



ANALYSIS OF AMMONIA AND AEROSOL CONCENTRATIONS AND DEPOSITION NEAR THE FREE TROPOSPHERE AT Mt. MITCHELL, NC, U.S.A.

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Abstract—Measurements of airborne (gaseous and aerosol), cloud water, and precipitation concentrations of ammonia (NH_3) and ammonium (NH_4^+) compounds were made at Mt. Mitchell State Park (Mt. Gibbs, ~2006 m MSL), North Carolina. Measurements were made from May to September during 1988 and 1989. An annular denuder system was used to determine gaseous NH_3 and particulate NH_4^+ and nitrate (NO_3^-) compounds. Measurements of NH_4^+ in cloud and rain water samples were made during the same time period. Mean concentrations of gaseous NH_3 were $0.62 \mu\text{g m}^{-3}$ for 1988 and $1.47 \mu\text{g m}^{-3}$ for 1989. Mean concentrations of fine particulate NH_4^+ were $1.24 \mu\text{g m}^{-3}$ for 1988 and $0.89 \mu\text{g m}^{-3}$ for 1989. The NH_4^+ concentrations in the cloud water were 214 and $147 \mu\text{eq l}^{-1}$ for the 1988 and 1989 field seasons, respectively. The concentrations of NH_4^+ in precipitation were quite low compared to cloud ionic values in both 1988 and 1989 at 14 and $15 \mu\text{eq l}^{-1}$, respectively. The estimated mean total deposition of NH_4^+ over the sampling period (5 months) of 1988 and 1989 was about 0.38 and $0.67 \text{ g N m}^{-2} \text{ season}^{-1}$, respectively. Cloud water interception contributed more nitrogen (~70%) to the total deposition than combined wet (~15%) and dry (~15%) deposition. © 1998 Elsevier Science Ltd. All rights reserved.

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1. INTRODUCTION

Air pollution is suspected of being one of the stress factors that may contribute to forest decline in the eastern United States and Europe (Cowling, 1985, 1989; Papke and Krahl-Urban, 1988; Joslin *et al.*, 1992). At Mt. Mitchell State Park in North Carolina (elevation ~2038 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 (Woodman and Cowling, 1987).

Atmospheric nitrogen deposition (wet and dry deposition) has been suggested as one of the factors that may have triggered the forest dieback in Europe (e.g. Nihlgard, 1985). The deposition of nitrogen-containing pollutants on foliage and soils may inhibit the

hardening-off processes by which needles protect themselves from frost injury during severe winter weather (Friedland *et al.*, 1988). Nitrogen deposition may also cause nutrient imbalances in coniferous forests (Hornung *et al.*, 1995). Therefore, it is important to establish the extent to which nitrogen is supplied by atmospheric deposition throughout the growing season (Lovett, 1991; Johnson, 1992; Joslin *et al.*, 1992).

In this paper we present measurements of NH_3 and NH_4^+ compounds during the summer (May–August) of 1988 and 1989. We estimate the relative contribution of NH_3 and particulate NH_4^+ dry deposition, cloud vapour deposition, and rainfall to overall nitrogen deposition.

2. EXPERIMENTAL

A 16.5 m meteorological tower was installed at Mt. Gibbs (~2006 m MSL), just outside the Mt. Mitchell State Park, about 2 km southwest of Mt Mitchell. An aluminum walk-up tower 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

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cloud collectors, one passive (ASRC-type [Falconer and Falconer, 1980]) and one active (Caltech-type [Daube *et al.*, 1987]).

Ambient gaseous NH_3 , nitric acid (HNO_3), nitrous acid (HNO_2) and fine particulate measurements were made using an Annular Denuder System (ADS) (Possanzini *et al.*, 1983). The ADS consisted of an impactor pre-separator to remove coarse aerosols, three annular denuder tubes in series to collect gases, and a filter pack to collect fine aerosols. The dimensions of the denuders used in this study were 217 by 28 mm with a 1 mm annular space between the two concentric tubes. The first denuder tube was coated with a 0.1% solution of NaCl to collect HNO_3 . The second denuder, for the collection of other acidic gases (SO_2 and HNO_2), was coated with a solution of 1% glycerine, 1% Na_2CO_3 , and 1% methanol in distilled water. The third denuder was coated with 1% citric acid in methanol to collect NH_3 . Each denuder was charged with 10 ml of solution and then capped and rotated to completely coat the annular surfaces. The tubes then were dried with dry zero air.

The annular denuder assembly was transferred to the field in a shipping 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 16.5 l min^{-1} . Most measurements were made over a 24 h period. The samples were immediately extracted with deionized water in the field, and analyzed for NH_4^+ by colorimetry, and for NO_3^- and SO_4^{2-} by ion chromatography.

The immersion of the top of the tower in a cloud for more than 15 min, as noted by an observer and an optical cloud detector (Mallant and Kos, 1990), was defined as the start of a cloud event. Manual cloud water collection (hourly bulk samples) then commenced at the top of the tower, and the liquid water content (LWC) of the cloud was measured hourly by a gravimetric technique (Valente *et al.*, 1989). Cloud collection was almost continuous from May to September in 1988, while during 1989, samples were collected only during two intensive periods (15 May to 15 June, and 15 July to 15 August). Cloud water was analyzed for pH, soluble Cl^- , NO_3^- , SO_4^{2-} , and total dissolved Ca^{2+} , Mg^{2+} , K^+ , Na^+ , and NH_4^+ . 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 Acid Deposition Program (NADP) in Urbana, Illinois. In addition, internal and external audits were performed by the U.S. Environmental Protection Agency (EPA) at the field site and in the chemical laboratory throughout each sampling season.

Rainfall chemical analyses for Mt. Gibbs were obtained from the NADP (Peden *et al.*, 1986). 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 the amount of precipitation. The samples were collected weekly and analyzed for major chemical species.

Continuous gas-phase measurements of ozone, SO_2 , and nitrogen oxides were also made (Aneja *et al.*, 1991, 1994). Oxides of nitrogen, measured with a Monitor Lab Model 8840 analyzer, were generally lower than the detection limit for the analyzer (~ 2 ppb).

3. DEPOSITION MECHANISMS

Deposition pathways include dry, wet, and cloud interception. Dry deposition involves the exchange of

trace gases and aerosols from ambient air to the collection surface. The dry deposition process is highly dependent on the aerodynamic characteristics of the near surface boundary layer, the physical and chemical nature of the depositing material, the nature of the canopy (the collecting surface), and the physiological characteristics of the biological components in the canopy. Wet deposition involves the deposition of chemical species by precipitation. Cloud deposition can be taken as a combination of wet and dry deposition mechanisms.

3.1. Dry deposition model

The dry deposition flux, F_d , can be represented as: $F_d = -\chi V_d$ where χ is the concentration of the pollutant at a given height, and V_d is the deposition velocity. V_d was calculated using the "Big Leaf" model (Hicks *et al.*, 1987). V_d was estimated at 8 mm s^{-1} for gaseous NH_3 (Aneja *et al.*, 1986) and 1 mm s^{-1} for particulate NH_4^+ (Asman and Janssen, 1987).

3.2. Cloud deposition model

The cloud deposition flux (F_c) is calculated using Lovett's (1984) multilayer model. V_d is the ratio of concentration of cloud droplets, χ_d , and the turbulent resistance for cloud deposition, R_i , which is mediated primarily by impaction (subscript *i*). Hence

$$F_c = -\frac{\chi_d}{R_i} \quad (1)$$

where

$$R_i = 0.5 \left(\frac{dz_i}{K_{di}} + \frac{dz_{i-1}}{K_{di-1}} \right), \quad K_d = K_m = ku^*(z-d) \quad (2,3)$$

K_d is the turbulent diffusivity for cloud droplets, 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 above the ground. Calculations of R_i were confirmed using through fall measurements. χ_d may be calculated using an assumed droplet size distribution (e.g. Best, 1951) or a distribution obtained experimentally using a Forward Scattering Spectrometer Probe. A standard size distribution was assumed here.

3.3. Wet deposition

Pollutants can be scavenged by rain drops and delivered to environmental surfaces by rainfall. The rainfall, or wet deposition, flux (F_w) is computed as $F_w = I_p C_p$ where I_p is the precipitation intensity obtained in terms of precipitation amount collected within a projected time scale (e.g. m h^{-1}), and C_p is the concentration of the pollutant of interest in the precipitation.

4. RESULTS AND DISCUSSION

4.1. Ambient nitrogen pollutant concentrations

The mean, standard deviation, and the range of concentrations of gaseous NH_3 , HNO_3 , HNO_2 and nitrogen oxides, together with fine particulate NH_4^+ , SO_4^{2-} , and NO_3^- are given in Table 1. The mean NH_3 concentrations were 0.62 and $1.47 \mu\text{g m}^{-3}$, respectively, for 1988 and 1989. The mean NH_4^+ aerosol concentrations were 1.24 and $0.89 \mu\text{g m}^{-3}$, respectively, for the 1988 and 1989 sampling seasons. Figure 1 illustrates seasonal trends in NH_3 and NH_4^+ concentrations.

The dominant aerosol anion was SO_4^{2-} at $\sim 4.3 \mu\text{g m}^{-3}$ in both years. Nitrate concentrations were much lower compared with SO_4^{2-} and NH_4^+ (0.11 and 0.22 for 1988 and 1989, respectively). There was a linear correlation between the concentrations of NH_4^+ and SO_4^{2-} ions ($r^2 = 0.89$), with a molar ratio of 2:1 between NH_4^+ and SO_4^{2-} . The observed anion/cation balance for the teflon filter and the observed low concentrations of particulate NO_3^- suggest that the aerosol at Mt. Mitchell is predominately ammonium sulphate. The 2:1 mole ratio suggests that H_2SO_4 aerosol was completely neutralized by NH_4^+ .

4.2. Relation of ambient ammonia and particulate ammonium with emission sources

To understand potential sources of NH_3 and particulate NH_4^+ measured at the site, the emission inventory for NH_x ($= \text{NH}_3 + \text{NH}_4^+$) (EPA, 1995) in the

surrounding region was analyzed. Despite the mountainous nature of the region surrounding Mt. Mitchell, emissions are still significant. The average $\text{NH}_x - \text{NH}_3$ emission density in a 120 km radius around the site is about $0.49 \text{g m}^{-2} \text{yr}^{-1}$. Most of the emissions from the region are gaseous NH_3 from animal waste (79%) and from fertilizer usage (7%). Industrial emissions of NH_3 and particulate NH_4^+ are minor. The emission strength in a 120 km radius around the monitoring site varies relatively little – the average emission strength is $0.59 \text{g m}^{-2} \text{yr}^{-1}$ in the Northeast quadrant, $0.53 \text{g m}^{-2} \text{yr}^{-1}$ in the Northwest, $0.44 \text{g m}^{-2} \text{yr}^{-1}$ in the Southeast, and $0.39 \text{g m}^{-2} \text{yr}^{-1}$ in the Southwest. The nearest large industrial sources of NH_x are 100–150 km away.

Figure 1 indicates that the largest total concentration of NH_x in 1988 occurs at the beginning of the growing season, and generally declines as the summer progresses. The average monthly concentrations of NH_3 and NH_4^+ in 1988 were $2.81 \mu\text{g m}^{-3}$ in May, $2.39 \mu\text{g m}^{-3}$ in June, $0.97 \mu\text{g m}^{-3}$ in July, and $1.41 \mu\text{g m}^{-3}$ in August. (Too few measurements were made in 1989 to analyze seasonal trends.) The seasonal trend shown in 1988 may be related to the application of nitrogen fertilizer and animal waste to crops, which is highest in North Carolina in Spring (e.g. Olson *et al.*, 1988; R. Mikkelsen, 1995, N. Carolina State University, pers. comm.)

Although emissions of NH_4^+ are minor compared with NH_3 , ambient NH_4^+ concentrations were double NH_3 on average. This suggests that NH_3 was converted to NH_4^+ in the process of atmospheric transport to this high altitude site. Analysis of the time series of concentrations of gaseous NH_3 and particulate NH_4^+ (Fig. 1) suggests that the transition between NH_3 and NH_4^+ is a rapid process. For instance, between 3 May and 5 May 1988 concentrations shift from high NH_4^+ and low NH_3 to high NH_3 and low NH_4^+ and then back to high NH_4^+ and low NH_3 . This rapid transition is also indicated by some indications of an anti-correlation between NH_3 and NH_4^+ for the daily sampling (Fig. 1).

4.3. Cloud water and precipitation concentrations

The NH_4^+ ion concentrations in the cloud water were 214 and $147 \mu\text{eq l}^{-1}$ for the 1988 and 1989 field seasons, respectively. The ionic concentrations in the cloud water were lower in 1989 compared to the previous years. Ammonium contributed $\sim 15\%$ to the total ionic concentration in the cloud water. The concentrations of NH_4^+ in precipitation were quite low (Table 2) compared to cloud ionic values in both 1988 and 1989; 14 and $15 \mu\text{eq l}^{-1}$, respectively. The other major ionic concentrations in precipitation samples were also small compared with corresponding cloud values.

4.4. Deposition estimates

Table 3 gives estimated dry deposition and wet deposition fluxes of NH during the 1988 and 1989

Table 1. Mean, standard deviation, and range of daily concentrations of the gaseous and fine aerosol nitrogen species measured at Mt. Mitchell

Species	Concentration ($\mu\text{g m}^{-3}$)*	
	1988	1989
Gas phase		
HNO_3	1.14 ± 0.96 (0.13–5.62)	1.40 ± 0.59 (0.55–2.60)
HNO_2	0.30 ± 0.05 (0.09–1.53)	0.30 ± 0.04 (0.02–0.70)
NH_3	0.62 ± 0.79 (0.01–4.98)	1.47 ± 1.16 (0.20–3.23)
NO_x	2.16 ± 1.76 (<14)	5.3 ± 4.1 (<15)
Particulate phase		
NH_4^+	1.24 ± 1.04 (0.01–4.72)	0.89 ± 0.90 (0.24–2.32)
SO_4^{2-}	4.35 ± 3.22 (0.21–18.13)	4.33 ± 3.16 (0.50–11.82)
NO_3^-	0.11 ± 0.04 (0.02–0.21)	0.22 ± 0.10 (0.10–0.78)

*Measurements made during May to September.

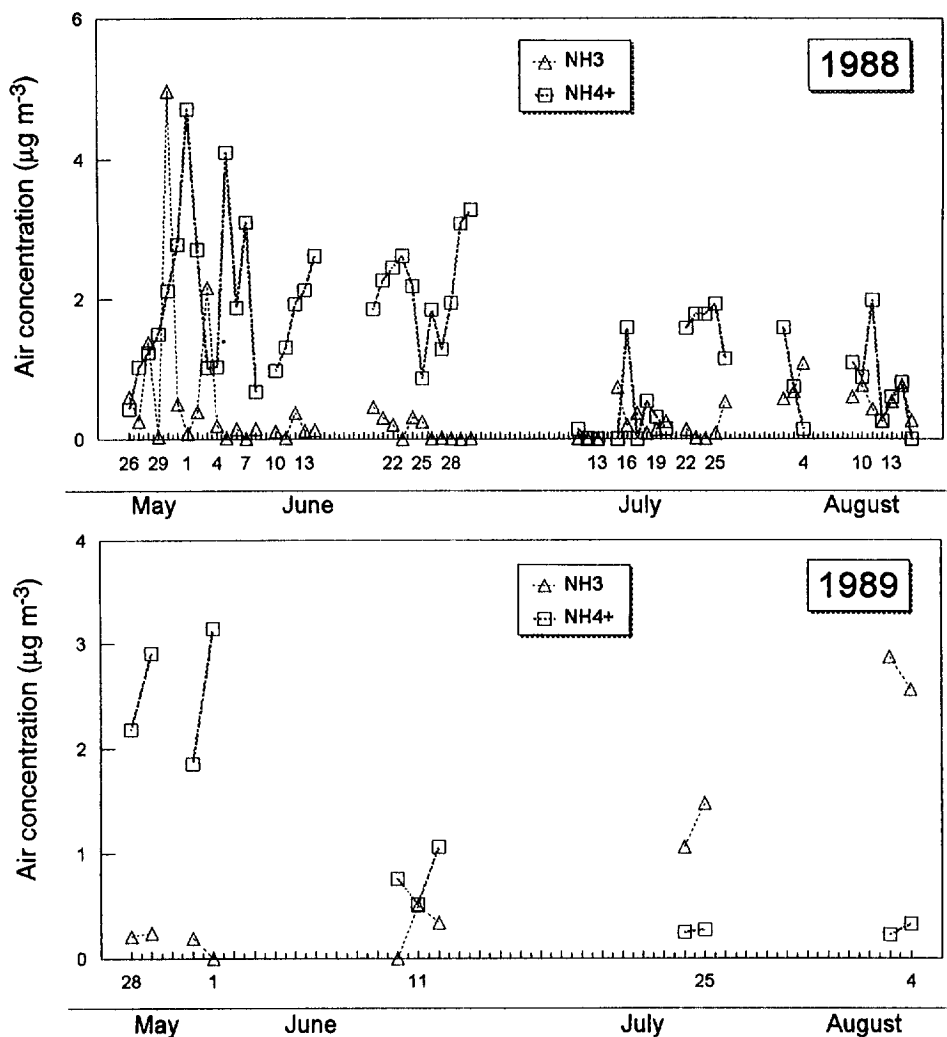


Fig. 1. Seasonal trends in ambient air concentrations of gaseous ammonia and aerosol ammonium measured at Mt Mitchell.

Table 2. Mean concentrations of NH_4^+ in cloud water and rainfall at Mt. Mitchell

	Cloud NH_4^+ concentration ($\mu\text{mol l}^{-1}$)	Rainfall NH_4^+ concentration ($\mu\text{mol l}^{-1}$)
1988	214 ± 192	14.0 ± 13.0
1989	147 ± 118	15.2 ± 4.7

growing seasons. Dry deposition fluxes were estimated using the measured air concentrations and the model-estimated dry deposition velocities (Aneja *et al.*, 1986). Ammonium dry deposition included deposition due to gaseous NH_3 and particulate NH_4^+ . Dry deposition fluxes were estimated only for the growing season (May to September) when the actual measurements were made. The estimated dry deposition values for NH_3 were 45 and 100 mg N m^{-2}

season⁻¹ for 1988 and 1989, respectively. The contribution from aerosol NH_4^+ to the deposition was very small (12 and 9.3 mg N m^{-2} season⁻¹ for 1988 and 1989, respectively). Tjepkema *et al.*, (1981) estimated a considerably higher NH_4^+ deposition rate—about 250 mg N m^{-2} year⁻¹—using a deposition velocity of 7.2 mm s^{-1} for pines. If this NH_4^+ deposition velocity was applied to the Mt. Mitchell test results, dry deposition of NH_4^+ would be considerably higher (about 94 and 72 mg N m^{-2} season⁻¹ for 1988 and 1989, respectively).

Wet deposition is divided into precipitation and cloud interception. The rainfall mean NH_4^+ deposition rates were estimated to be 29 and 132 mg N m^{-2} season⁻¹ for 1988 and 1989, respectively. Hourly cloud water NH_4^+ deposition estimates were computed using the cloud deposition model. The observed cloud frequency (cloud immersion time) were 30% and 40% for 1988 and 1989, respectively. The hourly deposition fluxes were calculated using the volume

Table 3. Estimated dry, cloud water and wet deposition of reduced nitrogen species at Mt. Mitchell

Species	Deposition (mg N m ⁻² season ⁻¹) ^a	
	1988	1989
Dry deposition		
NH ₃	45 ± 34	100 ± 59
NH ₄ ⁺	12 ± 9	9.3 ± 4
Cloud water deposition (NH ₄ ⁺) ^b	295 ± 131	430 ± 220
Rainfall (NH ₄ ⁺)	29 ± 21	132 ± 41
Total	380	670

^aSeason: May–September (5 months).

^bCloud frequency was 30% in 1988 and 40% in 1989.

of water deposited per hour (as output from the model) and the measured ionic concentrations. Hourly fluxes were then used to compute the flux for the growing season (May to September)—295 and 430 mg N m⁻² season⁻¹ for 1988 and 1989, respectively (Table 3). Saxena and Lin (1990) reported cloud ionic mass fluxes for Mt Mitchell during the growing season (May to September) of 1986 and 1987. Their deposition fluxes were similar—238 and 441 mg N m⁻² season⁻¹ for 1986 and 1987, respectively.

Total NH_x deposition was estimated at 0.38 and 0.67 g N m⁻² season⁻¹ in 1988 and 1989, respectively. Nitrate deposition at the site has been estimated at 0.62 and 0.72 g N m⁻² season⁻¹ for 1988 and 1989, respectively (Aneja *et al.*, 1994). Based on these estimates for reduced nitrogen and nitrate, total nitrogen deposition was 1.0 and 1.4 g N m⁻² season⁻¹ in 1988 and 1989, respectively.

5. CONCLUSIONS

The relative amounts of cloud and rain deposition are important because cloud-water deposition is the factor which differentiates wet deposition in mountains from that in low-lands. Comparing the deposition from dry, wet (precipitation), and cloud interception, we can conclude that cloud water interception contributed more nitrogen (~70%) to the total deposition of NH_x than wet (~15%) or dry (~15%) deposition. Dry deposition may be higher (accounting for up to 25% of total deposition), depending on the deposition velocity that is used for NH₄⁺. Similarly, dry deposition of NH₃ is uncertain as both deposition and emission fluxes may occur within the forest; the present estimates are likely to be conservative, however, and actual NH₃ dry deposition may be larger. The estimated mean total deposition of NH_x over the sampling period (5 months) of 1988 and 1989 was ~0.38 and 0.67 g N m⁻² season⁻¹, respectively.

Critical nitrogen loads for coniferous tree ecosystems have been reported at 1–5 g N m⁻² yr⁻¹ (Hornung *et al.*, 1995). Therefore, the NH_x deposition predicted for this site is significant, especially when considered along with oxidised nitrogen deposition. Total nitrogen deposition was estimated at 1.1 g N m⁻² season⁻¹ in 1988 and 1.4 g N m⁻² season⁻¹.

No correlation was found between trends in NH₃ and NH₄⁺ concentrations and wind speed or direction. Further research is planned by the U.S. EPA in modeling the transport of NH_x, and acid gases with the Regional Particulate Model (RPM) to assess possible control strategies for acid aerosols and acid deposition in the Eastern U.S.

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