measurements generally included zero and span checks weekly and multipoint calibrations twice during the measurement season. Calibrations for these analyzers were based on National Institutes of Standards and Technology (NIST) traceable reference standards.

Ambient gaseous nitric acid, nitrous acid, ammonia, and fine particulate measurements were made utilizing the Annular Denuder System (ADS) technique.<sup>25</sup> The annular denuder system consisted of an impactor pre-separator to remove the coarse aerosol fraction, three annular denuder tubes in series to collect gases, and a filter pack to collect aerosols. The specific dimensions of the denuders used in this study were 217 by 28 mm with a 1-mm annular space between them. The first denuder tube, for the collection of nitric acid, was coated with a 0.1 percent solution of NaCl. The second denuder tube for the collection of other acidic gases (sulfur dioxide and nitrous acid) was coated with a solution of one percent glycerine and one percent Na<sub>2</sub>CO<sub>3</sub> solution in a one percent mixture of methanol and distilled water. The third denuder for the collection of ammonia from the air stream was coated with one percent citric acid in methanol. A 10-ml portion of the solution was introduced into the respective denuders, which were then capped and rotated to completely coat the annular surfaces. The tubes then were dried with dry zero air. The artifacts of denuder collection of HNO<sub>3</sub>, NH<sub>3</sub>, and HONO have been reported by several researchers.<sup>26,27</sup>

The annular denuder assembly was transferred to the field in a ship-

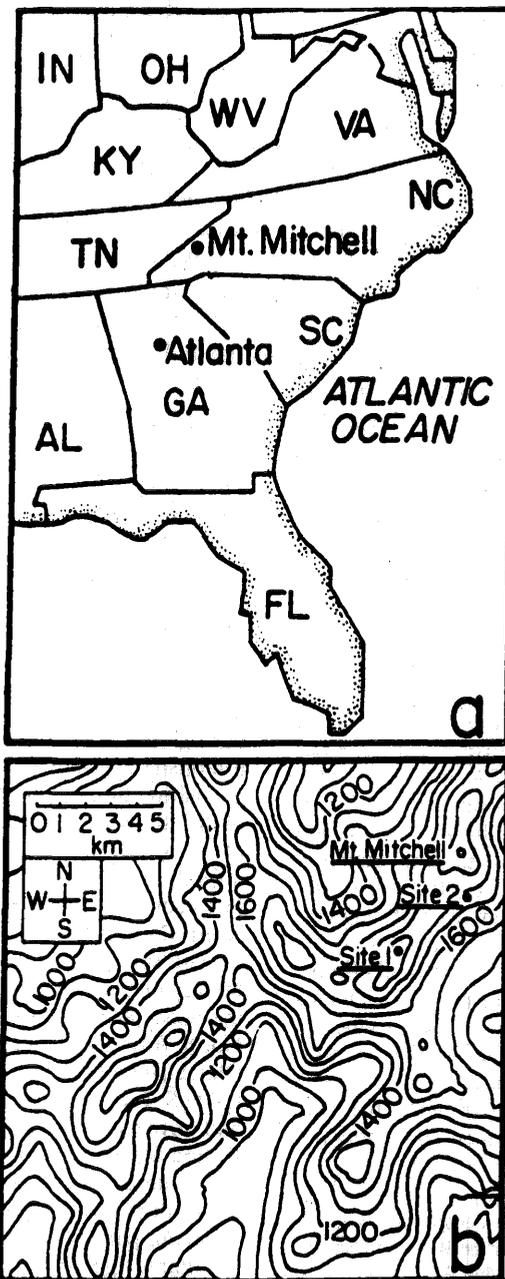


Figure 1. (a) Map of southeastern United States showing the location of Mt. Mitchell. (b) Topographical map of the Mt. Mitchell area showing the location of Site 1.

ping case and installed in a box designed to shield against precipitation, with the inlet opening extending from the bottom of the box. The assembly was operated in a laminar mode at a constant flow rate of 16.5 l/m. Most measurements were made during a 24-hour period. Shorter time periods (12 and four hours) also were used to study the diurnal variability of the nitrogen compounds. The samples were immediately extracted with deionized water in the field, and analyzed for  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  by ion chromatography and for  $\text{NH}_4^+$  by colorimetry.

Rainfall chemical analyses for Mt. Gibbs were obtained from the National Atmospheric Deposition Program (NADP).<sup>28</sup> The NADP collector was co-located at the site. The NADP monitoring station used an Aerochem Metrics wet/dry precipitation collector to collect a cumulative weekly sample of precipitation, and a rain gauge with an event pen to make a second measurement of precipitation amount. These samples were collected weekly and analyzed for major chemical species.

### Deposition Processes

Deposition pathways include wet, dry, and cloud interception. Wet deposition involves the deposition of chemical species by precipitation. The dry deposition process is highly dependent on the aerodynamic characteristics of the near-surface boundary layer, the physical and chemical natures of the depositing material, the nature of the canopy (collecting surface), and the physiological characteristics of the biological components present in the canopy. Cloud deposition may be taken as a combination of wet and dry deposition mechanisms because the chemical uptake processes occur similarly to dry deposition.

#### Dry Deposition Model

Dry deposition may be defined as the aerodynamic exchange of trace gases and aerosols from ambient air to the collection surface. These processes include gravitational settling of particles and transport by turbulent eddies, molecular diffusion, and inertial impaction. Dry deposition is characterized by the deposition velocity ( $V_d$ ), which can be calculated from the "Big Leaf" model,<sup>29</sup>

$$V_d = (R_a + R_b + R_c)^{-1} \quad (1)$$

where both the aerodynamic and diffusive boundary layer resistances,  $R_a$  and  $R_b$ , are functions of the wind speed ( $u$ ) and the standard deviation in the wind direction ( $\sigma_\theta$ ).

$$R_a = \frac{1}{u\sigma_\theta^2} \quad (2)$$

$$R_b = \frac{1}{u^*} \left( \frac{Sc}{Pr} \right)^p \quad (3)$$

The terms  $Sc$  = Schmidt number and  $Pr$  = Prandtl number, and the friction velocity ( $u^*$ ) can be approximated from the aerodynamic resistance:<sup>29</sup>

$$R_a = \nu u^{*-2} \quad (4)$$

For a highly soluble and reactive gas such as nitric acid and ammonia, the canopy resistance ( $R_c$ ) is expected to be much less than the aerodynamic and boundary layer resistances, so that

$$V_d \approx (R_a + R_b)^{-1} \quad (5)$$

It can be shown that the deposition velocity varies with the wind speed and standard deviation in wind direction, as follows:

$$V_d \approx \frac{u\sigma_\theta^2}{1 + \sigma_\theta} \quad (6)$$

The dry deposition flux ( $F_d$ ) can be represented as

$$F_d = V_d[c] \quad (7)$$

where  $[c]$  is the concentration of the pollutant measured at a given height.

#### Cloud Deposition Model

The deposition process for cloud water is a function of the free stream velocity of the droplets, the concentration of droplets (liquid water content of the cloud), the droplet size distribution, and the size, shape, and distribution of elements protruding into the flow. Lovett<sup>30</sup> developed a multiple-layer model in which the vertical turbulent transport of droplets is controlled by the aerodynamic resistances between model layers and between the top layer and the air above the canopy. The transfer of cloud droplets from the surrounding air to the canopy has been modelled by direct analogy to Ohm's law.

The cloud deposition flux ( $F_c$ ) is calculated as the ratio of the concentration of cloud droplets ( $V_i$ ) to the turbulent resistance ( $R_i$ ). Hence,

$$F_c = \frac{V_i}{R_i} \quad (8)$$

where

$$R_i = 0.5 (dz_i/K_{di} + dz_{i-1}/K_{d,i-1}) \quad (9)$$

and  $K_d$  is the turbulent diffusivity for cloud droplets,

$$K_d = K_m = k u^* (z-d), \quad (10)$$

$K_m$  is the diffusivity of momentum,  $k$  is von Karman's constant (0.41),  $u^*$  is the friction velocity,  $d$  is the zero plane displacement, and  $z$  is the height within the canopy.

$V_i$  may be calculated assuming a droplet size distribution<sup>31</sup> or obtained experimentally using an FSSP.

A modified version of the cloud deposition model, CDM,<sup>30</sup> was used in estimating the cloud-water volumetric deposition rate per unit area. The CDM requires four meteorological parameters (namely, temperature, wind speed, solar radiation, and relative humidity) and a cloud physical parameter (namely, the liquid water content of the clouds). The cloud deposition model is sensitive to changes in the cloud drop size distribution and canopy top wind speed. Since the meteorological measurements were made at the top of a 16.5-m tall meteorological tower, a logarithmic profile equation was used to estimate winds at the top of the canopy.<sup>32</sup> The cloud frequency estimates (immersion time) were based on the measurements with the cloud detector.<sup>21</sup>

#### Rainfall Deposition

Pollutants can be scavenged by raindrops and delivered to environmental surfaces by rainfall. The rainfall (i.e., wet deposition flux,  $F_w$ ) is computed as

$$F_w = I_p C_p \quad (11)$$

where  $I_p$  is the precipitation intensity obtained in terms of precipitation amount collected within a projected time scale (e.g.,  $\text{cm h}^{-1}$ ), and  $C_p$  is the concentration of the pollutant of interest in the precipitation.

Results and Discussion

Ambient Nitrogen Pollutant Concentrations

The mean, standard deviation, and range of concentrations of nitric acid, nitrous acid, ammonia, NO<sub>x</sub>, and fine particulate sulfate, nitrate, and ammonium are given in Table I. The mean concentrations of nitric acid for all sampling periods in 1988 and 1989 were 1.14 ± 0.96 µg/m<sup>3</sup> and 1.40 ± 0.59 µg/m<sup>3</sup>, respectively. The observed concentrations of gaseous nitric acid ranged from 0.13 to 5.62 µg/m<sup>3</sup>. The concentrations observed at Mt. Mitchell, which is considered a "pristine" site, were comparable to values reported in other remote locations<sup>33-38</sup>; however, the observed maximum values tended to approach some of the measurements made in urban locations.<sup>39,40</sup> Nitrous acid concentrations were found to be low (~0.3 ± 0.05 µg/m<sup>3</sup> for both 1988 and 1989). The mean ammonia concentrations were 0.62 ± 0.79 µg/m<sup>3</sup> and 1.47 ± 1.16 µg/m<sup>3</sup>, respectively, for 1988 and 1989. The mean concentrations of NO<sub>x</sub>, measured using a chemiluminescence analyzer, were found to be 2.16 ± 1.76 µg/m<sup>3</sup> and 5.3 ± 4.1 µg/m<sup>3</sup> for the 1988 and 1989 field seasons, respectively.

Particulate sulfate dominated the aerosol fraction, followed by particulate ammonium. The mean concentrations of particulate ammonium and sulfate aerosols were 1.24 ± 1.04 µg/m<sup>3</sup> and 4.35 ± 3.22 µg/m<sup>3</sup> for the 1988 sampling season, and 0.89 ± 0.90 µg/m<sup>3</sup> and 4.33 ± 3.16 µg/m<sup>3</sup> for the 1989 sampling season. Nitrate concentrations were much lower compared to sulfate and ammonium (0.11 ± 0.04 µg/m<sup>3</sup> and 0.22 ± 0.10 µg/m<sup>3</sup> for 1988 and 1989, respectively). An ionic balance of the ions showed a good coefficient of determination (r<sup>2</sup> = 0.89) between fine particulate sulfate and ammonium (Figure 2). The straight line in Figure 2 represents a 2:1 mole ratio between ammonium and sulfate. The observed anion/cation balance for the teflon filter and the observed low concentrations of particulate nitrate suggest that the aerosol at Mt. Mitchell is predominantly ammonium sulfate.

The mean concentration of NO<sub>x</sub> was higher in 1989 than in 1988. The levels of nitric oxide (NO) were always very low, usually lower than the detection limit of the instrument. The

Table I. Mean, standard deviation(s), and range of concentrations of the gaseous and fine aerosol nitrogen species measured.

Species	Concentration (µg/m <sup>3</sup> ) <sup>a</sup>	
	1988	1989
<b>Gas</b>		
HNO <sub>3</sub>	1.14 ± 0.96 (0.13 - 5.62)	1.40 ± 0.59 (0.55 - 2.60)
HNO <sub>2</sub>	0.30 ± 0.05 (0.09 - 1.53)	0.30 ± 0.04 (0.02 - 0.70)
NH <sub>3</sub>	0.62 ± 0.79 (0.01 - 4.98)	1.47 ± 1.16 (0.20 - 3.23)
NO <sub>x</sub>	2.16 ± 1.76 (< 14)	5.3 ± 4.1 (< 15)
<b>Particle</b>		
NH <sub>4</sub> <sup>+</sup>	1.24 ± 1.04 (0.01 - 4.72)	0.89 ± 0.90 (0.24 - 2.32)
SO <sub>4</sub> <sup>2-</sup>	4.35 ± 3.22 (0.21 - 18.13)	4.33 ± 3.16 (0.50 - 11.82)
NO <sub>3</sub> <sup>-</sup>	0.11 ± 0.04 (0.02 - 0.21)	0.22 ± 0.10 (0.10 - 0.78)

<sup>a</sup>Measurements made during May through September.

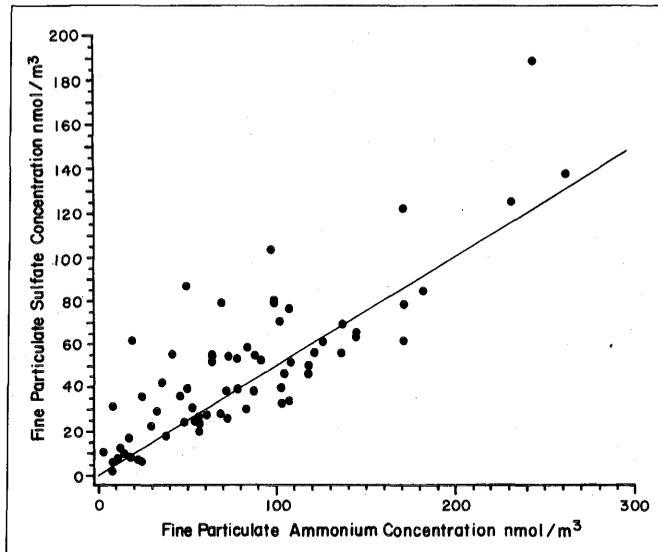


Figure 2. Ionic balance between fine particulate ammonium and sulfate aerosol concentrations.

precision associated with the ADS measurements was observed to be good, based on the three co-located sampling runs during the season which provided similar concentrations (e.g., 1.27 and 1.16 µg/m<sup>3</sup> for HNO<sub>3</sub> in one paired sampling). The laboratory and field blanks suggested no source of contamination.

Cloud Water Concentrations

The mean concentrations of nitrate in the cloud water samples were 238 µequ/l in 1988 and 135 µequ/l in 1989 (Table II). The ammonium ion concentrations were 214 and 147 µequ/l for the 1988 and 1989 field seasons, respectively. The ionic concentrations in the cloud water were lower in 1989 compared to previous years. Nitrate and ammonium contributed ~13 and ~15 percent, respectively, to the total ionic concentration in the cloud water.

Precipitation Concentrations

The concentrations of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> in precipitation were quite low (Table II) compared to cloud ionic values in both 1988 and 1989 (26.4 and 17 µequ/l for NO<sub>3</sub><sup>-</sup>, and 14 and 15 µequ/l for NH<sub>4</sub><sup>+</sup>). The other major ionic concentrations in the precipitation samples also were quite low compared to the corresponding cloud values.

Deposition Estimates

Dry deposition fluxes were estimated using the measured air concentrations and the model estimated dry deposition velocities. The dry deposition velocity for gaseous ammonia (8 · 10<sup>-1</sup> cm/s) was obtained from Aneja et. al.<sup>41</sup> Dry deposition fluxes were estimated only for the growing season (May through September) when the

Table II. Mean concentrations (µmol/l) of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> in cloud water and rainfall.

Year	Cloud Concentration (µmol/l) <sup>a</sup>		Rainfall Concentration (µmol/l) <sup>a</sup>	
	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>
1988	238 ± 236	214 ± 192	26.4 ± 18.8	14.0 ± 13.0
1989	135 ± 107	147 ± 118	16.6 ± 4.7	15.2 ± 4.7

<sup>a</sup>The ± values are one standard deviation (1σ).

**Table III.** Estimated dry deposition of the gaseous and aerosol nitrogen species (kg/ha/season) (Season: May through September).

Species	1988	1989
HNO <sub>3</sub>	2.6 ± 1.2	3.6 ± 1.98
NO <sub>x</sub>	1.5 ± 0.52	3.3 ± 1.48
NH <sub>3</sub>	0.55 ± 0.41	0.21 ± 0.72
NH <sub>4</sub> <sup>+</sup>	0.16 ± 0.11	0.12 ± 0.05
NO <sub>3</sub> <sup>-</sup>	0.02 ± 0.01	0.03 ± 0.01

actual measurements were made. The estimated dry deposition fluxes of nitric acid, NO<sub>x</sub>, ammonia, particulate ammonium, and particulate nitrate are given in Table III. Nitric acid dry deposition was estimated to be 2.6 and 3.6 kg/ha for the 1988 and 1989 field seasons, respectively. The estimated deposition values for NH<sub>3</sub> were 0.55 and 0.21 kg/ha for the two field seasons. The estimated dry deposition for gaseous NO<sub>x</sub>, primarily nitrogen dioxide, was 1.5 kg/ha/season in 1988, and 3.3 kg/ha/season in 1989. Gaseous NO<sub>x</sub> dry deposition was comparable to gaseous nitric acid deposition in 1989. The contribution from aerosol nitrates and ammonium to the deposition was very small (0.02 and 0.16 kg/ha/season). Particle nitrate was not deposited in significant quantities<sup>42,43</sup> because of the observed low concentration values and the low deposition velocities (1 × 10<sup>-3</sup> m/s); however, nitric acid deposition was significant.

Hourly cloud water nitrate and ammonium deposition estimates (Tables IV and V) were computed using the cloud deposition model, which requires the mean meteorological data and the liquid water content of the clouds as input data. The observed cloud frequency (cloud immersion time) from the cloud detector was 30 and 40 percent for 1988 and 1989, respectively. The hourly deposition fluxes were calculated using the volume of water deposited per hour (as output from the model) and the measured ionic concentrations. The mean hourly deposition for cloud NO<sub>3</sub><sup>-</sup> was 20.0 and 16.0 g/ha for the 1988 and 1989 field seasons, respectively. Cloud ammonium ion deposition rates were 4.3 and 4.8 g/ha/hour for the 1988 and 1989 field seasons, respectively. The growing-season (May through September) deposition fluxes were 17.3 and 18.4 kg/ha for NO<sub>3</sub><sup>-</sup>, and 3.8 and 5.5 kg/ha for NH<sub>4</sub><sup>+</sup> for 1988 and 1989, respectively. Saxena and Lin<sup>44</sup> reported cloud ionic mass fluxes for Mt. Mitchell during the growing season (May through September) of 1986 and 1987. Their deposition fluxes were 8.79 and 18.47 kg/ha for NO<sub>3</sub><sup>-</sup>, and 3.06 and 5.67 kg/ha for NH<sub>4</sub><sup>+</sup> for 1986 and 1987, respectively. These values are similar to those observed during 1988 and 1989.

The rainfall deposition fluxes for nitrate varied from 0.44 to 1.63 kg/ha/month for the 1988 sampling season; they varied from 0.85 to 2.40 kg/ha/month for the 1989 sampling season. The mean ammonium deposition amounts were estimated to be 0.1 and 0.33 kg/ha/month for 1988 and 1989, respectively. The total wet deposition in 1989 was higher than 1988 (6.6 kg/ha/season in 1988, compared to 8.4 kg/ha/season in 1989).

**Table IV.** Estimates of ionic mass fluxes (kg/ha/season) in cloud water and rainfall.

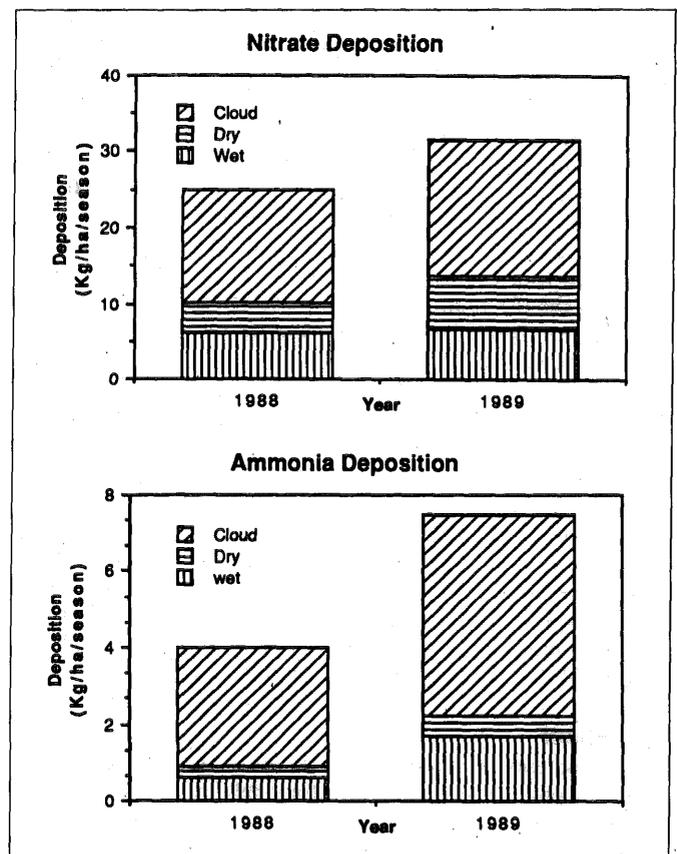
Year	Cloud Frequency Percent	Growing Season Deposition (May through September) kg/ha/season			
		Clouds		Rainfall	
		NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>
1988	30	17.3 ± 4.93	3.8 ± 1.68	4.0 ± 2.8	0.37 ± 0.27
1989	40	18.4 ± 7.3	5.5 ± 2.8	6.5 ± 1.82	1.7 ± 0.53

**Table V.** Estimated total deposition of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> for the period May through September. Units are kg/ha/season.

Deposition	NO <sub>3</sub> <sup>-</sup>		NH <sub>4</sub> <sup>+</sup>	
	1988	1989	1988	1989
Wet	6.0	6.7	0.6	1.7
Dry	4.2	6.9	0.3	0.5
Cloud	17.3	18.4	3.8	5.5
TOTAL	27.5	32.0	4.6	7.7

Estimates of the total deposition of nitrate and ammonium from wet deposition, dry deposition, and cloud interception are summarized in Table V. In this table, nitrate dry deposition includes deposition due to gaseous nitric acid, NO<sub>x</sub>, and particulate nitrate. Ammonium dry deposition includes deposition due to gaseous ammonia and particulate ammonium.

The relative amounts of cloud and rain deposition are important because cloud water deposition is the factor that differentiates mountains from lowlands. A schematic comparison of the deposition fluxes for NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> due to the above three mechanisms is given in Figure 3. Comparing the deposition from dry, wet (precipitation), and cloud interception, we conclude that cloud water interception contributed more nitrogen (~60 percent) to the total deposition than combined wet (~20 percent) and dry (~20 percent) deposition. The estimated mean total deposition of NO<sub>3</sub><sup>-</sup> over the sampling period (five months) of 1988 was ~27.5 kg/ha. Wet (i.e., rainfall) nitrate deposition for the same period was 6 kg/ha (about 22 percent of the total nitrate deposition), while the dry deposition of nitrate for 1988 was ~4.2 kg/ha/season (contributing about 18 percent of the total



**Figure 3.** Total deposition of nitrate and ammonium by wet, dry, and cloud water deposition processes.

nitrate deposition). For the 1989 field season, wet and dry deposition contributed ~21 and ~22 percent, respectively, for the total deposition. For ammonium ion deposition, cloud deposition contributed more than 70 percent toward the total ammonium deposition.

### Conclusions

Ambient measurements for primary nitrogen compounds were made during May through September of 1988 and 1989 at Mt. Mitchell State Park (Mt. Gibbs), North Carolina. Significant quantities of nitric acid (mean  $\sim 1.25 \mu\text{g}/\text{m}^3$  and range 0.13 to  $5.62 \mu\text{g}/\text{m}^3$ ) and ammonia (mean  $\sim 0.75 \mu\text{g}/\text{m}^3$  and range 0.01 to  $4.98 \mu\text{g}/\text{m}^3$ ) were found to be present in the gaseous form. Particle nitrate concentrations were low and undetectable for most sampling periods. Sulfate (mean concentration  $\sim 3.2 \mu\text{g}/\text{m}^3$ ) dominated the aerosol fraction, followed by particulate ammonium (mean concentration of  $\sim 1.2 \mu\text{g}/\text{m}^3$ ). Mean concentrations of nitrate and ammonium ions in cloud water samples were 238 and  $214 \mu\text{mol}/\text{l}$  in 1988, and 135 and  $147 \mu\text{mol}/\text{l}$  in 1989, respectively. Similarly, the concentrations of nitrate and ammonium ions in rainfall were 27 and  $17 \mu\text{mol}/\text{l}$  in 1988, and 14 and  $15 \mu\text{mol}/\text{l}$  in 1989, respectively.

Based on our estimates of nitrate deposition, cloud deposition contributed more nitrate and ammonium to the total deposition than dry and wet deposition combined. The total nitrogen deposition at Mt. Mitchell for the growing seasons (May through September) of 1988 and 1989 was estimated as  $\sim 9.8$  and  $\sim 13.2 \text{ kg N}/\text{ha}/\text{season}$ , respectively. Extrapolation of these growing season fluxes to annual nitrogen deposition could be erroneous, because concentrations of nitrogen species during the winter season are unknown. However, in the absence of winter measurements, an extrapolated mean annual nitrogen deposition flux for 1988 and 1989 was estimated as  $\sim 30$  and  $\sim 40 \text{ kg N}/\text{ha}/\text{year}$ , respectively. Argen<sup>45</sup> predicted that nitrogen-saturated forests would begin to appear after 20 to 25 years if the nitrogen deposition rate was in the range of  $30 \text{ kg}/\text{ha}/\text{year}$ . The annual nitrogen requirement (i.e., 'critical load' of the Smoky Mountains forest as given by the Integrated Forest Study (IFS)<sup>46</sup>) was  $\sim 32 \text{ kg N}/\text{ha}/\text{year}$ , and a 'critical load' of 10 to  $20 \text{ kg N}/\text{ha}/\text{year}$  has been published<sup>47</sup> for forest ecosystems in Europe. Though the mean estimated value for 1988 is within the required amount of the IFS value, the 1989 deposition flux ( $\sim 40 \text{ kg N}/\text{ha}/\text{year}$ ) is higher than that suggested by the IFS required amount, thus bringing into question the effect of over-fertilization, primarily by airborne deposition, on the forest ecosystem.

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