Tellus (1993), 45B, 209–227
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TELLUS
ISSN 0280–6509

Atmospheric deposition to a high-elevation forest at Whiteface Mountain, New York, USA

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(Manuscript received 13 January 1992; in final form 26 October 1992)

ABSTRACT

Atmospheric deposition rates have proven difficult to quantify in mountainous settings but must be estimated in order to assess the potential impact of air pollution on high-elevation ecosystem processes. We measured major ion concentrations in precipitation, cloud water and aerosols as well as the concentrations of the pollutant gases SO_2 and HNO_3 vapor in a subalpine spruce-fir forest at Whiteface Mountain, New York, USA, for a 4-yr period beginning in June of 1986. Deposition of S, N and major elements to this forest at 1050-m elevation was estimated using direct flux measurements and deposition velocities that were calculated with inferential models. The validity of model flux estimates was evaluated using mass-balance calculations for chemically conservative elements. Combined estimates of cloud water plus dry deposited ion fluxes based on micrometeorological modeling agreed with mass-balance derived estimates of these fluxes to within ~25%. Annual N deposition averaged 16.7 kg N ha^{-1} yr^{-1} with 32% contributed by cloud water deposition and 25% by HNO_3 vapor deposition. Annual S deposition averaged 16.3 kg S ha^{-1} yr^{-1} with 37% deposited by clouds and 11% due to SO_2 deposition. These values are substantially lower than previous estimates of S and N deposition to high-elevation forests of the northeastern USA and characterize pollutant deposition rates in the elevational range of average cloud base. Scavenging of aerosols and gases by cloud droplets with subsequent deposition to the forest canopy was found to be 12 to 30 times more efficient than dry deposition processes for transferring atmospheric N and S, respectively, to the forest. Direct effects of the atmospheric flux of N and S to the forest have been detected, including canopy assimilation of N and high SO_4 fluxes in soil solutions.

1. Introduction

Atmospheric deposition processes have long been recognized as important components of nutrient cycles in forest ecosystems. Enhanced levels of atmospherically deposited nitric and sulfuric acid are suspected to adversely affect the health of forest tree species (Vann et al., 1992) and disrupt normal nutrient cycling patterns (Schulze 1989; Aber et al., 1989). The rate of pollutant deposition to forests is controlled by environmental variables such as geographic location and elevation as well as biological variables (Lovett and Kinsman, 1990). The three primary vectors of atmospheric deposition to high-elevation forest ecosystems are rainfall, cloud water interception and dry deposition.

Schlesinger and Reiners (1974) and Lovett et al. (1982) showed the importance of cloud water deposition to the water and nutrient regimes of high-elevation forests. The contribution of dry deposition processes to the total atmospheric transfer of pollutants to low-elevation forests has been quantified by several investigators (Eaton et al., 1978; Lindberg et al., 1986; Shepard et al., 1989). These studies showed that dry deposition

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contributed significant fractions of the total atmospheric flux of S and N. High-elevation forests have been shown to experience greater total deposition rates than adjacent low-elevation forests in the northeastern USA (Lovett and Kinsman, 1990; Lindberg et al., 1988), but these rates remain poorly quantified.

Increased deposition of H_2SO_4 and HNO_3 has been shown to increase the concentration of base cations in soil solutions and accelerate their removal from soil exchangeable pools potentially reducing the nutrient status of soils (Reuss and Walthall, 1990). Strong acid inputs also result in Al mobilization to streams (Cronan and Schofield, 1990). Exposure to acidic cloud water has been demonstrated to reduce the winter hardiness of red spruce (Vann et al., 1992; DeHayes et al., 1991) which have experienced significant winter injury in recent years (Friedland et al., 1984). These observations illustrate the sensitivity of nutrient cycles in high-elevation forests to changing atmospheric loadings of nutrient and pollutant elements.

This study estimated the atmospheric deposition of major pollutant and nutrient elements to a subalpine spruce-fir forest at Whiteface Mountain, New York (NY), over a 4-year period beginning in June of 1986. Our primary objective was to characterize the average annual deposition rate of S and N species in order to improve our understanding of how atmospherically deposited S and N influence nutrient cycling patterns and processes in high-elevation forests.

2. Methods

2.1. Site description

The primary measurement site was located at 1050-m elevation on the northwest slope of Esther Mt., a subpeak of the Whiteface Mt. massif, in northeastern NY, USA (44°22′N, 73°54′W). Regional transport of pollutants to Whiteface is predominantly from the west (Husain and Dutkiewicz, 1990). The forest canopy is composed of balsam fir (*Abies balsamea* (L.) Mill.), red spruce (*Picea rubens* Sarg.) and paper birch (*Betula papyrifera* var. *cordifolia* Reg.). Tree density, basal area, height and leaf area are shown in Table 1. The canopy is rough with a relatively uniform surface at a height of approximately 15 m, above which the tops of individual spruce and fir trees protrude to heights of 16–22 m. Spruce and fir needles comprise 84% of the canopy leaf area which totals $8.2\,m^2\,m^{-2}$ during the growing season. The average slope at the measurement site is 15%. This forest receives an average of 132 cm of precipitation annually with 30% in the form of snow. Precipitation is dominated by snow during the period November through March, which will be referred to subsequently as the freezing season; April through October will be referred to as the nonfreezing season. The growing season extends from June through September. A meteorological and sampling tower (18-m height) was located at 1050-m elevation. Secondary meteorological stations were located at 950-m and 1150-m elevation. The vegetation and soils of the site have been described by Friedland et al. (1991) and Battles et al. (1992).

2.2. Vegetation and leaf area distribution

Vegetation was characterized by counting and measuring the diameter-at-breast-height (dbh) of trees on four 0.1 ha circular plots (Friedland et al., 1991). Regression equations to predict tree height from dbh were developed from measurements made in adjacent plots (Battles et al., 1992). The amount of leaf biomass was calculated using the

Table 1. *Forest canopy characteristics at the 1050-m elevation measurement site on Whiteface Mountain, NY*

Species	Live density (stems ha^{-1})	Total density (stems ha^{-1})	Live basal area ($m^2\,ha^{-1}$)	Maximum height (m)	Total leaf area ($m^2\,m^{-2}$)
Red Spruce	87.5	160	7.5	22	2.3
Balsam Fir	2060	2505	16.2	18	4.6
Paper Birch	67.5	72.5	4.1	15	1.3

measured tree diameters, estimated tree heights and allometric equations for each tree species (Whitakker et al., 1974; Friedland et al., 1991). The total leaf area for an individual tree was then calculated for the leaves of each species. The surface area conversion factor for birch leaves was determined by weighing and measuring the leaf area of a large number of birch leaves harvested from areas surrounding the measurement plots. The conversion factor for spruce needles was determined in a similar manner by A. Gordon (Ontario Ministry of Natural Resources, personal communication). The conversion factor for fir needles was calculated from data collected by Marchand (1983). The distribution of leaf area with height in the canopy was modeled by partitioning the total calculated leaf area for an individual tree according to the volume of crown space for that tree which intersected a given height layer above the forest floor. The position and size of crown space volumes for individual trees were calculated using average ratios of crown dimensions to tree height determined for each species from measurements of crown shapes on a subset of trees in the vegetation plots.

2.3. *Precipitation and throughfall*

Precipitation was collected on an event basis with a combination of automated NADP wet-only type collectors (Aerochemetrics, FL USA) and manually opened and closed polyethylene collectors of the same size (641 cm^2 collection area). Precipitation events were defined on a real-time basis. Collections were made at three locations: a small clearing at 950-m, the top of the meteorological tower at 1050-m and another small clearing at 1150-m elevation. The 1150-m site was operated only during the nonfreezing season and only after 1986. Snowfall was collected in a 130 L polyethylene container at the 950-m clearing during the freezing season. Precipitation chemistry was not measured at the above sites during the first growing season of the study period (June through September of 1986). During the 1986 growing season precipitation chemistry was obtained from a MAP3S (MAP3S, 1982) site at 600-m elevation on the southeast side of Whiteface Mountain. Precipitation amounts were meaured during this period at the 1050-m site with a recording rain gauge.

Throughfall was collected in the same type of manually-operated containers as precipitation. 5 replicate samplers were located randomly within each of 4 plots adjacent to the meteorological measurement site. Collections were made weekly during the nonfreezing season of 1986 and then on a wet-only basis for each precipitation event during the non-freezing seasons of 1987–1989. All samples were stored at 4°C until analysis. Throughfall samples were filtered through 0.4 μm polycarbonate membranes prior to storage. Storage times varied between 4 months during the first 2 years of the study and several weeks during the final 2 years.

2.4. *Cloud water*

Cloud water was sampled from the top of the meteorological tower using an ASRC passive cloud water collector (for a description see Mohnen and Kadlecek, 1989). Samples were collected over periods of 0.25 to 1 h during non-precipitating cloud immersion conditions. Samples were chilled with ice until transported to the laboratory where they were stored at 4°C until analysis. The average liquid water content (LWC) of cloud during the sample period was determined from the volume of water collected, the measured wind speed and the collection efficiency of cloud collector elements calculated according to the method of Mohnen (1988a). Cloud water was sampled during the nonfreezing season only. During freezing conditions, super-cooled cloud droplets deposit as rime ice, which is considerably more difficult to collect. Therefore, freezing season LWC and ion concentrations were estimated from non-freezing season values and winter/summer ratios that were determined from a large set of winter and summer cloud water samples collected at the Whiteface Mt. summit observatory between the years 1984 and 1987 (Kadlecek et al., 1985, 1988).

2.5. *Dry deposition*

Air concentrations of particles 0.3 to ~ 3 μm equivalent spherical diameter (esd) were determined by volume sampling with in-line Zefluor™ (Gelman, USA) PTFE filters from the top of the meteorological tower during the nonfreezing season and from the top of an auxiliary tower at the 950-m site during the freezing season. In both sampling locations the air inlet faced down and was protected by a conical rain shield. In August of 1988, electric service was discontinued to the

primary sampling site and all subsequent air concentration measurements were made at the Whiteface Mt. summit observatory (1483 m). Both the 1050-m site and the summit observatory are assumed to have similar air concentrations of particles and gases (see SO_2 below). Air concentrations of HNO_3 vapor were determined from NO_3^- collection on Nylasorb™ (Gelman, USA) filters mounted downstream from the PTFE filter in the filter pack (cf. Lindberg et al., 1989). Filters were exposed during dry air conditions for periods of 12 to 48 h to flow rates of 0.3 $m^3 s^{-1}$ in 1986–1988 and 0.6 $m^3 s^{-1}$ during 1989 and 1990. Coarse particle (>2.5 μm esd) sedimentation rates to polycarbonate petri dishes (Lindberg and Lovett, 1985) were measured at the same times and locations as the filters were exposed. Air concentrations of SO_2 were determined continuously with a pulsed fluorescence SO_2 analyzer (TECO, USA) located at the ASRC summit observatory. Hourly SO_2 concentrations generally agreed within 10% between the summit and the 1050-m site during several months of concurrent measurements (data not shown).

The problem of particle NO_3 vaporization from the PTFE filters which subsequently may be captured by the Nylasorb™ filters within the filter pack apparatus has been discussed by Lindberg et al. (1990). They have reported that the use of the Nylasorb™ filter in series with a PTFE filter is satisfactory for determining particle NO_3 and HNO_3 vapor concentrations under the exposure conditions outlined above.

2.6. *Meteorological measurements*

Air temperature, relative humidity, wind speed and wind direction were monitored continuously above the canopy at the meteorological tower. Total short-wave solar radiation was measured continuously at the 950-m site. Fifteen-minute average values were computed in a datalogger and retained on magnetic tape. The period of time during which the forest was immersed in cloud, experiencing precipitation or dry conditions was determined primarily from frequent observations made by field personnel. Due to gaps in the observation record, approximately 10% of the cloud immersion record was determined using a Mallant cloud detector (Mohnen, 1988a) and analysis of the relative humidity trace (Vong et al., 1990).

2.7. *Chemical analysis*

Chemical analyses of samples for the ions NO_3^-, $SO_4^=$, Cl^-, NH_4^+, K^+, and Na^+ were performed by ion chromatography at ASRC Whiteface Mountain Field Station (WFMFS) and at Dartmouth College. Aluminum, Ca and Mg were determined by graphite furnace and flame atomic absorption spectrophotometry at Dartmouth College and at Oak Ridge National Laboratory (ORNL). Total-N was determined by block digestion and auto-analyzer analysis for NH_4^+ at ORNL. Hydrogen ion activity was determined at ASRC WFMFS by pH electrode (Orion-Ross model #810300). All chemical analyses including filter pack extractions used the methods, protocols and quality assurance procedures of the Integrated Forest Study (Lindberg et al., 1989).

3. Deposition calculations

While the calculation of atmospheric deposition due to precipitation is relatively straightforward, the estimation of vapor, dry aerosol and cloud water deposition is subject to a great degree of uncertainty. Methods of estimating dry and cloud deposition have been reviewed by Hosker and Lindberg (1982), Lovett (1988) and Lovett and Kinsman (1990). We estimated dry and cloud deposition using inferential models driven by meteorological measurements and descriptions of forest canopy structure (cf. Mueller and Weatherford, 1988; Saxena et al., 1989; Saxena and Lin, 1990; Lindberg et al., 1990; Shepard et al., 1989; Mueller, 1991). We used a modified version of the Hicks et al. (1987) big-leaf dry deposition model for suspended particles and gases and a modified version of the Lovett (1984) cloud water deposition model. We are aware that these one-dimensional inferential techniques developed for simplified terrain are subject to potentially serious error when applied to mountainous terrain and we have attempted to account for the primary sources of error discussed by Hicks and Meyers (1988).

The main weakness associated with the application of the one-dimensional models to complex terrain is the representation of turbulent transfer as an entirely vertically diffusive process (Hicks and Meyers, 1988). In mountain settings, the horizontal component of the wind vector may dominate, and steep slopes may expose some frac-

tion of the canopy as a horizontal cross section to the wind. These effects combine to either lower the aerodynamic resistance of the canopy to the transfer of momentum and mass or produce an advective flux of aerosols to upper sections of the canopy. We have modified existing inferential models, as discussed below, to partially account for these conditions at our site. In addition, the northwest face of Whiteface Mountain rises 900 m across a distance of 5 km from relatively uncomplicated topography to the west and north. The lack of complex topography directly upwind reduces the likelihood that the measurement site is subject to large-scale vertical flow separations.

3.1. Cloud droplet deposition

Cloud droplet deposition velocities were calculated using a modified version of the multiple-resistance model developed by Lovett (1984). The model divides the canopy into several vertical layers within which wind speed, LWC and the droplet size distribution are assumed constant. The resistance to droplet transfer between layers is determined from the inverse of the turbulent diffusivity for droplets integrated over the depth of the layer being considered. The turbulent diffusivity for droplets at the top of the canopy is calculated by analogy with that for momentum after Thom (1975) and the profile of droplet diffusivity with height inside the canopy is taken to be a function of the downward cumulative canopy surface area (Waggoner, 1975). The resistance to droplet transfer across the leaf boundary layer is described as the inverse of the product of the mean horizontal wind speed within a layer and an empirically determined capture efficiency for droplets of a given size. The capture efficiency of fir needles and twigs for cloud droplets in the size range 4–32 μm was determined as a function of the Stokes number in wind tunnel experiments by Thorne et al. (1982). The calculation of mean horizontal wind speeds within the canopy from a wind speed value measured above the canopy is discussed below. The model also calculates the droplet flux due to gravitational settling. The mathematical structure of the model and method of solution are described in detail by Lovett (1984). Below we discuss several modifications to Lovett's original model that we have made in order to adapt it for use at the Whiteface site.

A wind speed profile was measured at the meteorological tower, which allowed the calculation of in-canopy wind speed extinctions consistent with the observed penetration of the wind into the forest stand at Whiteface. Our measured wind speed profiles were reasonably consistent with Lovett's (1984) formulation of the wind speed attenuation as a function of the downward cumulative canopy surface area,

$$u_h = u_{ct}(\alpha\ \mathrm{csai}_h), \tag{1}$$

where u_h is the wind speed at a given height in the canopy, u_{ct} is the wind speed at the canopy top, α is the wind speed extinction coefficient and csai_h is the downward cumulative surface area of canopy elements at a given height. While the fit of the modeled wind profile, using Lovett's value of $\alpha = -0.27$, (determined empirically for a 10.6 m high balsam fir stand on Mt. Moosilauke, New Hampshire) to the measured wind profile at our site was good, wind speeds in the upper 4 m of the canopy were underpredicted by 12% (Fig. 1). Lovett's (1984) work and our own experimentation with his model indicated that most cloud droplet interception occurs in the upper 3 to 5 m of the canopy and that the rate of droplet capture is strongly dependent on wind speed. For these reasons, we used a value of $\alpha = -0.18$, which more closely described wind penetration into the upper portions of the forest canopy (approximately 15 m to 20 m above the ground surface) at the 1050-m measurement site (Fig. 1).

The roughness length (z_0) and zero plane displacement height (d), which describe the scale of turbulence over a canopy, were then calculated for all wind speeds using the observed in-canopy wind speed extinction and the measured canopy surface area distribution, using the method presented by Lovett and Reiners (1986). We used this wind-speed-dependent parameterization of d and z_0 to calculate the aerodynamic resistance to momentum and cloud droplet transfer to the internal canopy space. Mueller (1991) has also used this type of modification to Lovett's (1984) model to quantify cloud water deposition to a high-elevation spruce-fir forest on Whitetop Mountain in Virginia, USA.

Lovett's (1984) model computes the boundary layer resistance to droplet transfer of several different canopy surface types such as fir needles, twigs and boles. The component resistances are

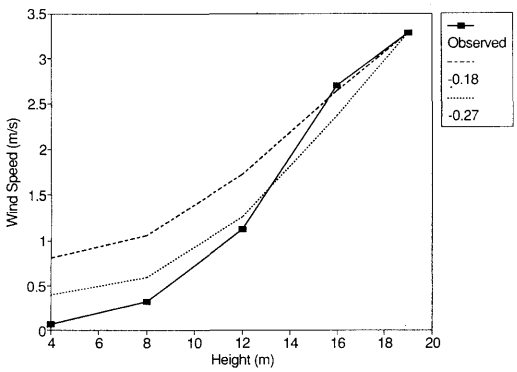

Fig. 1. Measured (solid line) and modeled wind speed profiles for average conditions in the spruce-fir canopy at 1050-m on Whiteface Mt., NY. The wind speed extinction coefficient (-0.27, see text) determined by Lovett (1984) gives a good overall fit (dotted line) but underestimates the average wind speeds near the top of the canopy by 12%, where most cloud droplet interception is believed to take place. In this study we used a wind speed coefficient of -0.18 (dashed line), which more accurately describes wind speeds in the critical region of the canopy.

then combined in parallel to form the integrated boundary layer resistance for the total canopy surface area. We adapted the model for a multi-species canopy by extending the number of canopy surface components to include spruce needles and birch leaves. The capture efficiency for spruce needles was assumed to have the same dependence on the Stokes number as fir needles and was calculated using the empirical formula of Thorne et al. (1982). Capture efficiencies (CE) of birch leaves were modeled as a function of the Stokes parameter (S) using the formula proposed by Bache (1979)

$$\mathrm{CE} = S^{1.7}, \quad \text{for} \quad S < 0.1, \tag{2a}$$

$$\mathrm{CE} = S^2/(S+0.6)^2, \quad \text{for} \quad S > 0.1, \tag{2b}$$

after Mohnen (1988b).

Refinements were also made to the way in which the continuous cloud-droplet size distribution is represented in the cloud water model. We modeled the droplet size distribution as a function of LWC according to the function described by Best (1955), in a similar manner to Lovett (1984), except that we have discretized the continuous droplet size frequency distribution into a much larger number of size classes. Numerical experiments with our version of the model and the canopy structure data used for this study showed that Lovett's original choice of 3 droplet size classes resulted in an underestimation of cloudwater deposition velocities on the order of 30% for meteorological conditions typical of the growing season. We found that 500 size classes provided a reasonable discretization of the droplet size distribution with which the model results approached the limiting value of V_d within $\sim 0.05\%$ in an acceptable amount of computational time on a 20-Mhz IBM-386 computer. The sensitivity of the model to the choice and weighting of representative droplet diameters results from the dependence of V_d on the square of the stokes parameter which is itself a function of the square of the droplet diameter.

Monthly average meteorological values for cloud immersion conditions were calculated from the meteorological data set and the modified model was used with these values to calculate an average monthly cloud water deposition velocity. These monthly average deposition velocities were multiplied by the cloud immersion time for the month to compute total monthly cloud water deposition. Seasonal totals of cloud water deposition were multiplied by seasonal average cloud water chemical concentrations to determine ion deposition rates.

3.2. Aerosol particle and gas deposition

The Hicks et al. (1987) multiple-resistance model for aerosol particle and gas deposition to forest canopies was modified for use at the Whiteface site. This model treats the canopy as a "big leaf" or single surface approximation of the entire canopy. Deposition velocities are determined from analysis of three component resistances operating in series, an aerodynamic resistance, a leaf boundary-layer resistance and a foliar resistance.

The Hicks et al. (1987) model uses the standard deviation of the horizontal wind direction (σ_θ) as a measure of the scale of turbulence and as a predictor for the aerodynamic resistance to particle and gas transfer. We replaced this with the method presented above (in the discussion of cloud droplet deposition) for calculating wind-speed-dependent parameterizations of d and z_0. The wind-speed-dependent values of d and z_0 were

then used to calculate the bulk aerodynamic resistance (R_a) of the canopy,

$$R_a = u/u^{*2}, \quad (3)$$

where u^*, the friction velocity, is given by

$$u^* = (uk)/\ln[(h_u - d)/z_0], \quad (4)$$

for which u is the mean wind speed at height h_u and k is von Karmen's constant, after Thom (1975).

The leaf boundary layer resistance is modeled as a function of the Schmidt number (the ratio of the kinematic viscosity of air to the diffusivity of a trace gas species or brownian diffusivity of a particle). We modified both the dry deposition and cloudwater deposition models to calculate atmospheric properties such as the density and kinematic viscosity of air as functions of the ambient vapor pressure, temperature and atmospheric pressure. Temperature and pressure dependent particle and gas diffusivities were also added to the dry deposition model. The original models use standard-temperature-pressure values of these parameters.

The foliar resistance is modeled as the combination of a stomatal resistance operating in parallel with a cuticular resistance. Stomatal resistance to trace gas transfer is modeled analogously to resistance to water vapor transfer through the stomata (Baldocchi et al., 1987). The model was adapted for use with a multi-species canopy by restructuring the calculation of the canopy resistance term as a leaf-area-weighted combination of the foliar resistance calculated for spruce, fir and birch leaves.

The original model estimates the deposition velocity of submicron to micron size aerosols assuming Brownian diffusion and gravitational settling are the dominant transfer processes. The deposition velocity of particles in the size range 2–10 μm esd was estimated based on the empirical formulation of Wesely et al. (1983), which specifies a linear dependence on the product $\sigma_\theta u$. In practice, deposition velocities for coarse particles at Whiteface calculated with this approximation appeared to be excessively large, probably due to typical values of $\sigma_\theta u$ at our high-elevation location that are much higher than the conditions encountered by Wesely et al. (1983). Therefore, we estimated the deposition velocity of the moderately coarse fraction (1.5 to $\sim 3\,\mu$m) of aerosols sampled by our filter pack system by adding an inertial impaction (with rebound) term based on the work of Slinn (1982) to Hicks et al.'s (1987) formulation of aerosol deposition by brownian diffusion and gravitational settling.

We assumed that the aerosol mass sampled by our filter pack system (Subsection 2.5) represented two primary particle populations, submicron to micron size particles containing primarily NH_4 and SO_4 and moderately coarse (1 to $\sim 3\,\mu$m esd) particles containing K, Na, Ca, Mg and NO_3. We based this assumption on the particle size distributions reported for these elements by Lindberg and Lovett (1985) and Davidson et al. (1985). We assumed that most NO_3 was derived from either oceanic sources or reaction of HNO_3 with alkaline aerosols and therefore, present in the moderately coarse suspended particle fraction (Lindberg et al., 1990). Submicron NH_4NO_3, produced by gas to particle conversion during reaction of NH_3 and NO_3 vapors, was assumed to be insignificant considering the apparently low NH_3 air concentrations (discussed below, cf. Lindberg et al., 1990). We modeled the deposition velocities of these two particle populations based on single representative aerodynamic diameters for each population. We chose 1 μm esd as representative of the NH_4 and SO_4 particle population based on the analysis of Davidson et al. (1985) who demonstrated that while the mode of the SO_4 particle size distribution may be $< 1\,\mu$m, the mode of the SO_4 mass flux distribution will tend to be shifted toward larger particle sizes. We assumed the second particle fraction had a mass median diameter of 2.5 μm after Lindberg and Lovett (1985). Both of these aerosol populations are discussed subsequently as the suspended particle fraction of the total dry deposition flux. The coarse particle fraction refers to particles deposited entirely by gravitational settling as measured by deposition rates to horizontal surrogate surfaces according to the method of Lindberg and Lovett (1985, see also Subsection 2.5).

Monthly average deposition velocities for particles and gases were calculated from hourly deposition velocities, computed using the modified Hicks et al. (1987) model and hourly averages of meteorological measurements made during dry periods. These monthly deposition velocities were combined with the average air concentration of

particles and gases for a given month to compute monthly average particle and gas deposition rates. If particle or gas concentration data were not available for a particular month (due to inefficient sampling of short duration dry periods), we calculated deposition rates on the basis of average air concentrations representative of the season to which the month belonged.

4. Results and discussion

We sampled 80 to 100% of the precipitation events which occurred during each year of the study. Approximately 80% of the nonfreezing, nonprecipitating cloud periods were sampled. The measurement site was immersed in cloud (including precipitating and nonprecipitating clouds) an average of 10% of each year (Table 2). Dry deposition sampling was complicated by frequent rainfall and short-duration dry periods. We successfully obtained filter pack samples during 31 out of the 48 months of the study. Sulfur dioxide measurements were available for 70% of the study period. There was considerable temporal variation between seasons (data not shown) and between years for both atmospheric concentrations and depositions (Tables 3, 4). We have not reported standard errors associated with temporal variation because they do not reflect the actual confidence interval of the measurement (Siros, 1990). The statistical uncertainties associated with flux estimates computed using mechanistic models such as we have used are difficult to quantify and often assumed to be large. Assessments of large uncertainties arise from the propagation of measurement errors through the calculations as well as uncertainty associated with the mathematical description of the physical processes of droplet, particle and vapor deposition. However some investigators have reported good agreement between deposition rates estimated with inferential models and deposition of cloud water or aerosols estimated from canopy throughfall measurements (cf. Lovett, 1984; Lindberg et al., 1990). We have attempted to constrain our estimates of atmospheric deposition based on mass balance considerations including throughfall and soil water fluxes. A discussion of measurement and estimate uncertainties is presented in section 4.5.

4.1. Precipitation

The concentrations of major ions in precipitation (Table 4) were similar to values reported for a nearby MAP3S (1982) station at 600-m elevation on Whiteface Mountain. Precipitation chemistry and deposition at Whiteface were also similar to the long-term record at the Hubbard Brook Experimental Forest (HB) in northern New Hampshire (Likens et al., 1977). Hubbard Brook experienced more S deposition in precipitation (12.8 kg ha^{-1} yr^{-1}) than Whiteface (WF) (8.5 kg ha^{-1} yr^{-1}), but this is more likely a result of a difference between the measurement periods (1964–1974 and 1986–1990) than a difference in regional deposition rates. Husain and Dutkiewicz (1990) reported a reduction in regional SO_2 emissions of 20% between 1977 and 1986. The average annual deposition of N via precipitation was virtually the same at both WF and HB, 6.7 and 7.0 kg ha^{-1} yr^{-1}, respectively, despite the difference in sampling periods. Nitrogen deposition via precipitation during 1986 and 1987 at the nearby Huntington Forest (HF) in Newcomb, New York (Shepard et al., 1989) was similar (6.6 kg ha^{-1} yr^{-1}) and S deposition (10.8 kg ha^{-1} yr^{-1}) was slightly greater than the values for the same period at Whiteface (Table 5). Average annual precipitation was slightly lower at HF (90 cm) than at WF (115 cm) during 1986 and 1987. The 4-yr average annual precipitation rate at WF (132 cm yr^{-1}) was identical to the long term average at HB.

4.2. Cloud water

The average deposition velocity for cloud droplets varied from 17.5 cm s^{-1} during the

Table 2. *Cloud exposure of the forest at 1050-m elevation on Whiteface Mountain, NY*

Year	1986	1987	1988	1989	Average
cloud immersion (% of hours)	6	9	9	16	10
liquid water content (g m^{-3})	0.20	0.24	0.32	0.62	0.36

Table 3. *Water fluxes (in cm yr^{-1}) to and through the forest canopy at 1050-m elevation on Whiteface Mountain, NY*

Year	1986	1987	1988	1989	Average
precipitation	117	112	124	174	132
cloud water	6.9	12.5	17.1	76.9	28.4
total input	124	125	141	251	160
throughfall	114	121	114	192	135

dormant season of 1986 to 27 cm s^{-1} during the growing season of 1989. These deposition velocities correspond to water deposition rates of 0.02 mm h^{-1} and 0.12 mm h^{-1}, respectively. Estimated annual cloud water deposition to the spruce-fir forest at WF ranged from 6.9 to 77 cm yr^{-1} with an average deposition rate of 28 cm yr^{-1}. The large year-to-year variation in deposition rates was a function of variable cloud LWC, windspeed and the length of time the forest was immersed in cloud (Tables 2 and 3). Both cloud LWC and immersion frequency are subject to large annual variations at the 1050-m measurement site, which is often near the altitude of cloud base at Whiteface Mountain (Mohnen, 1988b).

Lovett et al. (1982) estimated the annual cloud water deposition rate at 1220-m elevation on Mount Moosilauke, New Hampshire (MM) to be 84 cm yr^{-1}, which is reasonably comparable with our estimated deposition rate of 77 cm yr^{-1} for 1989. Schaefer and Reiners (1990) recently revised the estimate of annual cloud water deposition at MM from 84 cm yr^{-1} to 40.5 cm yr^{-1}. If the latter value is more representative of average conditions at MM, then compared to an average deposition rate of 28 cm yr^{-1} at 1050-m elevation at WF it may indicate an increase of roughly 0.08 cm yr^{-1} m^{-1}-elevation in the cloud water deposition rate for this region. Sherbatskoy and Bliss (1984) estimated annual cloud water deposition to be 154 cm yr^{-1} at 1110-m elevation on Madonna

Table 4. *Concentration of elements in wet deposition to the 1050-m forest site on Whiteface Mountain, NY*

Precipitation

Year	H^+	Ca^{2+}	Mg^{2+}	K^+	Na^+	NH_4^+	NO_3^-	Cl^-	SO_4^{2-}	TN
1986	50.7	10.8	2.6	1.9	1.4	13.7	21.5	3.0	18.4	35.2
1987	46.8	6.0	1.6	0.7	1.3	16.3	24.2	2.4	40.1	40.5
1988	46.7	8.4	1.5	1.3	1.3	11.7	23.9	2.9	37.3	35.6
1989	43.1	8.4	2.0	1.2	2.1	15.4	24.1	1.6	36.5	39.5
Avg	46.8	8.4	1.9	1.1	1.5	14.3	23.4	2.4	40.6	37.7

Cloud water

Year	H^+	Ca^{2+}	Mg^{2+}	K^+	Na^+	NH_4^+	NO_3^-	Cl^-	SO_4^{2-}	TN
1986	211	20.0	6.0	3.0	4.0	137	107	7.1	248	245
1987	343	20.0	6.0	3.0	4.0	197	188	10.1	366	385
1988	64.6	11.0	3.0	0.9	0.8	23.5	18.3	1.3	53.3	41.7
1989	90.4	8.4	2.0	3.1	3.5	58.9	47.8	5.1	100	107
Avg	122	10.7	2.9	2.7	3.2	73.5	62.4	5.2	132	136

Throughfall

Year	H^+	Ca^{2+}	Mg^{2+}	K^+	Na^+	NH_4^+	NO_3^-	Cl^-	SO_4^{2-}	TN
1986	62.8	28.7	4.6	11.2	3.7	10.8	15.7	5.8	80.5	45.8
1987	80.3	32.8	10.4	12.6	4.0	17.5	38.6	7.2	94.5	75.5
1988	54.5	24.1	6.5	13.5	2.6	9.2	31.0	5.8	60.5	54.7
1989	52.9	31.5	3.9	6.6	2.4	15.1	25.7	3.4	49.6	60.2
Avg	62.6	29.3	6.3	10.9	3.2	13.1	27.7	5.5	71.3	59.0

Concentrations are reported in μmol(+/−) l^{-1} except for total N (TN) which is reported in μmol l^{-1}.

Table 5. *Deposition of elements in wet and dry deposition to the 1050-m forest site on Whiteface Mountain, NY*

Precipitation

Year	H	Ca	Mg	K	Na	NH_4-N	NO_3-N	Cl	SO_4-S	TN
1986	0.60	2.36	0.36	0.44	0.38	2.24	3.52	1.23	9.07	5.76
1987	0.53	1.35	0.22	0.32	0.33	2.57	3.81	0.95	7.22	6.38
1988	0.58	2.09	0.22	0.65	0.38	2.04	4.15	1.26	7.42	6.19
1989	0.76	2.94	0.42	0.78	0.84	3.76	5.89	0.96	10.20	9.64
Avg	0.62	2.19	0.31	0.55	0.48	2.65	4.34	1.10	8.48	6.99

Cloud water

Year	H	Ca	Mg	K	Na	NH_4-N	NO_3-N	Cl	SO_4-S	TN
1986	0.15	0.28	0.05	0.08	0.06	1.33	1.04	0.18	2.76	2.38
1987	0.43	0.50	0.09	0.15	0.11	3.43	3.28	0.44	7.30	6.72
1988	0.11	0.38	0.06	0.06	0.03	0.56	0.44	0.08	1.51	1.00
1989	0.70	1.29	0.19	0.92	0.62	6.34	5.16	1.39	12.38	11.50
Avg	0.35	0.61	0.10	0.30	0.21	2.92	2.48	0.52	5.99	5.40

Dry deposition

Year	H	Ca	Mg	K	Na	NH_4-N	NO_3-N	Cl	SO_4-S	TN
1986	0.36	0.21	0.05	0.18	0.43	0.15	5.07	0.02	1.51	5.22
1987	0.23	0.23	0.17	0.24	0.58	0.10	3.19	0.66	1.46	3.29
1988	0.45	0.39	0.32	1.44	1.45	0.19	6.24	0.59	2.50	6.43
1989	0.16	0.23	0.10	0.90	1.05	0.02	2.18	0.15	1.89	2.19
Avg	0.30	0.26	0.16	0.69	0.88	0.11	4.17	0.36	1.84	4.28

Total atmospheric deposition

Year	H	Ca	Mg	K	Na	NH_4-N	NO_3-N	Cl	SO_4-S	TN
1986	1.11	2.85	0.47	0.71	0.87	3.73	9.64	1.42	13.34	13.37
1987	1.19	2.08	0.48	0.70	1.02	6.10	10.29	2.06	15.98	16.39
1988	1.14	2.85	0.61	2.15	1.85	2.79	10.83	1.93	11.43	13.61
1989	1.62	4.46	0.72	2.60	2.51	10.11	13.22	2.50	24.47	23.33
Avg	1.26	3.06	0.57	1.54	1.56	5.68	10.99	1.98	16.31	16.68

Throughfall

Year	H	Ca	Mg	K	Na	NH_4-N	NO_3-N	Cl	SO_4-S	TN
1986	0.72	6.53	0.64	4.96	0.98	1.71	2.49	2.33	14.66	7.28
1987	0.98	7.97	1.53	5.96	1.12	2.97	6.56	3.09	18.39	12.83
1988	0.63	5.52	0.90	6.02	0.68	1.47	4.96	2.33	11.08	8.75
1989	1.03	12.16	0.90	4.94	1.06	4.07	6.93	2.30	15.31	16.22
Avg	0.84	8.05	0.99	5.47	0.96	2.56	5.24	2.51	14.86	11.27

Depositions are reported in kg ha^{-1} yr^{-1}.

Mt., Vermont (MD). This relatively high deposition rate probably reflects their method of scaling the collection rate of cloud water collectors to the collection rate for the forest canopy. They did not use a micrometeorological modeling approach.

The average LWC-weighted concentrations of major ions in cloud water were 1.3 to 5.1 times greater than in precipitation (Table 4). Ions with gas phase precursers (NO_3^-, SO_4^{2-}, NH_4^+) had the highest cloud/rain enrichment ratios (2.7–5.1) while those with dominantly particulate transport modes (Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^-) had lower enrichment ratios (1.3–2.5). Annual enrichment ratios were generally inversely proportional to average annual cloud LWC. The observed cloud/rain enrichment ratios are consistent with the generally higher scavenging efficiency of cloud droplets than rain droplets (Junge, 1963) and are comparable to values obtained in other studies of cloud water chemistry (cf. Weathers et al., 1988). The chemistry of cloud water varied significantly within (data not shown) and between cloud events (data not shown) and annually (Table 4). Such temporal variation has been well documented and it attributable to synoptic meteorology, air mass history, cloud LWC and position of the sampling location relative to cloud base (Vong et al., 1990; Mohnen and Kadlecek, 1989).

The combined effects of position relative to cloud base and cloud LWC on average ion concentrations in cloud water can be illustrated by a comparison between cloud water sampled at the 1050-m site and the ASRC summit observatory on Whiteface Mountain. The 1987 growing season LWC-weighted average ion concentrations reported here for the 1050-m site (Table 6) are generally higher than those reported for the same season at the Whiteface summit station (1483 m) by Mohnen (1988a). The data for these two sites may be also be expressed as air concentrations during cloud:

$$C_a = C_c \times \mathrm{LWC}, \qquad (5)$$

where C_a is the ion concentration in air and C_c is the ion concentration in cloudwater, assuming a scavenging efficiency of 100% (Junge, 1963). Since the in-cloud air concentrations computed with equation (5) are very similar between the two sites, the variation in cloud water chemistry appears to be due primarily to differences in cloud LWC.

Table 6. *Comparison of growing season LWC-weighted average cloud water ion concentrations measured at the 1050-m site and the summit (1485-m) of Whiteface Mountain during 1987*

	Cloudwater concentration (μM l^{-1})		Air concentration[a] (nM m^{-3})	
	1050 m	Summit[b]	1050 m	Summit
H	302	180	874	829
Ca	10.0	8.5	29.0	38.9
K	3.0	1.6	8.7	7.2
Mg	3.0	1.5	8.7	6.7
Na	4.0	1.9	11.6	8.5
NH_4	228	119	662	547
NO_3	127	82	368	375
SO_4	230	118	668	542
Cl	10.1	4.5	29.1	20.7

[a] Air concentration during cloud calculated using equation (5), assuming 100% scavenging efficiency and cloud LWC of 0.29 g m^{-3} for the 1050 m site (Table 4) and 0.46 g m^{-3} for Whiteface summit (Mohnen, 1988a).
[b] Mohnen (1988a).

Cloud water NO_3^- and SO_4^{2-} concentrations for individual years at the WF 1050-m site were similar to values reported from other locations in New England (Tables 4 and 7). The 4-yr average concentrations at WF were similar to 1-yr averages reported for 1110 m at Madonna Mountain, Vermont (MD) (Scherbatskoy and Bliss, 1984) but were much lower than the values reported for 1220 m at Mount Moosilauke, New Hampshire (MM) measured in 1980 and 1981 (Lovett et al., 1982). The difference between the ion concentrations reported here and those reported for MM are most likely due to temporal variation in atmospheric chemistry because the 1980–1981 concentrations at MM fall within the range of values measured at the Whiteface summit station during 1979 (Falconer and Kadlecek, 1980; Lovett et al., 1982).

The reported estimates of annual S and N deposition by cloud water at MM and MD, which represent deposition rates in the early 1980s, are 10 times greater than our estimate for WF (Table 7). These considerable differences arise mainly from the variation in estimated cloud water depositions of 84, 154 and 28 cm yr^{-1} at MM, MD and WF respectively, although concentrations (as noted above) were higher at MM as well. The discrepencies between our estimates and the previously

Table 7. *Comparison of cloud water concentrations ($\mu mol(+/-)l^{-1}$) and estimated depositions ($kg\ ha^{-1}\ yr^{-1}$) between Whiteface Mt., NY, Mt. Moosilauke, NH and Madonna Mt., VT*

Site	Elevation m	Concentrations H^+	NH_4^+	NO_3^-	SO_4^{2-}
Whiteface Mt.	1050	122	74	62	136
Mt. Moosilauke[a)]	1220	288	108	195	342
Mt. Moosilauke[b)]	1220	270	102	180	330
Madonna Mt.[c)]	1110	122	na	69	172
Site	**Water cm**	**H**	**Deposition NH_4-N**	**NO_3-N**	**SO_4-S**
Whiteface Mt.	28.4	0.35	2.9	2.5	6
Mt. Moosilauke[a)]	84	2.4		23	46
Mt. Moosilauke[b)]	40.5	1.1	5.9	10	21
Madonna Mt.[c)]	154	2.3		22	54

[a)] Lovett et al. (1982).
[b)] Schaefer and Reiners (1990).
[c)] Scherbatskoy and Bliss (1984).

published values may reflect temporal variation in water deposition and atmospheric chemistry as much as canopy structure differences or varying geographic and elevational settings. In addition, the two previous studies extrapolated to annual estimates from relatively small data sets for chemistry, LWC and immersion time. In light of the magnitude of the temporal variation observed at WF, even our 4-yr average may not be a good estimate of the long-term average cloud water flux at this site.

4.3. Dry deposition

Dry deposition velocities (V_d) calculated using our modified version of the Hicks et al. (1987) big-leaf model fell within a range of values reported for similar settings. Monthly average V_d for HNO_3 vapor ranged from 0.75 to 7.8 cm s^{-1}, with an average of 3.8 cm s^{-1}. Hicks and Meyers (1988) reported average summer V_d for HNO_3 vapor in the range of 2.5 to 5 cm s^{-1}, using meteorological measurements made at 600-m elevation on the southeast side of Whiteface Mountain. Lindberg et al. (1990) reported a warm season average V_d of 1.9 and 2.4 cm s^{-1} for HNO_3 vapor at a loblolly pine site in Oak Ridge, Tennessee (TN), and a Norway spruce site in Göttingen, Germany. Lindberg et al. (1988) estimated a minimum HNO_3 deposition velocity for a high-elevation spruce stand in the Smoky Mountains, TN, of 1.8 cm s^{-1}, using a canopy mass balance for NO_3, and an average value of 4.2 cm s^{-1}, using the Hicks et al. (1987) model.

Monthly average V_d values for SO_2 ranged from 0.11 to 1.16 cm s^{-1}, with an annual average of 0.39 cm s^{-1}. Hicks and Meyers (1988) reported a summer average of 1 cm s^{-1} at WF, and Lindberg et al. (1990) reported 0.34 and 0.40 cm s^{-1} for the warm season at Oak Ridge and Göttingen. Eaton et al. (1978) calculated the V_d of SO_2 at Hubbard Brook, NH to be 0.9 cm s^{-1} using an ecosystem mass balance technique. Cadle et al. (1985) measured an SO_2 V_d to snow of 0.15 cm s^{-1} (at temperatures $> -3°C$) and 0.06 cm s^{-1} (at temperatures $< -3°C$) in northern Michagan.

Monthly average values of V_d for 1 μ aerosols at Whiteface varied from 0.02 to 0.24 cm s^{-1} with an annual average of 0.08 cm s^{-1}. Lindberg et al. (1990) reported deposition velocities for submicron particles of 0.06 and 0.17 cm s^{-1} at Oak Ridge and Göttingen based on the submicron radionuclide tracer model of Bondietti et al. (1984). Eaton et al. (1978) estimated an average value of V_d for submicron-micron size aerosols (as SO_4) of 0.1 cm s^{-1} at Hubbard Brook. The coarse population of the suspended particles at Whiteface (modeled using an aerodynamic diameter of 2.5 μm) had monthly average deposition velocities which ranged from 0.18 to 3.29 cm s^{-1} with an annual average of 1.06 cm s^{-1}.

Table 8. *Average and range of monthly air concentrations of suspended particles and gases measured at Whiteface Mountain, NY during 1986–1989*

	Ca	Mg	K	Na	NH_4	NO_3	HNO_3	Cl	SO_4	SO_2
Avg	2.87	2.21	7.09	13.7	39.1	3.68	25.2	3.54	24.0	60.4
Min	nd	nd	nd	nd	0.30	nd	7.67	nd	nd	8.31
Max	10.8	7.05	54.5	94.1	190	17.5	97.4	12.3	122	181

nd: not detected.
Values are given in nmol m^{-3}.

Air concentrations of SO_2, HNO_3 vapor and particles (Table 8) were generally lower than the values reported for Tennessee or Göttingen, reflecting the greater distance of WF from major pollutant sources than the aforementioned sites. Although we did not measure NO_2 for this study, Hanson et al. (1989) estimated an annual average NO_2 air concentration of 2 nL L^{-1}, an average deposition velocity of 0.18 cm s^{-1} and an annual NO_2-N deposition rate of 0.08 kg N ha^{-1} yr^{-1} for Whiteface Mountain. We estimated the air concentration of NH_3 from the air concentration of NH_4 using the average NH_3/NH_4 ratio (0.1) given for the eastern USA by Lindberg et al. (1990). By this estimate, NH_3 averages 4.1 nmole m^{-3} which is less than half the concentration estimated for Oak Ridge, TN and ~1/40 the concentration estimated for Göttingen, BDR by Lindberg et al. (1990).

The average annual dry deposition of N at Whiteface was 4.28 kg ha^{-1} yr^{-1} (or 4.36 kg ha^{-1} yr^{-1} including NO_2). The dry N flux for 1986–1987 (Table 5) was 17% less than the value estimated for the nearby Huntington forest of 5.1 kg ha^{-1} yr^{-1} (Shepard et al., 1989). Total dry

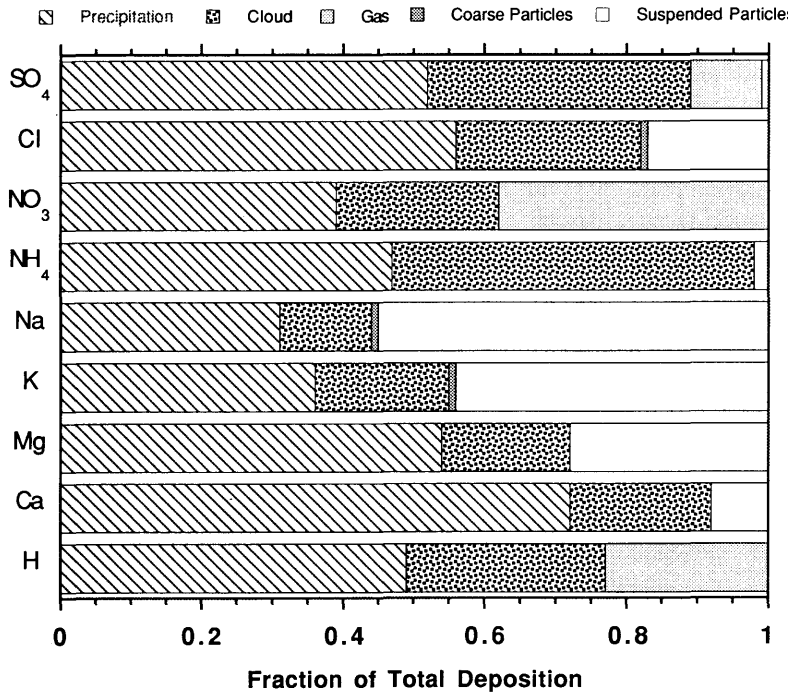

Fig. 2. Relative contributions of precipitation, cloud, gas phase, coarse and fine particle deposition to the 4-yr average annual atmospheric deposition of major ions at the 1050-m elevation forest site, Whiteface Mountain, NY, USA.

deposition of S to the 1050-m site at Whiteface averaged 1.8 kg ha^{-1} yr^{-1}. Shepard et al. (1989) reported 2.2 kg ha^{-1} yr^{-1} S dry deposition during 1986 and 1987 at Huntington Forest which was 30% greater than our estimates for WF for the same period. Likens et al. (1990) estimated the long-term average dry deposition of S to the Hubbard Brook experimental forest to be 6.7 kg ha^{-1} yr^{-1} using watershed mass-balance methods. Again, temporal variation may explain the large difference between the WF and HB estimates of S deposition rates, as the HB estimate reflects the average of the time period 1964–1987. Although Likens et al. (1990) did not observe a temporal trend in their watershed mass-balance estimates of S dry deposition, they did observe a 40% decrease in S wet deposition over the period, consistent with the trend in aerosol sulfate concentrations reported by Husain and Dutkiewicz (1990).

4.4. *Total atmospheric deposition*

Precipitation accounted for 30% to 70% of total deposition for all elements measured (Fig. 2). Cloud water deposition contributed significantly to total deposition of all elements and amounted to over 50% of the total NH_4 deposition. Gas phase dry deposition was most important for N, contributing 38% of the NO_3 as HNO_3 vapor. Suspended aerosol particle dry deposition was important for the cations Na, K, Mg and Ca, and contributed between 9 and 56% of their total deposition. Submicron SO_4 particle deposition contributed 1%, SO_2 vapor deposition 10% and cloud water deposition 37% of total S deposition. Coarse particle ($> \sim 2.5\ \mu m$) deposition as measured by sedimentation rates to surrogate surfaces was generally unimportant for all elements (Fig. 2). The relative contribution of each deposition process as well as total atmospheric input varied substantially from year to year (Fig. 3). Annual variations in cloud water deposition contributed most of the year-to-year variation in the total atmospheric deposition of N and S.

Differences in proximity to pollution sources and differences in sampling periods make it difficult to directly compare deposition rates at the high elevation (1050 m) Whiteface site with low elevation sites in the region. However, total atmospheric deposition is probably greater at high elevation sites than at immediately surrounding low elevations (Lovett and Kinsman, 1990). One way to assess the influence of elevation on total atmospheric deposition rates is to compare the relative efficiency of cloud droplet scavenging and deposition to dry deposition processes. For inland forests of the northeastern USA, cloud immersion is only significant at high elevations (>900 m) (Siccama, 1974; Lovett and Kinsman, 1990). Average annual cloud water deposition rates for N at the 1050-m site on Whiteface Mt. ranged from 1.3 to 8.7 g ha^{-1} h^{-1}, while annual average dry deposition rates ranged from 0.3 to 0.8 g ha^{-1} h^{-1}. Cloud scavenging and deposition was an average of 12 times more efficient than dry processes in transfering atmospheric N to the forest canopy over the 4 years of the study. Cloud scavenging was even more effective for S than N, averaging 30

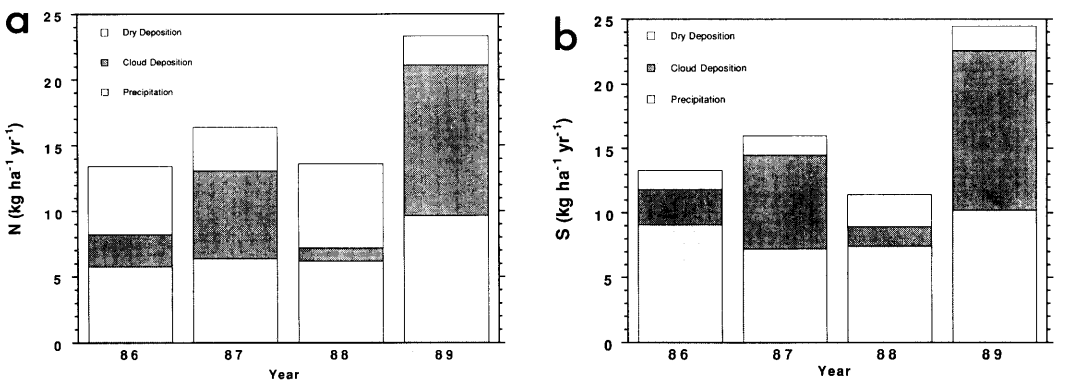

Fig. 3. Annual contribution of precipitation, cloud water and dry deposition processes to the total atmospheric flux of N (a) and S (b) to the 1050-m elevation forest at Whiteface Mountain, NY, USA.

times the efficiency of dry scavenging processes. Average cloud deposition rates for individual years ranged from 2.0 to 9.0 g S ha^{-1} h^{-1}, while dry deposition rates ranged from 0.2 to 0.3 g S ha^{-1} h^{-1}. In the absence of significant vertical gradients in air concentrations (Lovett and Kinsman, 1990), total atmospheric deposition rates should be lower below 900-m elevation than above average cloud base. Assuming cloud immersion hours are replaced by dry hours at low elevations, forests located there should receive an average of 12 to 30 × less N and S, respectively, than adjacent high-elevation forests during those time periods.

4.5. Evaluation of modeled deposition flux uncertainty

Uncertainties associated with the measurement and estimation of model parameters and input data for the Lovett (1984) cloud water deposition model have been estimated by Mohnen (1988b). Mueller (1991) has conducted a sensitivity analysis of a modified Lovett (1984) model to variations in the most important input parameters. Several of the input data requirements to which the model is most sensitive, LWC and wind speed measurement, appear to have statistical uncertainties of approximately 25%. However, other critical parameters such as droplet size spectra and droplet capture efficiency may have statistical uncertainties on the order of 100% (Mohnen, 1988b). An indeterminant amount of uncertainty is also introduced into the final model result by empirical formulae, simplified mathematical descriptions of physical processes and various assumptions used to construct the models. All of the above-mentioned factors make it impractical to assign a useful value to the overall model uncertainty via analysis of input data uncertainties and model formulation.

Because it is impractical to assess the accuracy of the cloudwater model by propagating error rates, attempts have been made to quantify model performance by comparison with cloud deposition rates estimated from throughfall collections (Mueller et al., 1991) and artificial collectors (Joslin et al., 1990). We made similar attempts to test the cloud model but were unable to collect a useful data set due to frequent rainfall periods during cloud immersion. Uncertainties in dry deposition fluxes computed with the Hicks et al. (1987) model are also impractical to estimate due to similar difficulties in propagating statistical uncertainties through the model.

We have attempted to assess the overall validity of the modeled dry and cloud water deposition fluxes using canopy and whole-ecosystem mass balance approaches (cf. Lovett, 1988). The elements most likely to exhibit conservative behavior in the canopy are Na, Cl and S. These elements are considered conservative tracers of atmospheric inputs because they are not easily leached from the forest canopy and do not appear to be readily adsorbed or assimilated by the canopy. Lindberg and Garten (1988) have demonstrated the conservative behavior of S in deciduous and coniferous canopies and have indicated that SO_2 deposition should not necessarily be included in a canopy mass-balance, because it is deposited primarily through the stomata to the internal areas of the leaf. Sulfur may also behave conservatively in the soil due to the lack of SO_4 adsorption at this site (Harrison and Johnson, 1991); however, organic sulfur dynamics in the soil column may compromise this approach (Fuller et al., 1986). The results of canopy mass balance calculations for these 3 potentially conservative elements are presented in Table 9. A mass balance calculation is also shown for S in the ecosystem as a whole, which includes SO_2 deposition. We have made the assumption that all SO_2 is deposited to internal areas of foliage and is released to the soil through tree roots (Schulze, 1989) or is deposited directly to the soil and snow during the freezing season.

If our assumptions about conservative behavior (e.g., throughfall = precipitation + cloud water + dry deposition) are valid, then the combined cloud and dry deposition model estimates agree with the mass balance estimates of cloud + dry deposition to between 8 and 66% for individual years (Table 9). Lynch and Corbett (1989) have recommended use of at least 3 to 5 yr of data when assessing the mass balance of S in forest ecosystems; therefore, we consider the 4-yr-average mass balance as the most appropriate measure to compare with the micrometeorological model results. The canopy mass balances for Na and Cl exhibited 4-yr-average estimates of cloud + dry fluxes that agree with the model estimates to within 25% and 32% respectively. Both canopy and ecosystem mass balances for S showed good agreement (Table 9). The ecosystem mass balance

Table 9. *Canopy and ecosystem mass balance assessment of cloud water and dry deposition estimates*

Year	1989			1988			1987			1986		
	Na	Cl	S	Na	Cl	S	Na	Cl	S	Na	Cl	S
Total Dep	109.0	70.7	705	80.6	54.4	288	44.6	58.2	457	37.7	40.1	674
Total + Gas			763			357			498			716
Canopy mass balance												
TF + SF	46.1	64.9	478	29.8	65.8	347	48.6	87.2	575	42.6	65.8	458
Net TF[a)]	−62.9	−5.8	−227	−50.8	11.4	58.9	4.0	29.0	118	4.9	25.7	−217
% difference[b)]	−58%	−8%	−32%	−63%	21%	20%	9%	50%	26%	13%	64%	−32%
Ecosystem mass balance												
Export[c)]			1263			494			620			613
Net ecosystem[d)]			500			134			121			−104
% difference			66%			38%			24%			−15%

Values are given in moles $ha^{-1}\ yr^{-1}$.

[a)] Net TF = throughfall − precipitation − cloud − dry deposition (particles).

[b)] % difference = [net flux/total deposition] × 100. Negative values indicate overestimates of total deposition.

[c)] Friedland and Miller, unpublished data for soil solution SO_4 fluxes below the root zone. See Friedland et al. (1991) for description of soil water flux estimates.

[d)] Net ecosystem = export − precipitation − cloud − dry deposition (Σ particles + SO_2).

for S exhibited a 4-yr-average discrepancy of 29% and the canopy mass balance averaged a difference of just 5%. There are, of course, additional sources of uncertainty associated with the throughfall and soil solution fluxes used in the mass balance calculations (cf. Friedland et al., 1991; Friedland and Johnson, 1985). For example, S may have been released from storage in the forest floor organic S pool and contributed to the apparent "imbalance" of the whole ecosystem mass balance for S. However, we find it encouraging that mass balance estimates of cloud + dry deposition fluxes for three different elements agree well on both an individual year and a 4-yr average basis with fluxes based on the micrometeorological model results.

Given the agreement between the tracer mass balance analysis and the inferential models, we conclude that a reasonable assessment of the uncertainty of our total deposition estimates is on the order of ±25%. Still, the estimates of cloud water and dry deposition rates should be interpreted with consideration of the significant uncertainty inherent in the modeling techniques used to obtain them (Hicks and Meyers, 1988). The relatively good agreement between our estimates of atmospheric deposition and canopy or ecosystem mass balances does not guarantee that our modeling of cloud water or dry deposition is accurate. The modeled fluxes, the precipitation fluxes and the throughfall or soil water fluxes could have compensating errors. Due to the large annual variations observed, it is also apparent that additional years of measurements are necessary to improve our understanding of atmospheric fluxes. However, the results of the comparison of modeled fluxes with mass balance calculations do indicate that our estimates are reasonable representations of the magnitudes of the processes of atmospheric transfer of pollutant and nutrient elements to high-elevation forests.

5. Conclusions

Four years of continuous measurements of precipitation, cloud water, air chemistry and meteorology have provided an opportunity to refine previous estimates of atmospheric deposition rates of major elements to high-elevation forests of the northeastern USA. Significant annual variability was observed in the meteorological factors controlling the flux of nutrients and pollutants to a high-elevation forest. Of primary relevance was the amount of time during which the forest

was immersed in cloud. Canopy and ecosystem mass-balance calculations supported the applicability of an inferential micrometeorological modeling approach to estimating cloud water and dry deposition of nutrient and pollutant elements to a subalpine spruce-fir forest at Whiteface Mountain, NY.

The immersion of this high-elevation forest in cloud for an average of 10% of the year significantly enhanced the overall efficiency of the transfer of atmospheric particles and gases to the forest canopy. Cloud water deposition was, on average, 12× more efficient at transfering atmospheric N to the forest canopy than dry deposition processes. Cloud water deposition processes were 30× more efficient than dry deposition at scavenging atmospheric S.

Total S deposition to the 1050-m forest at Whiteface Mountain ranged from 11 to 24 kg ha^{-1} yr^{-1} during 4 years of measurement. Total N deposition ranged from 13 to 23 kg ha^{-1} yr^{-1} over the course of the study. This rate of N deposition is also roughly 10 times the rate of deposition to forests unaffected by industrial pollution (Aber et al., 1989). Thus, the spruce-fir ecosystem at Whiteface has probably experienced a recent (this century) and significant increase in N input. This change in N supply may result in alterations of previously established N and cation cycles in this ecosystem as suggested by Schulze (1989), Aber et al. (1989) and Friedland et al. (1991). The difference between total atmospheric deposition of N and the N flux in throughfall of 4.4 kg ha^{-1} yr^{-1} (Table 5) indicates retention of N in the forest canopy (Friedland et al. 1991). Direct uptake of N by the canopy, substituting for N that would have otherwise been assimilated through tree roots, has been suggested as a cause of nutrient imbalances in foliage (Schulze, 1989). High-elevation forests of the northeastern USA which receive enhanced N (especially NH_4) inputs from cloud water interception may be particularly susceptible to this type of alteration of nutrient cycles.

6. Acknowledgements

We gratefully acknowledge the tremendous efforts made by C. White, D. Foley and R. MacDonald in the collection of cloud water and other samples. We thank J. Schneider, A. M. Kebschull and R. Hopkins for analytical work. D. Wolfe, R. Prinz and B. Michaelfelder provided technical assistance. R. Boyce and three anonymous reviewers made helpful comments on earlier versions of this manuscript. This research was funded by a grant from the Electric Power Research Institute to Oak Ridge National Laboratories and by grants from the Northeast Forest Experiment Station, Spruce-Fir Cooperative within the joint US EPA-USDA Forest Service, Forest Response Program. The FRP is part of the National Acid Precipitation Assessment Program. This paper has not been subjected to EPA or Forest Service policy review and should not be construed to represent the policies of either agency. This research was also supported by a grant to AJF from the Andrew W. Mellon Foundation.

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