ABSTRACT

MENON, SURABI. Role of Sulfates in Regional Cloud-Climate Interactions

(Under the direction of V.K. Saxena and R.R. Braham Jr.)

Aerosols affect the radiation budget of the earth-atmosphere system by directly reflecting or absorbing solar radiation and also indirectly, by altering the cloud albedo through changes in the cloud condensation nuclei concentration (CCN). Increases in CCN concentrations result in an increase in the cloud droplet number concentration (N). Assuming the cloud liquid water content (LWC) stays the same, this will result in smaller cloud droplet sizes. Thus, this will increase cloud reflectance and cloud lifetime as cloud cover also increases. An accurate quantification of the aerosol forcing effect is still not possible due to the complexity involved in understanding aerosol processes and their effects on climate. There has also been a lack of a coordinated effort toward linking surface and in situ observations, as well climate model results and satellite data. Due to the spatial and temporal heterogeneity in aerosol forcing, regional effects are important. In this dissertation, the direct and indirect radiative forcing effects of aerosols – primarily sulfates and to lesser extent soot aerosols at a site located in the southeastern U.S. are investigated by means of surface observations, modeling results and satellite data.

During the summers of 1993-96, field experiments were conducted at Mt. Mitchell, North Carolina, at a site representative of the southeastern U.S. to determine the effect of pollutants on the cloud microphysical and optical properties. Analyses of the results from empirical relationships are used to obtain an estimate of the contribution of

sulfates to indirect radiative forcing. Concurrent measurements of size resolved chemical concentrations, light scattering and absorption coefficients, aerosol size distribution and optical depth measurements were obtained during the winter of 1997 for cloud-free skies. Data from these measurements are used to investigate the chemical-physical-optical interaction between aerosols and to determine the direct forcing effect of aerosols by means of a column forcing model.

Cloud water sulfate concentration is used as a measure of anthropogenic pollution. Back-trajectory analysis is used to identify the source of the air masses classified as polluted continental, continental and marine. The effect of anthropogenic pollution on cloud microphysical properties such as LWC, N, effective radii (R_{eff}), CCN activation spectrum, cloud optical depth and reflectivity are investigated. The relationship between R_{eff} and sulfate for different air masses, as well as the N-sulfate mass relationship, suggests that the counteracting effect of sulfates on greenhouse warming for the southeastern U.S. would be of a magnitude greater than -4.0 W m^{-2} obtained by previous modeling studies. Acidity variations between cloud droplets of different sizes indicated that on an average, smaller drops are enriched in sulfates, nitrates and ammonium, whereas, larger droplets have higher concentrations of sodium, calcium and magnesium. As part of a closure experiment cloud albedo calculated from in situ measurements was compared to that retrieved from the Advanced Very High Resolution Radiometer data for four years (1993-96). The nonlinear relationships between the cloud microphysical/optical properties and the sulfate content imply the existence of an optimum level for the sulfate concentration that would affect cloud albedo.

In terms of the direct forcing effect, wintertime forcing obtained for an internal mixture of sulfate and soot aerosols is much lower than that obtained during summer, due to reduced sulfate concentrations in winter. A quantitative measure of the direct forcing indicates higher magnitudes both for summer and winter than is obtained from previous modeling results. Analyses of the direct and indirect radiative forcing effect of sulfates for the southeastern U.S. indicate that the negative forcing effect is of greater magnitude than is predicted by modeling results. Thus, reduction in sulfate emissions would have a significant impact on climate for the southeastern U.S.

ROLE OF SULFATES IN REGIONAL CLOUD-CLIMATE INTERACTIONS

by

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BIOGRAPHY

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1. RADIATIVE FORCING DUE TO ANTHROPOGENIC AEROSOLS

1.1 Introduction

Anthropogenic aerosols perturb the radiation field sufficiently to warrant their inclusion in any climate forcing calculations. These particles are composed of various chemical species, mainly sulfates (from SO_2), organic matter (from gaseous precursors and biomass combustion), elemental carbon (from fuel combustion), ammonium (from biological sources and fertilizers) and some nitrate (from nitrogen oxides, NO_x) (Penner et al., 1994). The scattering and absorption of visible radiation by aerosols change the planetary albedo (the direct effect), thereby affecting the forcing of the earth-atmosphere system. The indirect forcing mechanism by anthropogenic aerosols has been thought to be comparable though of opposite sign to that caused by anthropogenic CO_2 (Charlson et al., 1987; 1992). Soluble anthropogenic aerosols can act as cloud condensation nuclei (CCN). The concentration of CCN along with other variables such as the updraft velocity, available water in the cloud, supersaturation, etc., determine the number of cloud droplets that can form which in turn is related to the cloud optical depth (τ) and cloud reflectivity. Increasing CCN concentrations at constant liquid water content (LWC) resulting in decreasing cloud droplet sizes, could also act to suppress drizzle production, and increase fractional cloudiness (Albrecht, 1989). For example, Albrecht (1989) deduced that an increase in low cloud cover by 4% would result in an increase in global albedo by 0.02 similar to the change in reflectivity associated with a 30% increase

in CCN concentration as estimated by Charlson et al. (1987). Therefore, due to this cloud-mediated effect, the radiation balance of the earth-atmosphere system is modified.

Aerosol particles are mainly found in industrial regions and in areas of biomass burning. Thus, they are non-uniformly distributed over the globe. Changes in emissions will have a greater effect on the concentration of tropospheric aerosols than on the concentrations of greenhouse gases (IPCC, 1995). This is because of the difference in the residence time of tropospheric aerosols, which is of the order of a few weeks, whereas, the residence time of greenhouse gases ranges from decades to centuries. Due to the spatial and temporal heterogeneity in the distribution of aerosols, the observed aerosol effects are expected to be mostly regional. The global average direct radiative forcing due to sulfates has been calculated by various modeling studies to be around -0.6 to -1.5 W m^{-2} and is estimated to be uncertain by a factor of 2 (Charlson et al., 1991, Kiehl and Briegleb, 1993, Boucher and Anderson, 1995). However, quantification of the indirect forcing is still under debate due to the large uncertainty in the relationship between aerosol number distribution and anthropogenic pollution (Chuang et al., 1997). Studies that estimate the contribution of sulfates to indirect radiative forcing usually use empirical observations and coupled chemistry-climate models to relate the sulfate mass concentration to sulfate aerosol concentration (e.g., Jones et al., 1994, Boucher and Lohmann, 1995). The estimates obtained from these studies range from -1.0 to -1.3 W m^{-2} for the global average. Hansen et al. (1993) gave a global mean forcing of -0.25 W m^{-2} using the same sulfate distribution, but accounted for some aerosol absorption. Taylor and Penner (1994) obtained a value of -0.9 W m^{-2} for global mean forcing due to

anthropogenic sulfate aerosols, using a coupled sulfur chemistry and climate model. The exact value of the negative forcing caused by sulfate aerosols cannot be calculated with confidence due to inadequate knowledge of their sources and geographical distribution. Thus, the magnitude of a global-mean forcing is still unresolved due to the fundamentally different nature of the two forcing mechanisms, both spatially and temporally.

Kiehl and Briegleb (1993) observed that major changes in radiative forcing from sulfate aerosols and greenhouse gases are more pronounced over eastern USA, central Europe and eastern China. The effect of sulfate aerosols on temperature and cloud reflectivity can be most easily observed in these areas (IPCC, 1995; NRC, 1996). On a regional scale, the eastern parts of the U.S. should undergo a cooling trend, if any, which would result from increasing cloud reflectivity and manifest itself in surface temperature records. In an analysis of the annual mean maximum temperature at 52 stations in the Southeast, Saxena et al. (1997) have shown a decrease in temperature of ~ -0.28 C during the period 1949-94 (46 years). In their analysis of surface-air temperatures in the United States for 1910-87, Dettinger et al. (1995) indicated a cooling trend for the southeastern region and long-term warming for the southwestern U.S. Over a continental landmass, high concentrations of CCN have a direct effect on cloud albedo and, by inference, produce an important cooling perturbation on regional climate. Although the relationship between cloud albedo and CCN has not yet been fully established theoretically, direct impact of CCN on cloud albedos have been reported by Coakley et al. (1987) when they analyzed ship exhausts and the cloud reflectances. Radke et al. (1989) found that enhanced reflectances in the 0.63 and 3.7 μm channels observed over ship tracks

accounted for increased cloud droplet concentrations and smaller cloud droplets in ship tracks. The effect of anthropogenic CCN on cloud radiative properties was also found in satellite observations of marine stratocumulus clouds modified by emissions from ships. Longitudinal variations of cloud albedos using monthly averaged results of observations from Earth Radiation Budget Experiment (ERBE) observations have been shown for two polluted ocean areas in the Northern Hemisphere and compared to those of remote clean areas in the Southern Hemisphere by Kim and Cess (1993). Their study implied a decrease in cloud albedo with distance from the continent for the Northern Hemisphere whereas the Southern Hemisphere showed no such link.

Recent literature suggests that carbonaceous and other non-sulfate aerosols are also significant and comparable to sulfate aerosols in terms of climate forcing, although parallel organic and sulfate measurements are extremely limited (Penner, 1995). Sulfates are known to dominate aerosols in the eastern U.S., whereas in the western U.S., organic aerosol concentrations are greater or equal to sulfate concentrations (Penner, 1995). Carbonaceous aerosols may enhance warming, whereas, hygroscopic aerosol may counteract it. Thus, the monitoring of carbonaceous aerosols is necessary in order to investigate its effect on cloud albedo properties.

The scientific community has recognized the potential importance of the indirect effect of aerosols on radiative forcing and has sought to reduce the uncertainty in determining this effect. Due to complexities involved in quantifying this effect, a new initiative has been launched recently by the National Aeronautical and Space Administration (NASA) to provide a quantitative assessment of radiative forcing caused

by atmospheric aerosols during the 20 year period of satellite observations. This would include a link between satellites, models and in situ and surface data. The results presented in this study would aid such efforts to resolve the aerosol forcing effect in terms of the regional observations and relationships that are obtained between aerosol chemical, physical and optical properties and aerosol-cloud interaction.

1.2 Objectives of this study

The main objective of this investigation is to obtain an estimate of the magnitude of the direct and indirect climatic effect of aerosols – primarily sulfates and black carbon – on a regional scale in the Southeast. This is accomplished by analyzing the role of aerosols with particular emphasis on the effect of sulfate-rich aerosols on cloud microphysical properties and on the optical properties both in cloudy skies and in cloud-free skies from data taken at a remote mountain top site. Back trajectory analysis of the air masses is used to identify the sources of the air masses classified as polluted continental, continental and marine. Thus, it is possible to delineate the aerosol effect in continental and marine air masses.

Surface based measurements of cloud and aerosol (microphysical, chemical and optical) properties obtained at a site in the southeastern U.S. that is climatically significant in terms of radiative forcing is used to provide detailed information that will provide a sensitivity of climate to aerosol properties.

Direct forcing effect of aerosols:

- 1) Aerosol mass concentration, size distribution, chemical composition and optical properties are used in a column forcing model to determine the magnitude of the direct forcing effect.
- 2) The competing effect of soot and sulfate aerosols is analyzed to determine the critical value of the single scatter albedo that changes the sign of the forcing from a negative to a positive forcing.

Indirect forcing effect of aerosols:

In situ data are used to study the following:

- 1) Aerosol concentration, chemical composition and size distribution as a function of the source of the cloud forming air mass,
- 2) Sensitivity of cloud droplet number, droplet radius, liquid water content and cloud condensation nuclei concentration to the chemical composition in the air mass,
- 3) Chemical heterogeneity in cloud droplets to observe the variations in the chemical composition of small and large drops and its effect on cloud droplet spectra (Sulfate production rates are usually calculated using cloud water pH obtained from bulk samples that do not differentiate between large and small drops. However, due to the chemical heterogeneity in cloud droplets, acidity variations between large and small drops can have a significant impact on in-cloud sulfate production rates.),
- 4) Sensitivity of cloud optical depth and cloud albedo to the cloud microphysical parameters and sulfate content,

- 5) Comparison of cloud reflectance retrieved from the Advanced Very High Resolution Radiometer (AVHRR) data to cloud albedo calculated from measurements at Mt. Mitchell since 1993 as part of a closure study to assess the confidence level with which the in situ data can be used to obtain cloud albedo.

Measurements obtained from the field study conducted at Mt. Mitchell are used to establish a relationship between cloud water chemistry and the microphysical characteristics of clouds. Results from this field study are used to conduct sensitivity tests, which yield quantitative information used to assess the role of aerosols in climate forcing. This will aid in answering some of the questions raised on climate forcing by aerosols, answers that can be incorporated into climate models.

From the data obtained during these field experiments, case studies have been compiled and are described in chapters.

- 1) Chapter 2 gives a description of the effect of chemical composition and cloud microphysics on the cloud albedo. The cloud albedo was calculated from in situ observations and compared to that retrieved from the Advanced Very High Resolution Radiometer (AVHRR) data as part of a “local closure” study.
- 2) Chapter 3 describes the effect of sulfate content in different air masses (polluted continental, continental and marine) on N , R_{eff} , CCN spectrum, cloud optical depth and cloud albedo from four years of data. A comparison of the empirical relationships obtained from the field study with those used by climate models is used to obtain an estimate of the indirect forcing due to sulfates for the southeastern U.S.

- 3) Chapter 4 describes in detail the results from the 1995 field experiment. The role of sulfates in light scattering, the relationship between CCN and sulfate content, sensitivity of optical depth to N , R_{eff} and cloud liquid water path (LWP) and the sensitivity of cloud albedo retrieved from satellite data to the sulfate content and N are analyzed.
- 4) Chapter 5 includes an analysis of the chemical heterogeneity in small, large and bulk droplets and its relation to cloud droplet size distribution for continental and marine air masses.
- 5) Chapter 6 compares the cloud microphysical and chemical properties that were obtained by means of empirical relationships in the southeastern U.S. to those obtained in the northeastern U.S. This is used to highlight the dominant role played by sulfates in modifying the cloud properties and climate for the southeastern U.S.
- 6) Chapter 7 describes the results for the direct radiative forcing derived from a column forcing model using mass concentrations of sulfate and soot aerosols. It also describes the interaction between the chemical, physical and optical properties of aerosols.
- 7) Chapter 8 suggests the directions for future work in the field of aerosol forcing.

1.3 Results of this study

In terms of the direct forcing effect of aerosols, the values of the direct forcing obtained are -0.91 , -1.34 and -1.81 W m^{-2} for wintertime sulfate aerosols and $+0.08$, $+0.09$ and $+0.13 \text{ W m}^{-2}$ for soot aerosols for marine, continental and polluted continental

air masses, respectively. Thus, the presence of an internal mixture of soot and sulfate aerosols reduces the negative forcing due to sulfates. The reduced values for the direct forcing are -0.32 , -0.55 and -0.66 W m^{-2} for marine, continental and polluted continental air masses, respectively. Summer time values for the negative forcing due to sulfates range from -2 to -20 W m^{-2} . These values are much higher than those found during winter due to the higher sulfate concentrations during summer daytime conditions. The addition of soot resulted in a lower reduction in the sulfate forcing than was found for winter cases. Thus, even though sulfate is the dominant chemical species from all the chemical species identified, the presence of other species can affect the microphysical and radiative properties of clouds. In order to investigate variations of acidity between cloud droplets of different sizes as predicted in models, chemical inhomogeneity between cloud droplets of different sizes is analyzed. On average, smaller drops are enriched in SO_4^{2-} , NO_3^- , NH_4^+ and H^+ , whereas, larger droplets have higher values of Na^+ , Ca^{2+} , Mg^{2+} . However, samples were collected where the reverse was true. Droplets with higher Na^+ and Cl^- are usually associated with marine air masses and those with higher sulfates and nitrates are usually from the polluted continental sectors, indicating the transport of aerosols from different sectors to the Mt. Mitchell site. Acidity variations in cloud droplets suggest that droplet growth time is an important factor that determines if smaller drops are more acidic than larger drops and vice versa. Climate models that determine the indirect forcing effect usually relate droplet number concentration with the sulfate contents that are obtained from bulk samples. Accounting for the solute differences in

large and small droplets and its relation with cloud droplet size distribution, may either lead to an overestimation or underestimation of the indirect radiative forcing estimate.

In order to investigate the indirect forcing effect of aerosols, the effect of sulfate concentrations on cloud microphysical properties such as LWC, CCN concentration, N and R_{eff} was investigated. A linear relationship between CCN and N is obtained for low CCN concentrations. At higher CCN concentrations the relationship was more non linear, due to smaller number of CCN that grow to a size large enough to be activated as the peak supersaturations are lowered at high CCN concentrations. Almost 75% of the CCN are composed of sulfate. The lesser polluted air masses exhibit greater changes in CCN concentrations for smaller increases in sulfate mass concentrations as compared to the more polluted air masses. The trend in sulfate concentration since 1986 indicates greater increases during 1993-97 as compared to 1986-89. Differences in cloud droplet size from marine to polluted continental air masses are greater during 1993-97, suggesting greater atmospheric cooling (smaller droplets scatter more efficiently). Comparison of the differences in R_{eff} from marine to polluted continental air masses to the modeling results from Slingo (1990) suggest that these differences in R_{eff} due to the pollutant content in the air mass could help offset the warming due to greenhouse gases on a regional scale. The slope of the regression relationship between N and sulfate indicates the sensitivity of N to the sulfate content. The comparison of this slope with those obtained by modeling studies that determine the indirect effect suggests that the negative forcing effect of sulfates for the southeastern U.S. is greater than -4.0 W m^{-2} obtained by other modeling studies.

Sensitivity tests for cloud optical depth indicate that the liquid water path (LWP) and the effective radius of cloud droplets play a key role in determining the optical depth. The cloud albedo calculated from in situ measurements compared well with that retrieved from the Advanced Very High Resolution Radiometer (AVHRR) data for four years (1993-96) with a correlation coefficient of ~ 0.91 . Cloud albedo retrieved from satellite data and that calculated from surface observations, does not indicate a continual increase in cloud albedo with increasing sulfate content in the air mass. Cloud dynamical factors besides the microphysical parameters play an important role in determining the cloud albedo. The nonlinear relationships between the cloud microphysical/optical properties and the sulfate content of the air mass implies the existence of an upper level for the sulfate concentration that affects cloud reflectivity, as suggested by Wigley (1991).

Analyses of the direct and indirect radiative forcing effects of sulfates for the southeastern U.S. indicate that the negative forcing effect of sulfate aerosols is of greater magnitude than is predicted by modeling results. The reduction in sulfate emissions will have a significant effect on regional climate for the southeastern U.S. Thus, measures taken to control sulfate emissions must be carefully evaluated in view of its important climatic effects on a regional scale.

1.4 Importance of this study

Clouds are the most important variables that determine changes in the radiation balance of the earth-atmosphere system. To reduce the uncertainties in remotely sensed cloud properties, theoretical and empirical validation becomes necessary. Much of the

prior work at Mt. Mitchell was concentrated towards resolving the climatic effects of aerosols via its interaction with cloud properties and the ecological consequences of climate change on natural and/or human-influenced systems. Ground-based observations from the Mt. Mitchell site can be used to provide important validation to satellite measurements at a site that is climatically significant in terms of aerosol radiative forcing. In particular, validation of remotely sensed cloud properties such as effective size of cloud droplets, cloud optical depth and cloud reflectances can be assessed for errors by comparing these properties to those measured at our site. In addition to these cloud properties, the empirical relations between cloud microphysical, chemical and optical properties can be used to evaluate model parameterizations. This is important in view of the large uncertainty in quantifying the indirect effect and the necessity for comparing model predictions with observations as expressed by the scientific community.

Long-term ground-based measurements provide information that is not readily obtained from airborne measurements. Schwartz and Slingo (1996) have expressed a necessity for information of this kind. Because of the continuity of our measurements at a strategic location in the Southeast, which has been established as the region most affected by aerosols, our results will contribute to the upcoming IPCC assessment of the aerosol impact on regional climate. In addition, the analyses of the data sets will provide an improvement in our basic understanding of the fundamental factors that affect the regional environment. Regional variability in the aerosol forcing demand that observations of aerosols and its climatic impact be monitored on a continuous basis on a regional scale at strategic locations. Improvisation in model parameterizations would

greatly enhance the understanding of aerosol-cloud-climate interactions and the processes that affect this relationship. If reasonable climate change predictions are attainable on a regional basis, a better understanding can be obtained as to the causes of climate change due to anthropogenic influence.

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2. PHYSICO-CHEMICAL MEASUREMENTS TO INVESTIGATE REGIONAL CLOUD-CLIMATE FEEDBACK MECHANISMS

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2.1 Abstract

On a regional scale, cloud-climate feedback mechanisms are investigated by analyzing the impact of anthropogenic sulfur emissions on the microstructure and short-wave albedo of clouds formed at a mountain-top location and simultaneously observing these clouds by AVHRR (Advance Very High Resolution Radiometer) aboard the NOAA (National Oceanographic and Atmospheric Administration) satellites. Cloud droplet number concentrations (CDNC) and ionic composition of cloud water are measured in situ along with meteorological parameters. The thickness of the overlying clouds and the 48 h back-trajectories of air masses are determined from on site measurements and Hybrid Single Particle Lagrangian Integrated Trajectory (HY-SPLIT) model. In general, more acidic clouds were found to have smaller effective radii of droplets but larger CDNC. The short-wave albedo of clouds determined from in situ measurements decreased with an increase in the cloud water pH, which was largely affected by the sulfate concentration in the cloud forming air mass. For six coincidental cloud events, the AVHRR retrieved cloud albedo (channel 1, wavelength = 0.63 μm) agreed well with those determined from in situ microphysical measurements, the correlation coefficient being 0.95. These findings indicate that the sulfate contents of air masses are capable of influencing cloud-climate feedback mechanisms by changing the albedo of thin, continental clouds.

2.2 Introduction

Aerosols are implicated (IPCC, 1994) to produce indirect radiative forcing which alone could offset the greenhouse warming due to monotonous increase in greenhouse gases. Recent evidence points out (Leaitch et al., 1986; Pueschel et al., 1986; Leaitch et al., 1992; Kaufmann and Nakajima, 1993) that industrial emissions and biomass burning increase cloud condensation nuclei (CCN) and cloud droplet number concentrations (CDNC). Enhanced CDNC in marine clouds have been reported by Radke et al. (1989) due to effluents from ship tracks. They reported these clouds to have enhanced albedos relative to nearby uncontaminated clouds. Marine cloud albedos are highly sensitive to increases in CDNC (Platnick and Twomey, 1993; Taylor and McHaffie, 1993). Although these findings are significant, they do not help answer an important question raised by Wigley (1991): 'Could reducing fossil-fuel emissions cause global warming?'. Mostly burning of fossil fuels produces aerosols over land. An investigation of relationships between the sulfate content of an air mass, the microphysics of the ensuing continental cloud, and its albedo is needed. To this end, mountain top locations offer unusual and unique opportunities (see for example, Saxena et al., 1989; Saxena and Lin, 1990) because they are often immersed in thin clouds. For example, recent investigations from Whiteface Mountain, NY (Mohnen and Kadlecek, 1989); Mount Mitchell, NC (DeFelice and Saxena, 1994); Mount Areskutan, Sweden (e.g., Noone et al., 1990); Mount Rigi, Switzerland (e.g., Collett et al., 1993); and Mount Tsukuba, Japan (Akagawa and Okada, 1993) have produced valuable cloud microphysical data. Results from Cheeka Peak,

Washington (Anderson et al., 1994) have demonstrated complexity in establishing an unambiguous aerosol effect on CDNC.

The purpose of this paper is to present results from a field experiment conducted in Mount Mitchell (2,038 m MSL; 35°44'05" N, 82°17'15" W) State Park during 1993-94 aimed at establishing the relationship between cloud water acidity and effective radius of CDNC in thin clouds. For six cases, cloud albedos are determined from the AVHRR (Advanced Very High Resolution Radiometer) aboard the NOAA (National Oceanographic and Atmospheric Administration) satellites. These albedos are compared with the ones determined from coincidental *in situ* microphysical measurements.

2.3 Experimental Procedure

2.3.1 Experimental Site and Instrumentation

The site is located in the Mount Mitchell State Park, North Carolina, on Mount Gibbs, which is ~ 3.3 km southwest of Mount Mitchell. It consists of a 17.1-m walkup tower equipped with temperature, pressure, wind speed, wind direction, and humidity instruments, which provide continuous measurements near its top. A rotatable carriage, positioned on the tower's northern face, carries an ASRC (Atmospheric Science Research Center, Albany, New York) passive string collector (e.g., DeFelice and Saxena, 1990a; Kadlec et al., 1983), and a Particle Measuring System (PMS) forward-scattering spectrometer probe (FSSP) (Knollenberg, 1981) from the ground to as high as a meter above its top.

All cloud-water samples were obtained on an hourly basis using the ASRC collector, which is situated about 17.6 m above ground level (AGL). Cloud-droplet sizes were measured using the FSSP, which is situated just below the ASRC collector. The FSSP was calibrated in the field before and after each event, and at the beginning and at the end of each field season (15 May - 15 Aug) by PMS. The liquid water content (wl) was simultaneously obtained using the FSSP, ASRC, and a gravimetric device (Valente et al., 1989) during the study. The pH of the sample cloud water was immediately measured after collection and the cloudwater sample was subsequently prepared and refrigerated for later ionic analysis via ion chromatography. A cloud was designated and the measurements commenced when the visibility was reduced to 1 km for a continuous 15 minute period.

Backward air parcel trajectories were computed for each cloud event, ending at the time of the NOAA satellite passes. Nested Grid Model (NGM) data was used for three-dimensional boundary-layer trajectory runs. The Hybrid Single Particle Lagrangian Integrated Trajectory (HY-SPLIT) model (Draxler, 1992) was used for back-trajectory calculation as well as to compute representative soundings over the Mt. Mitchell site. The lifting condensation level (LCL) was found on a representative sounding by following the procedure given by Walcek and Taylor (1986). This method has previously been successfully applied to orographic clouds at Mount Mitchell by DeFelice and Saxena (1990b). The cloud thickness above the mountain top was estimated from the sounding diagrams. The cloud top was identified as that point in the sounding where the departure between dewpoint and ambient temperatures did not exceed 5C. The accuracy

of these trajectories, like all computed trajectories, is limited (Draxler, 1987; Draxler and Stunder, 1988) and depends on a variety of factors including wind field resolution, the type of computational scheme used, and the associated synoptic-scale meteorological conditions.

2.3.2 Calculation of in situ Cloud Albedo

From the data-set, the impact of the sulfate content of cloud water on cloud albedo was calculated. The FSSP measurements provide $CDNC(\text{cm}^{-3})$, cloud liquid water concentration ($w_l(\text{g m}^{-3})$) integrated over droplet size distribution, and effective cloud droplet radius ($r_e(\mu\text{m})$). The $CDNC$ is defined as

$$CDNC = \int n(r)dr \quad (2.1)$$

where $n(r)$ is the droplet size distribution and r is the droplet radius. The effective cloud droplet radius is defined as

$$r_e = \frac{\int r^3 n(r)dr}{\int r^2 n(r)dr}. \quad (2.2)$$

The liquid water content can be expressed as

$$w_l = \frac{4}{3} \pi \rho_w r^3 CDNC \quad (2.3)$$

where ρ_w is the density of water (1000 kg m^{-3}). From determining the cloud depth $H(\text{m})$ from sounding, knowing $CDNC$ and w_l , the optical depth of cloud (τ) is calculated as follows (Twomey, 1977),

$$\tau = H \left\{ 4.5 \pi \text{CDNC} \rho_w^{-2} \right\}^{1/3} \quad (2.4)$$

The albedo (A in %) may be evaluated using the relationship (Lacis and Hansen, 1974)

$$A = \frac{\tau}{\tau + 7.7} \quad (2.5)$$

Equations (2.4) and (2.5) were used to calculate *in situ* albedo for cloud events occurring at Mt. Mitchell when the microphysical measurements were taken within 300 meters of the cloud top.

2.3.3 Cloud Reflectivity Based on AVHRR Data

The AVHRR data from the polar orbiting NOAA-11, NOAA-12, and NOAA-14 satellites provide the visible (Channel 1, $\lambda = 0.63 \mu\text{m}$), near-infrared (Channel 3, $\lambda = 3.7 \mu\text{m}$), and thermal infrared (Channel 4, $\lambda = 11 \mu\text{m}$) information for this study. Visible albedo information was derived by scaling the raw visible counts by solar zenith angle and applying an anisotropic low (water) cloud reflectance factor. To perform this derivation, it is necessary to assume an optically thick cloud such that direct transmittance through the cloud does not occur. Temperature information is derived directly from the Channel 4 data by applying the satellite-specific calibrations. Clouds act as blackbodies at this particular wavelength. Care was taken to exclude clouds that contained ice by examining the cloud top temperature determined from AVHRR Channel 4. To further reduce the errors encountered with inhomogeneous vertical stratification (Nakajima and King, 1990) all convective type cloud events were excluded. Only orographic stratiform clouds which formed in the vicinity of Mt. Mitchell were

considered. Our sampling site was within 300 m from the cloud tops. A total of six satellite passes coincident with in situ measurements are presented below for comparison of calculated and remotely sensed cloud albedos.

2.4 Results and Discussion

The results of observed cloud events for the summer of 1993 are listed in Table 2.1. The mean values for CDNC, r_{ave} , w_l , and pH are shown for each population. To investigate the dependence of pH on cloud microstructure, 136 cases with coincident pH and FSSP data were sorted into three populations: $pH < 3.1$ ($n = 33$), $3.1 < pH < 3.7$ ($n = 71$), and $pH > 3.7$ ($n = 32$) based on the available data. The table shows that lower pH values are associated, on average, with higher number concentrations and smaller average radii of cloud droplets. In contrast, higher pH values are associated, on average, with lower number concentrations and larger average radii. Figures 2.1a and 2.1b show the variation of cloud water acidity (pH) with the effective droplet radius (r_e), and CDNC. In general, the lower pH values are associated with smaller r_e and larger CDNC. The correlation coefficients are 0.72 and -0.75 respectively.

For a comparison of short-wave albedos determined from the AVHRR measurements and the ones computed from in situ microphysical measurements at the mountain top, only those cases were selected for which the following conditions were met: (a) daytime cloud episodes with high sun angle, (b) non-precipitating and thin clouds, (c) cloud episodes which occurred coincident with the NOAA satellite 10 and 11 passes, and (d) clouds formed in air masses which had variable sulfate contents.

The results are given in Table 2.2. It can be seen that samples include cloud forming air masses with large variations in sulfate content. We use cloud water pH as an indicator for the pollution content of the cloud forming air masses. The concentrations of SO_4^{2-} and NO_3^- which are the dominant ionic species present, are higher in the low pH cases compared with the high pH cases. In all cases AVHRR measured albedos agree with the ones calculated from in situ measurements.

It is evident from Table 2.2 and Fig. 2.1c that lower cloud water pH which is associated with higher CDNC, resulting from increased sulfate content of the cloud forming air mass, leads to higher short-wave albedo. An increase in cloud droplet effective radius (Fig. 2.1a), usually associated with a decrease in sulfate content of the air mass, leads to a lower CDNC (Fig. 2.1b), and a decrease in cloud albedo. In general, effective radius (r_e) decreases as CDNC increases in conformity with the expected trend. The correlation coefficient between the cloud water pH and short-wave albedo derived from in situ measurements is -0.70.

In Fig. 2.2 are plotted short-wave cloud albedos, derived from in situ measurements (see Table 2.2), against those determined from channel one (wavelength $\lambda = 0.63 \mu\text{m}$) measurements of AVHRR. The correlation coefficient between these two is 0.95. The uncertainties in both are shown plotted in Fig. 2.2 and listed in Table 2.2. The agreement is good in spite of the fact that the depth of the overlying cloud above the mountain top varied by a factor of 3 (range: 88-276 m ACL) and the liquid water content varied by a factor of 3.7 (range: $0.07\text{-}0.26 \text{ g m}^{-3}$) for the six cloud events.

As is evident from Eq. (2.4), the optical thickness (τ) is directly proportional to the cloud thickness and varies as $(\text{CDNC})^{1/3}$. In Table 2.2, there are three cases with similar cloud thicknesses namely, cases of 19 Aug 93, 29 May 94, and 24 Jul 94. It can be seen that τ is almost identical for cloud events of 29 May 94 and 24 Jul 94 for which the liquid water content (w_l) and CDNC are similar. The case of 19 Aug 93 is the exception because w_l and CDNC are higher by a factor of two or more as compared with the other two cases. This difference is reflected in the in situ albedos.

For the remaining three cloud events in Table 2.2 (14 Jun 93, 19 Jun 93, 21 Jul 94), the optical thickness is within 6% in spite of large variations in CDNC which will be explained below as resulting from different air mass trajectories. The variation in τ is not so apparent because of the larger contribution of the thickness of the overlying cloud which ranged from 148-276 m AGL. In Table 2.3 are listed pH and ionic composition of the cloud water for the six cloud events. The pH is evaluated as: $\text{pH} = \log [1/\text{H}^+]$. The principal ions in the cloud water are: SO_4^{2-} , NO_3^- , NH_4^+ and H^+ . The sulfate accounts for a large fraction of cloud water acidity. The highest H^+ concentration is associated with the largest CDNC in general conformity with the trend shown in Fig. 2.1b.

In order to analyze the direct relationships between the sulfate content of the cloud forming air mass and the cloud albedo, four cases with contrasting physical and chemical properties were selected. These are discussed below. In Fig. 2.3 are shown 48 h back trajectories of air masses for these cases.

2.4.1 *June 14, 1993 vs. July 21, 1994*

It can be seen from Fig. 2.3 that the air mass leading to the cloud event on June 14, 1993 was contained close to the Mt. Mitchell site in the preceding 48 hours. Wind speeds were relatively low, and the air mass lingers over the Knoxville, TN urban area. In contrast, for the July 21, 1994 case, the air mass producing the cloud event at the site was maritime. By referring to Tables 2.2 and 2.3, we can deduce the following about the June 14 and July 21 cases. The June 14 case formed in a highly polluted continental air mass. The result is an optically thick ($\tau = 11$), highly reflective cloud. The AVHRR measured albedo for this cloud is 60%, and the albedo calculated from Eqs. (2.4) and (2.5) is 58%. The July 21 case, in contrast, formed in a much less polluted air mass. Sulfate concentration is down by 37% but nitrate concentration is roughly the same as compared with the June 14 case. The satellite picture (not shown) indicates the presence of convective activity at this time. The difference in CDNC and r_e is as much as 93% and 52% respectively. This confirms that the sulfate content of the air mass is crucial in determining the cloud microstructure and its reflectivity.

2.4.2 *August 19, 1993 vs. July 24, 1994*

The air masses of August 19 and July 24 are characterized by long back trajectories indicating limited residence times over industrial areas. The August 19 air mass traveled further northward over the Ohio River Valley receiving a taint of urban pollution. The July 24 cloud formed in a continental air mass and has a very low sulfate content. This is evident from Table 2.3, which shows the $\text{SO}_4^{=}$ content is ten times larger

for Aug 19, 1993. These factors result in an optically thick ($\tau = 6$), more reflective cloud for the event of August 19. The retrieved AVHRR albedo on August 19 is 35% and the calculated albedo is 43%. The July 24 case (see Fig. 2.3), has a very low AVHRR retrieved albedo of 22% and the calculated albedo of 24% from in situ measurements.

The results of the case studies indicate higher concentrations of sulfate lead to higher cloud droplet number concentrations. Since the clouds formed at our experimental site are moisture limited, the droplet radius ranged from 2.56 μm to 5.79 μm . The above four cloud events demonstrate that the cloud albedo depends upon the sulfate content of the air mass. A statistical composite of the results from a significant number of cases is needed to improve our confidence in the above findings. It must be pointed out that since orographic clouds have larger supersaturations, larger fractions of the sulfate aerosol forms cloud droplets.

2.5 Concluding Remarks

We have presented above the results of a "local closure" field study in which the retrieved AVHRR albedos of thin (88-276 m AGL), mountain-top clouds were compared with those determined from in situ microphysical measurements. The clouds formed in marine, continental, and continental/polluted air masses were investigated. Although during the summer field seasons (15 May - 15 Aug) of 1993 and 1994, we investigated 99 cloud episodes during which 944 cloud water samples were collected hourly, the results of our analysis of only six cloud events are presented above. The data analysis is not only very labor intensive, but also requires that several conditions be satisfied for

coincidental occurrence of satellite passes over the site, and cloud formation as mentioned in Section 3 above. In addition, the presence of cirrus clouds in the vicinity of the experiment site could produce artificially elevated values of cloud reflectivity and should be avoided. The cloud events, reported here, have satisfied all these conditions.

The following conclusions result from this study:

- The effective radius of cloud droplet size distribution is related to the cloud water acidity. The smaller the effective radius, the more acidic is the cloud water.
- The cloud water acidity may be considered as an indicator of the sulfate content of the air masses which form clouds at the site. Larger cloud droplet number concentrations (CDNC) are associated with more acidic clouds.
- The cloud albedo determined from in situ measurements increases as the cloud becomes more acidic. The correlation coefficient between the cloud water pH and albedo is -0.70.
- The albedo of six cloud events retrieved from AVHRR measurements (channel one, wavelength of $0.63\ \mu\text{m}$) agreed well with those determined from in situ microphysical measurements, the correlation coefficient being 0.95.

The above findings indicate that on a regional scale, the anthropogenic sulfur emissions are capable of altering the reflectivities of thin, continental clouds and this constitutes one of the significant cloud-climate feedback mechanisms.

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Table 2.1. Average microphysical values for three case populations grouped by pH. On average, pH is associated with low droplet concentration and large average radius, and vice versa. Liquid water content is essentially constant across populations.

	pH < 3.0	3.0 < pH < 3.7	pH > 3.7
Number of cases	18	71	24
pH range	2.51 – 2.99	3.01 – 3.68	3.74 – 4.74
Average pH	2.86 ± 0.03	3.28 ± 0.02	3.98 ± 0.04
CDNC (cm^{-3})	793 ± 36	589 ± 21	282 ± 22
Rave (μm)	3.35 ± 0.14	3.77 ± 0.08	4.99 ± 0.24
w_l (g m^{-3})	0.29 ± 0.03	0.29 ± 0.01	0.30 ± 0.02

Table 2.2. Relevant cloud characteristics and derived albedos for six cases coincident with AVHRR satellite retrievals.

Event date	CDNC (cm^{-3})	R_e (μm)	w_l (g m^{-3})	H (m)	τ	Albedo (%)	
						AVHRR	In situ
14 Jun, 1993	823 ± 150	2.88 ± 0.57	0.18 ± 0.03	148 ± 20	10.8 ± 1.5	60 ± 10	58.1 ± 3.4
19 Jun, 1993	218 ± 160	4.51 ± 0.92	0.19 ± 0.04	238 ± 51	11.5 ± 2.4	70 ± 5	59.3 ± 5.2
19 Aug, 1993	613 ± 100	3.36 ± 0.83	0.15 ± 0.03	105 ± 5	6.1 ± 0.3	35 ± 5	44.4 ± 1.1
29 May, 1994	237 ± 91	2.56 ± 0.80	0.09 ± 0.01	88 ± 3	2.7 ± 1.0	25 ± 3	26.3 ± 0.6
21 Jul, 1994	54 ± 15	5.79 ± 0.44	0.26 ± 0.05	276 ± 23	11.1 ± 0.9	56.5 ± 6.5	59 ± 2.1
24 Jul, 1994	231 ± 91	3.33 ± 0.90	0.07 ± 0.01	101 ± 10	2.5 ± 0.3	22 ± 6	24 ± 2.0

Table 2.3. Cloud chemical characteristics for six cases. Units for the chemical species are in $\mu\text{eq l}^{-1}$

Event	pH	Cl^-	NO_3^-	$\text{SO}_4^{=}$	H^+	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	Σ anions	Σ cations	Σ ions	difference
14 Jun, 93	2.84	31.88	40.73	664.2	1445	155.6	26.05	7.77	20.91	12.18	736.8	1668	2405	931.2
18 Jun, 93	3.77	39.21	24.76	162.1	169.8	73.22	51.59	6.98	23.35	13.74	226.1	338.7	564.8	112.7
19 Aug, 93	2.97	38.87	107.11	1110	1071.5	218.3	3.91	2.48	30.79	9.54	1256	1336	2593	80.37
29 May, 94	3.42	420.8	113.10	742.3	380.2	291.6	154.8	15.32	82.80	105.3	1276	1030	2306	-246.1
21 Jul, 94	3.47	15.74	41.06	419.5	338.9	88.83	6.39	2.05	8.23	3.90	476.3	448.2	924.6	-28.07
24 Jul, 94	2.92	8.00	8.00	105.0	1202	25.50	6.00	2.70	7.10	1.20	121.0	1245	1366	1124

Figure 2.1. Cloud water acidity (pH) vs coincident effective cloud droplet radius (R_e) (a), cloud water acidity (pH) vs coincident cloud droplet number concentration (CDNC) (b), and calculated cloud albedo (%) vs coincident cloud water acidity (pH) (c). The solid line represents the corresponding regression line for two cloud characteristics determined from in situ measurements

Figure 2.2. Albedo determined from in situ measurements vs coincident AVHRR albedo (channel 1, $\lambda = 0.63 \mu\text{m}$). The error bars are indicated. The solid line represents the direct one-to-one correspondence (correlation coefficient = 0.95) between the two independently derived albedos.

Figure 2.3. Air mass back trajectories for two highly reflective and two less reflective cloud events. The trajectories go back for 48 hrs.

3. ROLE OF SULFATES IN REGIONAL CLOUD-CLIMATE INTERACTIONS

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3.1 Abstract

During the summers of 1993-96, field experiments were conducted at Mt. Mitchell, North Carolina, in the southeastern U.S. The effect of anthropogenic pollution on cloud microphysical properties such as liquid water content (ω), cloud droplet number concentration (N), effective radii (R_{eff}), cloud condensation nuclei (CCN) activation spectrum and cloud reflectivity were investigated. Cloud water sulfate concentration was used as a measure of anthropogenic pollution. Back-trajectory analysis was used to categorize the cloud forming air masses that arrived at the site. The sulfates and nitrates emission inventories of the U.S. Environmental Protection Agency (EPA) were used to classify air masses as polluted marine (PM), polluted continental (PC) or as highly polluted (HP). Empirical values for the relationships between CCN- N , CCN-sulfate, N -sulfate and R_{eff} - N for different air masses have been obtained. A quantitative nonlinear relationship between CCN and N was obtained. The lesser polluted air masses exhibited greater changes in CCN concentrations for smaller increases in sulfate mass concentrations as compared to the more polluted air masses. The relationship between R_{eff} and N for different air masses, as well as the N -sulfate mass relationship, suggested that the counteracting effect of sulfates on greenhouse warming for the southeastern U.S. would be of magnitude greater than -4.0 W m^{-2} obtained by modeling studies. The nonlinear relationships between the cloud microphysical/optical properties and the sulfate content of the air mass implies the existence of an optimum level for the sulfate concentration beyond which cloud reflectivity stays unaffected. Analysis of three years of observational data established this level at $400\text{-}500 \mu\text{eq l}^{-1}$ of sulfate in the cloud water.

3.2 Introduction

During the past few years considerable attention has been focused on the cloud-mediated effect of aerosols on radiative forcing, due to the complexity involved in understanding the indirect effect as compared to the direct effect. Most estimates on the radiative forcing caused by tropospheric aerosols are made using modeling studies rather than observations of the distribution of aerosols and their optical properties (IPCC, 1994). The major causes of uncertainty in obtaining a quantitative estimate of the indirect forcing arise due to inadequate knowledge of the interaction between aerosol particles and cloud microphysical properties, as well as the temporal and spatial variability of aerosol and cloud distribution. Observational data that are related to the monitoring of the distribution of aerosol concentrations and cloud microphysical properties are unfortunately limited.

The indirect effect, also called the “Twomey effect”, arises due to changes in cloud condensation nuclei (CCN) concentrations which affect the cloud droplet number concentration (N). This in turn changes the optical depth (τ) of thin stratus clouds through the relationship $\tau \propto (N)^{1/3}$, thereby affecting its reflectivity. If the liquid water content in the cloud is unchanged, an increase in CCN concentration will result in smaller cloud droplet sizes, which would actually suppress drizzle production and increase fractional cloudiness (Albretch (1989). Albretch (1989) deduces that an increase in low cloud cover by 4% would result in an increase in global albedo by 0.02 similar to the change in reflectivity associated with a 30% increase in CCN concentration as estimated by Charlson et al. (1987). The effect of CCN on cloud albedos have already been

demonstrated in ship tracks by Coakley et al. (1987) through satellite observations, but sufficient evidence on regional and continental scale is still lacking.

The sensitivity of the energy balance to cloud albedo needs to be fully understood in order to obtain a realistic estimate of the indirect contribution. The debate concerning the magnitude of the contribution of both the direct and indirect effect of aerosols on radiative forcing still remains unresolved. Kiehl and Briegleb (1993) observed that changes in radiative forcing from sulfate aerosols and greenhouse gases are more pronounced over eastern USA, central Europe and eastern China, thus making the eastern USA a favorable site to monitor the effects of sulfates.

We have used measurements of CCN activation spectra, cloud liquid water content (ω), N , cloud droplet effective radii (R_{eff}) and the chemical composition of cloud water to study the effect of anthropogenic pollution on the microphysical properties of thin, non precipitating clouds at a remote mountain-top location in the southeastern U.S. Cloud water sulfate was used as an index of anthropogenic pollution. Cloud reflectivity was calculated based on cloud microphysical measurements to study the effect of sulfates on cloud radiative properties. In view of the sensitivity of cloud optical depth to N , we report here a quantitative relationship between CCN and N . This relationship would help assess the contribution of anthropogenic aerosols to modifications in the resultant cloud microphysical properties, which in turn affect the cloud radiative properties. Thus, first order estimates of the indirect climatic effect of sulfates can be obtained through empirical relationships between the variables determined from in situ measurements.

3.3 Methodology

3.3.1 Field Study Description

The experimental site is located in the Mount Mitchell (2038 m msl, at 35°44'05"N and 82°17'15"W) State Park on Mount Gibbs, North Carolina in the southeastern U.S. Continuous measurements of meteorological variables such as temperature, pressure, wind speed, wind direction and humidity are provided by means of instruments that are located atop a 17.1-m walk-up tower. The type of clouds formed for cloud events that are less than 8 h in duration are usually those due to orographic lifting. Cloud events that last for more than 8 h usually has clouds that form from frontal passages (Saxena and Lin, 1990). A passive string-type cloud water collector as described by Kadlecik et al. (1983) and a Particle Measuring System (PMS) Forward-Scattering Spectrometer Probe (FSSP) as described by Saxena et al. (1989); and Saxena and Lin (1990) are located on the tower's northern face, atop an elevator. Cloud water samples are obtained on an hourly basis using the passive string-type cloud water collector.

The sources of the cloud forming air masses were analyzed from their back trajectories obtained from the Hybrid Single Particle Lagrangian Integrated Trajectory (HY-SPLIT) model. The accuracy of these trajectories, like all computed trajectories, is limited as observed by Draxler (1987); and Draxler and Stunder (1988) and depend on a variety of factors including wind field resolution, the type of computational scheme used and the associated synoptic-scale meteorological conditions. The air masses that were identified from the back trajectory analysis were classified as highly polluted (HP),

polluted marine (PM) and polluted continental (PC) based on the SO_x and NO_x emission inventories obtained from the U.S. Environmental Protection Agency (EPA). Accordingly, the continental U.S. is divided into three sectors with the HP sector located between 290° and 65° azimuth relative to Mt. Mitchell, the PM sector between 65° and 210° and the PC sector between 210° and 290° . Deininger and Saxena (1997) have validated the back trajectories of the air masses that arrived at the site based on the principal component analysis of ionic concentrations found in cloud water. Ulman and Saxena (1997) have provided a detailed analysis of the dependence of cloud water pH upon the wind sector in which the cloud forming air mass originated.

3.3.2 Instrumentation

Cloud droplet sizes were measured using the FSSP located just below the passive string-type cloud water collector. The alignment of the optical measurement sensor is checked after every cloud event by recording the spectra that result when glass beads of varying sizes are introduced and is calibrated if the alignment is not proper. Before and after every field season the FSSP is factory calibrated. The cloud water collector is manually operated on an hourly basis upon the occurrence of a cloud event. Before and after every cloud event, the collector is cleaned by spraying distilled, deionized water on the collection strands to remove traces of chemicals that may have been present from previous sampling. The collector is enclosed in a clean bag after use to avoid contamination by dry aerosol impaction on the collection surfaces. The collected cloud water was used to calculate ω in terms of mass per unit volume. The pH of the cloud

water was measured immediately after collection and the cloud water sample was subsequently prepared and refrigerated for later ionic analysis via ion chromatography. The pH of a standard buffer solution was also measured at the same time as a check to ensure that the measured pH was accurate within 0.02 unit. A cloud was designated and the measurements commenced when the visibility was reduced to 1 km for a continuous 15 minute period.

The CCN spectrometer described by Fukuta and Saxena (1979 a,b) was operated from a shed located about 8 m to the north east of the tower. Its inlet is an inverted funnel (0.1 m diameter) that extends 0.5 m outwards and whose opening is 2 m above the top of the shed. The opening of the funnel is oriented perpendicular to the airflow past it. The spectrometer provides a continuous measurement of the CCN number concentration as a function of the supersaturations encountered during cloud formation as described by DeFelice and Saxena (1994).

3.4 Results and Discussion

3.4.1 Relationship between cloud condensation nuclei and cloud droplet number concentration

We present results obtained during a four year period between 1993 and 1996. In order to provide experimental evidence for the “Twomey effect”, establishing a relationship between CCN and N would be of importance. The CCN activation spectra were recorded for two years, 1995 and 1996. The CCN concentrations taken an hour prior to the cloud event are considered to be an indicator of the aerosols that would

activate as cloud droplets. The updraft in the clouds, mixing between the cloud and its environment and the ability of the particle to act as CCN determine the relationship between aerosol concentrations and cloud droplet concentrations as described by Pruppacher and Klett (1978). Back trajectory analyses for every hour as well as changes in wind direction during and prior to the cloud event were used to decipher a change in the source of the cloud forming air mass.

The cloud droplet concentration plotted as a function of CCN concentration (at 1% supersaturation) is shown in Fig. 3.1. As CCN concentrations increase the number of cloud droplets must also increase. The contribution of anthropogenic aerosols to modifications in the resultant droplet concentration has been investigated by previous researchers. A linear relationship between CCN and N was observed by Twomey and Warner (1967). However, Raga and Jonas (1993) reported that the sensitivity of cloud droplet concentration to aerosol particle concentration was much lower. Baker and Charlson (1990) and Ackerman et al. (1993, 1994) using models investigated the relationship between aerosol production rate (defined as the production rate of water-soluble particles that are large enough to nucleate cloud droplets at supersaturations found typically in clouds) and droplet concentration for marine stratus clouds. Both modeling studies indicate a strong dependence of CCN concentrations on the source strength. The Baker and Charlson (1990) model indicated a substantially large increase in droplet number concentration for an increase in particle production rate beyond $0.004 \text{ cm}^{-3} \text{ s}^{-1}$. Even a small fraction of anthropogenic aerosol production could be of significance over clean oceans as suggested by Toon (1994).

Jones et al. (1994) relate the aerosol concentration (A_{CB}) measured by a Passive Cavity Aerosol Spectrometer Probe (PCASP) below cloud base, to the cloud droplets that form on the aerosols which act as CCN by means of an exponential equation expressed as;

$$N = 375 (1 - \exp [-2.5 \times 10^{-3} A_{CB}]) \quad (3.1)$$

This equation is based on aircraft data obtained from a wide range of locations from Martin et al. (1994). They measured the CCN concentration with a thermal gradient diffusion chamber described by Saxena et al. (1970). The difference in CCN concentration and A_{CB} was found to be mainly dependent on the chemical composition of the air mass. For maritime air masses all the A_{CB} measured were found to be good CCN, but for continental air masses the A_{CB} was much higher than the CCN concentration.

Combining experimental data for the two years from our study, a logarithmic relationship between CCN and N is obtained and is given as;

$$N = 62.3 (\pm 0.024) \times \ln \text{CCN} - 192 (\pm 71) \quad (3.2)$$

with a correlation coefficient of 0.71. The difference in N obtained by using Eq. (3.1) versus that using Eq. (3.2) would approximately average to a 30% reduction in N if we assume that the concentration of CCN is the same as that of the A_{CB} . This reduction was for CCN ranging between 100 and 3000 cm^{-3} , with the maximum difference lying in the range between 500 and 1500 cm^{-3} . Although some differences do exist between the two equations, the basic underlying idea that arises from these equations is the non-linearity between A_{CB} , CCN and N.

The experimental data indicate that a linear relationship between CCN and N can be expected for lower values of CCN concentrations, but for high CCN concentrations, the increase in N may not be linear. This is not surprising since the chemical composition of the CCN, role of the updraft and vapor consumption by previously activated drops play a role in determining the number of particles that would get activated to form cloud droplets. Leaitch et al. (1986) report results where they found that N increases proportionally with the available CCN at low concentrations. However, for heavily polluted cases with weak convection, the supersaturation gets lowered due to the increased aerosols and vapor consumption thereby lowering the number of nuclei that get activated. Thus, increasing CCN in regions of high concentrations would have no effect on drop size distributions as is also indicated by our experimental observations. This suggests that the sensitivity of cloud reflectivity to N would be lowered for large increases in CCN concentrations. Our data suggest a qualitative non-linear relationship between CCN concentration and N that would have an affect on the cloud optical depth.

3.4.2 Relationship between cloud condensation nuclei and sulfate mass concentration

The slope of the regression line between the CCN concentration at a given supersaturation to the sulfate concentration gives the sulfate nucleation efficiency (Hegg et al., 1993). The 1995 data set resulted in a sulfate nucleation efficiency of $\sim 75 \text{ cm}^{-3} \text{ m}^3 \mu\text{g}^{-1}$ and indicated that 80% of the CCN were sulfate derived (obtained as the product of the sulfate nucleation efficiency and the ratio of the mean sulfate to the mean CCN concentration). Since most of the CCN are sulfate derived, one can expect a good

correlation between sulfate concentrations and CCN concentrations. Assuming that the cloud water sulfate concentration is the same as that of the sulfate mass concentration in the air mass, the sulfate mass concentration in mass per unit volume can be derived using the equation from Lin and Saxena (1991) as;

$$[SO_4^{=}]_{\text{air mass}} = [SO_4^{=}]_{\text{cloud water}} * \omega / \rho_w \quad (3.3)$$

where ρ_w is the density of liquid water.

This equation will hold for the entire cloud event if we assume that the sulfate concentration is conserved. The equation breaks down if the air mass varies with time during the event or if the entire sulfate is not incorporated into cloud droplets (Lin and Saxena, 1991). Leaitch et al. (1986) investigated the relationship between cloud water $[SO_4^{=}]$ and aerosol $[SO_4^{=}]$ and found an average cloud scavenging ratio for $[SO_4^{=}]$ to be ~ 73%. Hegg and Hobbs (1983) in their observations on scavenging of aerosol sulfates $[SO_4^{=}]$ in cloud water for moderate convective clouds, found an average of ~ 63% of aerosol sulfate that got incorporated in cloud water based on 12 cases. Using this relationship, the optimum effect of sulfates on CCN can be investigated for different air masses.

The relationship between CCN concentration at 1% supersaturation and sulfate mass concentrations for the 1996 data set is depicted in Fig. 3.2 for different air masses. For a 32% increase in the sulfate mass concentration, the CCN concentration increases by 57% as one goes from the PM to the PC sector, whereas, for a 76% increase in sulfate mass concentration, the corresponding increase in CCN concentration is only 25% as one goes from the PC to the HP sector. This implies the existence of an upper limit for the

sulfate mass concentration for which a linear increase in CCN concentration can be expected for a given range of CCN concentration and sulfate mass concentration.

Hegg (1994) tried to develop a functional relationship between CCN and sulfate mass concentration from four different data sets taken at different locations. He found the regional variability to be important for the individual data sets. To produce a 30% change in CCN concentration that would be of climatic importance, the sulfate mass should change by 76% for the entire data base that he considered. This is comparable to the values we obtained for the 25% change in the CCN concentration as one goes from the PC to the HP sectors. However, the change in the air mass from the PM to the PC sector indicated that a much smaller change in the sulfate mass could significantly alter the CCN concentration.

The susceptibility of the cleaner air mass to the sulfate concentration is fairly evident. Hegg (1994) further suggests that the sensitivity of the cloud albedo to changes in the sulfate concentration would be further reduced as compared to that for a similar fractional change in CCN concentration. The effect of cloud water sulfate on N and cloud albedo from experimental measurements would indicate such a reduction in the sensitivity, if it exists.

3.4.3 Relationship between cloud droplet number concentration and sulfate mass concentration

A large fraction of atmospheric sulfate stays on a time-averaged basis as solute in cloud droplets. This is due to the dominance of sulfate formation within clouds (Möller

1994). Principal component analysis of cloud water samples collected at the site indicated that sulfuric acid and nitric acid were most influential in cloud forming air masses from the HP sector, whereas, for the PM sector, sea salt particles were more abundant (Deininger and Saxena, 1997). Black carbon is a more suitable indicator of the degree of anthropogenic influence. Preliminary results of measurements of black carbon mass concentrations collected at the site indicated that higher black carbon mass concentrations were closely associated with high concentrations of cloud water sulfate which were usually from the HP sector. Here we use cloud water sulfate concentration as an indicator of anthropogenic pollution. Figure 3.3 shows the cloud water sulfate concentration as a function of the cloud water pH for the four years. The average correlation coefficient for the four years is 0.86. The concentration of sulfates in cloud water were found to be higher than that of other ionic species such as NH_4^+ , Cl^- , NO_3^- and salts of sodium, potassium, magnesium and calcium that were present in small amounts in the cloud water.

In order to obtain an estimate of the magnitude of the indirect effect, Boucher and Lohmann (1995) related N (obtained from empirical results) and the cloud optical properties (obtained from two general circulation models) to the sulfate aerosol mass concentration derived from a chemical transport model. They found the magnitude of the indirect effect ($\sim -1 \text{ W m}^{-2}$) to be similar to that of the direct effect but with larger uncertainties. The value obtained is dependent on the assumed relationship between sulfate aerosol mass and N , and is sensitive to the distinction between maritime and continental clouds. As an example we combined data from 1993 and 1996 since they

contained cloud forming air masses from all three sectors as opposed to 1995 which had very high values of sulfate mass concentrations from the HP sectors and did not have any PM cases.

The relationship between the logarithm of N as a function of the logarithm of sulfate mass is indicated in Fig. 3.4. The equations for N and sulfate mass concentrations are as follows:

$$\log_{10} [N]_{PM} = 0.49 (\pm 0.08) \log_{10} [m_s] + 2.29 (\pm 0.39) \quad (3.4)$$

$$\log_{10} [N]_{PC} = 0.52 (\pm 0.12) \log_{10} [m_s] + 2.15 (\pm 0.40) \quad (3.5)$$

$$\log_{10} [N]_{HP} = 0.47 (\pm 0.13) \log_{10} [m_s] + 2.33 (\pm 0.23) \quad (3.6)$$

with a mean regression line for all data sets given as;

$$\log_{10} [N] = 0.54 (\pm 0.09) \log_{10} [m_s] + 2.21 (\pm 0.39) \quad (3.7)$$

where m_s is the sulfate mass in $\mu\text{g m}^{-3}$ and N is in cm^{-3} .

Equation (3.7) is very similar to that obtained by Boucher and Lohmann (1995) that represents both maritime and continental clouds and is given as;

$$\log_{10} [N] = 0.41 \log_{10} [m_s] + 2.21 \quad (3.8)$$

The normalized shortwave indirect radiative forcing obtained by Boucher and Lohmann (1995) by using Eq. (3.8) is about -1.7 W m^{-2} for the entire Northern Hemisphere with the southeastern parts of the U.S. exhibiting a forcing of less than -4.0 W m^{-2} which is in agreement with the results of Jones et al. (1994). The higher value of the slope in Eq. (3.7) as compared to Eq. (3.8) indicates that the counteracting effect of aerosols on greenhouse warming in the southeastern U.S. would be higher than the estimated value of -4.0 W m^{-2} , as calculated by Boucher and Lohmann (1995). This is

inferred from the minimum and maximum values of the slopes that they obtained from the relationships between N and sulfate mass for various cloud types. Jones et al. (1994) used Eq. (3.1) in their calculations for estimating the indirect effect and obtained a value of -1.54 W m^{-2} for the Northern Hemisphere. They also used a log-log relationship between N and A_{CB} and cloud water sulfate concentrations from Leaitch et al. (1992), and obtained a value of -1.25 W m^{-2} for the indirect effect.

3.4.4 Relationship between cloud droplet effective radii and cloud droplet number concentration

Slingo (1990) investigated the effect of changes in low clouds to the earth's radiation budget. He used three different versions of the NCAR (National Center for Atmospheric Research, Boulder, CO) Community Climate Model (CCM) to model the changes that must take place in the low cloud amount, the cloud liquid water path (LWP) and R_{eff} in order to balance the forcing caused by doubling the carbon dioxide concentration. Results from the model suggest that for an assumed cloud droplet R_{eff} of $10 \mu\text{m}$, the R_{eff} must decrease by 21% for low clouds with a LWP of 50 g m^{-2} . Assuming $N \propto R_{eff}^{-3}$, for fixed LWP the increase in N must be between 60% and 102%. Table 3.1 indicates average values of sulfate concentration, N and R_{eff} for the three years from our study for cloud forming air masses from the HP, PC and PM sectors. The ratios of R_{eff} and N obtained for polluted and relatively cleaner air masses from our study were compared to experimental results from Leaitch et al. (1992) and modeling results from

Slingo (1990). These results indicate the fraction by which R_{eff} and N must be multiplied in order to counteract the forcing from the doubling of carbon dioxide.

Leaitch et al. (1992) observed that pollution increase over eastern North America was sufficient to offset the warming caused by the doubling of carbon dioxide. The values we obtained for changes in R_{eff} for the three different sectors lead us to similar conclusions, although the increases in N are not always as high as would be necessary to offset the warming effect. Han et al. (1994) found the effective radius to be a more sensitive indicator of anthropogenic influence. Previous analysis at the same site indicated that the optical depth was most sensitive to the LWP and R_{eff} and was more susceptible to changes in R_{eff} for lower acidity in cloud water as compared to more acidic cloud water.

On a regional scale, the southeastern parts of the U.S. should undergo a cooling trend if any, which would result from increases in cloud reflectivity and manifest itself in surface temperature records, for the observed high values of the sulfate concentrations. In the analysis of the arithmetic average annual mean maximum temperature at 52 stations in the southeastern U.S., Saxena et al. (1997) have shown a decrease in temperature of ~ -0.28 C during the period 1949-94 (46 years). Dettinger et al. (1995) in their analysis of surface-air temperatures in the United States for 1910-87 indicated a cooling trend for the southeastern region and long-term warming for the southwestern U.S.

3.4.5 Relationship between cloud albedo calculated from in situ observations and cloud water sulfate concentration

Saxena et al. (1996) have shown that the indirect or cloud-mediated effect of sulfate aerosols exists in the southeastern U.S. by analyzing the changes in cloud albedo that resulted from varying sulfate contents. Cloud albedo was calculated from in situ measurements and compared to satellite retrievals obtained from the Advanced Very High Resolution Radiometer (AVHRR) data as part of a “local closure” experiment. The reflectivity of thin continental clouds was found to be modified due to the effect of sulfates. Prior investigations had led to good correlation between satellite retrieved cloud albedo and in situ calculations. Since comparison of satellite and in situ calculations are very strenuous and limited in the number of cases that can be obtained, we use cloud albedo calculated from in situ measurements as a function of the cloud water sulfate concentration in the present study.

The data from three years (1993, 95, 96) were used. Two different ω intervals were chosen for $0.15 < \omega < 0.3 \text{ g m}^{-3}$ and for $0.3 < \omega < 0.5 \text{ g m}^{-3}$. The cloud thickness for all cases were between 100 and 300 m. The τ is calculated as shown by Twomey (1977),

$$\tau = H \{ 4.5\pi N(\omega)^2 \rho^{-2} \}^{\frac{1}{3}} \quad (3.9)$$

where the density (ρ) of liquid water is 1000 kg m^{-3} and the cloud thickness H in meters is obtained from the HY-SPLIT sounding. The albedo (A) can then be evaluated using the relationship (Lacis and Hansen, 1974),

$$A = \frac{\tau}{\tau + 7.7} \quad (3.10)$$

Figure 3.5 is for ω between 0.15 and 0.3 g m^{-3} , whereas, Fig. 3.6 is for ω between 0.3 and 0.5 g m^{-3} . Figure 3.5 suggests that reflectivity increases with sulfate

concentrations for lower values of sulfate concentrations. At higher sulfate concentrations, (beyond $400 \mu\text{eq l}^{-1}$) it almost stays constant, though the degree of correlation for the relationship between the two is not as good. This saturation in reflectivity implies that increasing sulfate emissions may not necessarily counteract the greenhouse warming, as the cloud reflectivity is only sensitive to low sulfate concentrations. Figure 3.6 also indicates that for higher ω values at high sulfate contents (beyond $400\text{-}500 \mu\text{eq l}^{-1}$), the reflectivity of the cloud reaches the saturation point.

However, at high sulfate contents beyond $1000 \mu\text{eq l}^{-1}$, an average decrease in reflectivity by almost 21% was noticed for three cases which are not shown in Fig. 3.6. The effect of varying solar zenith angle on these cases needs to be considered to investigate the cases more fully. Multiple scattering could cause the reflectivity to reach saturation as suggested by Bohren (1987), however the decrease in reflectivity could be due to the role of absorption particles such as black carbon (BC) particles and requires further investigation. As the soot volume fraction increases, cloud reflectivity was found to decrease in a series of modeling experiments conducted by Chylk et al. (1984). They found the effect to be more pronounced at visible wavelengths. Ambient BC aerosols were found to exhibit hygroscopic properties based on data taken by Hansen and Novakov (1989) in California. They found 80% of fresh urban ambient carbonaceous aerosol got incorporated into marine fog with lower percentages incorporated at higher total BC mass concentrations. The liquid water supply was found to be the limiting factor for this lower incorporation.

Our results from a three year data set indicate that for low ω values, an increase in reflectivity with increasing droplet concentrations is not found. However, at higher ω 's, the decrease in reflectivity observed at high sulfate concentrations could possibly be due to the competing effects of sulfates with other absorptive species. Thus, this suggests that there could be an upper limit to the effect that sulfates would have in increasing cloud reflectivity.

3.5 Climatic Importance

Higher SO_2 emissions in the Northern Hemisphere as compared to the Southern Hemisphere could lead to temperature differences between the two hemispheres, if caused by aerosols. An attempt was made by Schwartz (1988) to discern such interhemispheric differences, but none was found. Wigley (1991) suggested that this would place an upper limit on the magnitude of forcing related to anthropogenic SO_2 . This upper limit is quite evident for sulfate concentration, based on the analysis of our experimental results. Jones et al. (1994) suggest that reduction in sulfur emissions may lead to reductions in both the direct and indirect effect which would actually lead to an enhancement of greenhouse-gas warming. However, the magnitude of the indirect effect is dependent on the susceptibility of clouds to changes in aerosol concentrations. Therefore, it is quite obvious that any major change in cloud susceptibility and forcing would take place for less polluted clouds.

Twomey (1991) defined absolute cloud susceptibility (dA/dN) as the change that takes place in cloud albedo for a given change in N . Accordingly,

$$\frac{dA}{dN} = \frac{1}{3 \times N} [A(1 - A)] \quad (3.11)$$

where the two stream approximation for the cloud albedo was evaluated as;

$$A = \frac{\tau(1 - g)}{2 + \tau(1 - g)} \quad (3.12)$$

with g the asymmetry parameter for single scattering taken as 0.85 for droplets with radii greater than the wavelength of visible light, and τ is given as;

$$\tau = 2\pi \overline{r^2} N H \quad (3.13)$$

Figure 3.7 shows susceptibility of cloud albedo to N calculated from the 1995 data set as well as model simulations obtained from Taylor and McHaffie (1994). Taylor and McHaffie (1994) calculated susceptibility using the expression;

$$\frac{dA}{dN} = \frac{4\pi \rho_l}{9\omega} A (1 - A) k r_c^3 \quad (3.14)$$

where k is a constant which depends on the type of air mass. Experimental evidence indicates that susceptibility of cloud albedo would be greater for less polluted clouds, similar to simulations performed by Taylor and McHaffie. Hence, an upper limit for both N and sulfate concentration can be found which affects the increase in cloud reflectivity.

3.6 Concluding Remarks

Nonlinear relationships between CCN and N have been obtained which are similar to those used by Jones et al. (1994). The sublinear relationship between CCN and sulfate mass concentration suggests that susceptibility of cloud forming air masses to anthropogenic pollution would play a role in determining the response of the climate

system to changes in SO₂ emissions. The relationship between R_{eff} and N for different sulfate contents at the experimental site indicated that in the southeastern U.S. anthropogenic influences could already have offset any warming that could be expected from the doubling of CO₂. The empirical relationship between N and sulfate mass obtained from this study suggested that the counteracting effect of sulfate aerosols on greenhouse warming for the southeastern U.S. could be of magnitude higher than the -4.0 W m^{-2} estimated by modeling studies performed by Boucher and Lohmann (1995). A cooling effect was found to exist in surface temperature records for the southeastern U.S. that were analyzed by Saxena et al. (1997). Since the cooling effect has been reported in surface temperature records, the change in cloud reflectivity might have been partly responsible. Increases in cloud reflectivity from increasing sulfate content are significant at low sulfate contents (upto $400 \mu\text{eq l}^{-1}$) in cloud water. However at higher sulfate contents (beyond $400 \mu\text{eq l}^{-1}$), the reflectivity seems to reach saturation.

Other chemical species, such as nitrates as well as some other insoluble inorganics and organics have not been considered in this study, although it is quite possible that they would have some contribution to the indirect effect. There appears to be an upper limit to the sulfate concentration that changes the increase in cloud reflectivity and other cloud microphysical properties. Better estimates of this limit can be obtained by means of several such regional experimental studies. Monitoring the factors that contribute to the indirect effect must be made at few other locations so that an evaluation can be made on a global basis without involving too many approximations to reduce the uncertainty associated with the indirect effect. Due to the dominant role of

sulfate aerosols in the southeastern U.S. and its influence on cloud microphysical-radiative properties, monitoring the trends in sulfate concentrations needs to be continued. This is especially important in view of the expected decline in SO₂ emissions in eastern U.S. arising from the amendment of the Clean Air Act.

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3.7 References

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Table 3.1. Average values of cloud droplet number concentration (N), effective radii of droplets (R_{eff}) and cloud water sulfate concentration for 1993, 1994, 1995 and 1996. Comparison of MVR (Mean volume radius)/N with that from Leaitch et al., (1992) and R_{eff}/N from Slingo (1990) is shown. The ratios indicate the changes to be expected in N and R_{eff} to counteract the forcing due to doubling of CO_2 . Sources of cloud forming air masses are listed as polluted marine (PM), polluted continental (PC) and highly polluted (HP).

Source	$\text{SO}_4^{=}$ ($\mu\text{eq l}^{-1}$)				N (cm^{-3})				R_{eff} (μm)			
	1993	1994	1995	1996	1993	1994	1995	1996	1993	1994	1995	1996
PM	122	343	NA	94	333	234	NA	126	4.50	4.77	NA	5.01
PC	548	184	607	221	523	541	238	165	3.90	4.11	4.04	3.40
HP	1022	597	1996	422	594	754	286	166	3.03	3.15	3.90	2.67

Mt. Mitchell	R_{eff}/N			
	1993	1994	1995	1996
HP/PM	0.67/1.78	0.66/3.22	-	0.53/1.32
HP/PC	0.78/1.14	0.77/1.39	0.97/1.20	0.78/1.01
PC/PM	0.87/1.57	0.86/2.31	-	0.68/1.31

Leaitch	MVR/N	Slingo	R_{eff}/N
Stratiform	0.84/1.75	CCM1	0.79/2.02
Cumuliform	0.85/1.67	CCM2	0.85/1.65
		CCM3	0.83/1.72

Figure 3.1. Cloud droplet number concentration (N) from the FSSP cloud-droplet size distributions as a function of the cloud condensation nuclei (CCN) concentration (active at 1% supersaturation) for the 1995 and 1996 field seasons.

Figure 3.2. Average cloud condensation nuclei (CCN) concentration (active at 1% supersaturation) and average sulfate mass concentration as a function of different air masses for the 1996 field season.

Figure 3.3. Cloud water sulfate concentration as a function of cloud water pH for the four years from 1993 to 1996.

Figure 3.4. Logarithm of cloud droplet number concentration (N) from the FSSP cloud-droplet size distributions as a function of the logarithm of sulfate mass concentrations for air masses from the three different sectors. Data are from the 1993 and 1996 field seasons

Figure 3.5. Cloud albedo calculated from in situ measurements as a function of cloud water sulfate for liquid water content (ω) in the range between 0.15 and 0.3 g m^{-3} . Data is from the 1993, 1995 and 1996 field seasons.

Figure 3.6. Cloud albedo calculated from in situ measurements as a function of cloud water sulfate for liquid water content (ω) in the range between 0.3 and 0.5 g m^{-3} . Data is from the 1993, 1995 and 1996 field seasons.

Figure 3.7. Cloud droplet susceptibility calculated from in situ measurements as a function of cloud droplet number concentration (N). Comparison is made to model simulations taken from Taylor and Mc Haffie, (1994).

**4. OBSERVED EFFECTS OF SULFATES ON LIGHT SCATTERING,
CLOUD REFLECTIVITY AND CLOUD SUSCEPTIBILITY**

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4.1 Abstract

At a remote mountain top location in the southeastern U.S., measurements were made to estimate the contribution of sulfates in terms of its indirect radiative effects. The influence of long-range transport of anthropogenic emissions on cloud microphysical and optical properties at the mountaintop site was investigated. The sources of the cloud forming air masses were determined from back-trajectory analysis. Cloud water sulfate content was used as a surrogate for anthropogenic pollution. The relationship between the light scattering extinction coefficient and the sulfate content resulted in a sulfate-scattering efficiency of $6.0 \text{ m}^2 \text{ g}^{-1}$ at ambient relative humidity. The role of sulfates in changing the cloud condensation nuclei (CCN) concentration, cloud droplet number concentration (N), cloud droplet effective radii (R_{eff}) and cloud albedo was analyzed. The CCN-sulfate analysis indicated that most of the CCN were sulfate derived. The relationship between CCN and sulfate indicated a lowered sensitivity of CCN at high values of sulfate. Sensitivity tests for cloud optical depth indicated that it was most sensitive to R_{eff} and the liquid water path. Cloud albedo sensitivity to droplet concentration was found to be greater at lower values of cloud albedo. As part of a “closure experiment” we were able to compare the cloud albedo calculated from in situ measurements with that retrieved remotely from the Advanced Very High Resolution Radiometer (AVHRR) data. The cloud reflectivity retrieved from satellite was found to be dependent on the cloud water sulfate.

4.2 Introduction

The role of anthropogenic sulfate aerosols on both direct and indirect climatic effects is dependent on several parameters and has long been debated. A significant amount of short-wave radiation is backscattered by anthropogenic sulfur aerosols in cloud-free air and is referred to as the direct radiative forcing by sulfate aerosols. Through its effect on the activation spectrum of cloud condensation nuclei (CCN) and the consequent effect on cloud microphysics and cloud optical thickness (τ), anthropogenic sulfates modify the short-wave albedo of clouds and thereby, regional and global climate. This indirect radiative forcing mechanism by anthropogenic sulfate has been thought to be comparable though of opposite sign to that caused by the doubling of anthropogenic CO₂ [Charlson *et al.*, 1987; 1992]. Carbonaceous and other non-sulfate aerosols are also known to be important contributors to global climate change. However, there is still not enough data on the properties and distribution of these aerosols on a global scale to fully consider their climatic impact without much uncertainty.

Since anthropogenic SO₂ emissions are greater in the Northern Hemisphere than in the Southern Hemisphere, one would expect an increase in cloud albedo in the Northern Hemisphere due to both the direct and indirect radiative effect of sulfates. Kim and Cess [1993] investigated longitudinal variations of cloud albedos for two polluted ocean areas in the Northern Hemisphere with those of remote clean areas in the Southern Hemisphere and found a decrease in cloud albedo with distance from the continent for the Northern Hemisphere whereas no such link was found for the Southern Hemisphere. The forcing applied to the Northern Hemisphere will have an effect on the Southern

Hemisphere [IPCC, 1994] in terms of temperature. *Schwartz* [1988] attempted to discern such interhemispheric differences but no such indication was observed. However, *Dettinger et al.* [1995] in their analysis of surface-air temperatures in the United States for 1910-87, found a cooling trend for the southeastern region and long-term warming for the Southwest. This supports the findings of *Saxena et al.* [1997] which indicated a decrease of ~ -0.28 C in the average of annual mean maximum temperature at 52 stations in the southeastern U.S. (during the period 1949-94). Maximum negative forcing has been indicated for the southeastern U.S. by modeling studies [*Boucher and Lohmann*, 1995 and *Jones et al.*, 1994]. Thus, the forcing due to aerosols on a regional scale would be important in influencing regional climate.

Light scattering coefficient per unit mass of sulfate is thought to be a key parameter in establishing the role of sulfates in direct forcing [*Hegg et al.*, 1993]. The scattering of light is caused by submicron anthropogenic aerosols, produced in the atmosphere by chemical reactions of sulfur-, nitrogen-, and carbon-containing gases of which sulfur is predominant [*Charlson et al.*, 1992]. Cloud processed sulfate aerosols are known to be more efficient scatterers of light than the sulfate aerosols created only through gas-phase SO_2 oxidation [*Lelieveld and Heintzenberg*, 1992]. For background conditions, a value of $2\text{-}3 \text{ m}^2 \text{ g}^{-1}$ is usually used in climate models for the light scattering caused by sulfates [*Hegg et al.*, 1993] though, higher values are usually reported for the eastern U.S. [*Weiss et al.*, 1982]. *Waggoner et al.* [1976] obtained a mean value of $5 \text{ m}^2 \text{ g}^{-1}$ for the light scattering due to sulfates in their study located over southern Sweden.

Because of their chemical nature and size distributions, sulfate particles are known to be efficient CCN. Enhancement of CCN concentrations due to anthropogenic pollution can influence cloud radiative properties. The number of CCN that would be produced by a given amount of sulfate aerosol or the cloud drop nucleation efficiency of sulfates [Hegg *et al.*, 1993] would provide information as to the contribution of sulfates in modifying CCN concentrations and thereby, cloud microphysical properties. This is however dependent on factors such as regional location, supersaturation values, updraft speed, presence of chemical species other than sulfates, etc. Long-term measurements of cloud microphysical and chemical properties at remote sites can be used to infer trends in CCN concentrations and compositions [Hindman *et al.*, 1994] that can serve as inputs to cloud formation models. Since the indirect role of cloud forcing is most significant in the marine atmosphere, the variation in the cloud droplet nucleation efficiency of sulfates derived from different air masses is of importance.

Concurrent measurements of CCN, cloud droplet number concentration (N), cloud liquid water content (LWC), cloud water chemistry and light scattering extinction coefficient (b_{scat}) were obtained at a remote mountain top location in the southeastern U.S. during the summer of 1995. Cloud droplet effective radii (R_{eff}) were calculated from the drop-size distribution. Cloud optical depth (τ) and cloud albedo were calculated from in situ measurements and compared to the cloud albedo retrieved from the Advanced Very High Resolution Radiometer (AVHRR) data. Results from the observations presented in this study are used to analyze the sensitivity of above-mentioned cloud microphysical and optical properties to anthropogenic sulfate. Here, we

use cloud water sulfate as a surrogate for all anthropogenic species. The effect of differing air masses such as polluted continental, continental and marine on cloud properties will be taken into consideration. Thus, the regional climatic impact of sulfates for the Southeast can be analyzed from the results.

4.3 Methodology

4.3.1 Field Study Description

The experimental site is located on Mount Gibbs in the Mount Mitchell State Park (2038 m msl, at 35°44'05"N and 82°17'15"W), NC, in the southeastern U.S. The site is ideal for in situ cloud measurements as nearly seven out of ten days during the summer months have some kind of a cloud episode [Saxena *et al.*, 1989]. A 17.1-m walk-up tower equipped with temperature, pressure, wind speed, wind direction and humidity instruments provide continuous measurements. An elevator, positioned on the towers northern face, carries an Atmospheric Science Research Center passive string cloud water collector (ASRC) described by Kadlecek *et al.* [1983]. Cloud droplet size distribution was obtained by means of a Particle Measuring System (PMS) Forward Scattering Spectrometer Probe (FSSP) [Knollenberg, 1981] located below the cloud water collector. A cloud was designated and measurements commenced when visibility was reduced to 1 km for a continuous 15 minute period. The type of clouds formed for cloud events that are less than 8 h in duration are usually those due to orographic lifting. Cloud events that last for more than 8 h usually have clouds that are influenced by frontal passages [Saxena and Lin, 1990].

The sources of the cloud forming air masses were analyzed from their back trajectories obtained from the Hybrid Single Particle Lagrangian Integrated Trajectory (HY-SPLIT) model. The accuracy of these trajectories, like all computed trajectories, is limited [Draxler, 1987; Draxler and Stunder, 1988] and depends on a variety of factors including wind field resolution, the type of computational scheme used and the associated synoptic-scale meteorological conditions. The continental U.S. is divided into three sectors with the polluted continental (PC) sector located between 290° and 65° azimuth relative to Mt. Mitchell, the continental (C) sector between 210° and 290° and the marine (M) sector between 65° and 210°. This classification is based on the SO_x and NO_x emission inventory from the U.S. Environmental Protection Agency. *Deininger and Saxena* [1997] found sulfuric and nitric acid to be most influential in cloud forming air masses from the PC sector, whereas, for the M sector, sea salt particles were more abundant.

4.3.2 Instrumentation

The cloud droplet concentration measured from the FSSP is given as;

$$N = \int n(r)dr \quad (4.1)$$

where $n(r)$ is the number distribution for drops of radius r and dr is the droplet radius range. R_{eff} , the ratio of the moments of the drop-size distribution is given as;

$$R_{eff} = \frac{\int_0^{+\infty} r^3 n(r)dr}{\int_0^{+\infty} r^2 n(r)dr} \quad (4.2)$$

The FSSP was calibrated in the field before and after each cloud event, and at the beginning and at the end of each field season. Details of the calibration procedure can be obtained from *DeFelice and Saxena* [1994]. The cloud water collector is manually operated and cloud water samples are collected on an hourly basis upon the occurrence of a cloud event. The collector is cleaned by spraying distilled, deionized water on the collection strands before and after every cloud event, to remove traces of chemicals that may have been present from previous sampling. At the end of every cloud event the collector is enclosed in a clean bag to avoid contamination by dry aerosol impaction on the collection surfaces. The collected cloud water was used to calculate LWC in terms of mass per unit volume. The pH of the cloud water was immediately measured after collection and the cloud water sample was subsequently prepared and refrigerated for later ionic analysis via ion chromatography. The concentration of eight ionic species namely SO_4^{2-} , NO_3^- , NH_4^+ , Ca^{2+} , K^+ , Mg^{2+} , Na^+ and Cl^- were analyzed from each cloud water sample by means of ion chromatography (Cl^- , SO_4^{2-}), flow injection analysis (NO_3^- , NH_4^+) and ionically coupled plasma atomic emission spectroscopy (Ca^{2+} , K^+ , Mg^{2+} , Na^+). The pH of a standard buffer solution was also measured at the same time as a check to ensure that the measured pH was accurate within ± 0.04 units.

The CCN-Spectrometer [*Fukuta and Saxena*, 1979 a, b] was operated from a shed located about 8 m to the north east of the tower. Its air intake is an inverted funnel (0.1 m diameter) that extends 0.5 m out from and whose opening is 2 m above the top of the shed as well as the canopy. The opening of this funnel is oriented perpendicular to the airflow past it. The spectrometer provides a continuous measurement of the CCN

number concentration as a function of supersaturations as described by *DeFelice and Saxena* [1994]. Measured CCN activity spectra are expressed in the form

$$n = c S^k \quad (4.3)$$

where c and k are obtained empirically and n is the number of CCN per cm^3 that will be active at or below the supersaturation S (in %).

Light scattering extinction coefficient (b_{scat}) was measured using the Radiance Research M903 portable nephelometer that uses the geometry of a standard integrating nephelometer. The nephelometer was located at a shed about 50 m south of the tower, with an inlet above the canopy. The air Rayleigh scattering is directly calculated from pressure and temperature. The total scattering coefficient is converted to a light-scattering coefficient by subtracting the Rayleigh scattering. The nephelometer operates at 530 nm wavelength and measurements are obtained continuously every 15 minutes.

4.4 Sulfate-Scattering efficiency

Four consecutive days were selected from the 1995 (May-August) field season for analysis. The cases were chosen from the above four days for better coincidence of the measurements from the various instruments used. The air masses in which the cloud formed were continental. The measurements for b_{scat} were taken at the ambient relative humidity. The sulfate mass concentration in the cloud forming air mass ($[SO_4^-]$ air mass) in $\mu\text{g m}^{-3}$ can be obtained as;

$$[SO_4^-] \text{ air mass} = [SO_4^-] \text{ cloud water} * \text{LWC}/\rho_w \quad (4.4)$$

where ρ_w is the density of liquid water, assuming that all the sulfate concentration in the air mass is incorporated into cloud water [Lin and Saxena, 1991]. Leaitch *et al.* [1986] found an average cloud-scavenging ratio of $\sim 73\%$ for the relationship between cloud water $[SO_4^-]$ and aerosol $[SO_4^-]$. Hegg and Hobbs [1983] found an average of $\sim 63\%$ of sulfate aerosol was incorporated in cloud water from their observations on scavenging of sulfate aerosols in cloud water for moderate convective clouds. Here, we assume the entire sulfate in the air mass is incorporated in the cloud water in order to investigate the optimum effect of sulfates on light scattering and to avoid any assumption regarding the scavenging of sulfates.

The sulfate content in the cloud water during the first hour of the cloud event is used in Eq. (4.4) to estimate the sulfate mass concentration that would have been in the air mass just prior to the onset of the cloud event. The value for bscat ($\sim$ an hour prior to the cloud event) is correlated with the corresponding sulfate mass to illustrate the relationship between bscat and sulfate mass for the entire data set, as shown in Fig. 4.1. The regression equation is as given;

$$\text{bscat} = (6.0 \pm 0.6) [SO_4^-] + (5.0 \pm 1.2) \times 1.0E-05 \text{ m}^{-1} \quad (4.5)$$

with a correlation coefficient of 0.77. The slope of the regression line gives the sulfate-scattering efficiency, which in this case is $6.0 \pm 0.6 \text{ m}^2 \text{ g}^{-1}$. At a remote site in California, Lelieveld and Heintzenberg [1992] obtained values of the sulfate mass scattering coefficient for sulfates produced through cloud processing in the range of $5.8 \text{ m}^2 \text{ g}^{-1}$ to $7.8 \text{ m}^2 \text{ g}^{-1}$ that was dependent on the amount of sulfate present. Yuen *et al.*

[1994] report a range of sulfate-scattering efficiencies from previous investigators for sulfates produced through cloud processing to be between 3.7 to 7.8 m² g⁻¹ at ambient relative humidity.

The hygroscopic nature of anthropogenic aerosols as well as cloud dynamics would result in a large variability for the values obtained since the measurements were at ambient relative humidity. Though sulfates have been found to be the dominant contributor to cloud water acidity, the covariance of sulfates with other submicron particles such as nitrates, soot and organics (depending on the source of cloud forming air mass) is important and must be considered. The relationship between different aerosol mass concentrations and light scattering would provide a better estimate of the sulfate-scattering efficiency. Thus, the sulfate scattering efficiency that was obtained would best serve as a first order estimate of the effect of sulfates on light scattering at ambient relative humidity for background conditions in the Southeast.

4.5 CCN-Sulfate analysis

An important issue for indirect forcing is the sensitivity of cloud albedo to CCN or N, which is in turn related to the aerosol concentration. The CCN concentration at 1% supersaturation plotted as a function of the sulfate mass is indicated in Fig. 4.2. The regression equation for the best fit line is as given;

$$\text{CCN} = (60.4 \pm 10.6) [\text{SO}_4^-] + (129 \pm 95.8) \text{ cm}^{-3} \quad (4.6)$$

with a correlation coefficient of 0.78. The sulfate nucleation efficiency given in terms of the slope is $\sim 60 \text{ cm}^{-3} \text{ m}^3 \mu\text{g}^{-1}$. The finite value of the intercept indicates that not all

CCN were sulfate derived, for the linear relationship assumed. The sources of the air masses were C for all except five cases that were a mix of PC and C/PC air masses (air masses that traversed through both the continental and polluted continental sectors are labeled as C/PC). The sulfate mass ranged from ~ 8 to $30 \mu\text{g m}^{-3}$ and CCN concentrations ranged from 1100 to 1800 cm^{-3} for the PC and C/PC cases, whereas, the C cases had 1.5 to $7 \mu\text{g m}^{-3}$ for sulfate mass and between 130 to 900 cm^{-3} for CCN concentrations. Hegg [1994] obtained different slopes for the CCN-sulfate mass regression relationships for data taken at four different locations such as the NE Pacific, W. Washington, NE Atlantic and Virginia Coast ranging from 0.1 to $117 \text{ cm}^{-3} \text{ m}^3 \mu\text{g}^{-1}$. Thus, the regional variability of the slope and the decreasing values of the slope with increasing sulfate concentrations imply that a non-linear relationship might be more realistic [Hegg, 1994].

The relationship between CCN and sulfate determined from our empirical results would best serve as an indicator of the potential sulfate nucleation efficiency for the southeastern U.S. At high CCN concentrations, as more droplets compete for the same available water, the supersaturation gets lowered, thereby lowering the number of nuclei that would get activated. Hence, the supersaturation, available liquid water in the cloud, as well as cloud dynamics would give rise to the nonlinearity between CCN and sulfate concentration. The non-zero intercept for the regression between CCN and sulfate suggest that the other aerosols such as organics, that have not been measured at the site during 1995, could also act as potential CCN. Organics are known to account for a major

part of both total aerosol number concentration and the CCN fraction [Novakov and Penner, 1993].

Changes in the average values of sulfate, CCN, N and R_{eff} for PC and C type air masses for all the measurements obtained during the 1995 field season are listed in Table 4.1. No marine air masses were sampled during the observational period. Relatively high concentrations of CCN and sulfate were obtained for PC type air masses in conformity with the previous findings of the enhancement of CCN concentrations due to anthropogenic emissions [Twomey *et al.*, 1978, Hudson, 1991]. However, the PC type air masses had only slightly higher values of N and smaller R_{eff} as compared to the C type air masses with higher standard deviations indicating a high variability in the FSSP measurements. Changes in the dynamical conditions for the cloud events encountered could also cause fluctuations in the droplet size spectrum.

Analyses of data obtained from four previous years at Mt. Mitchell (1993-96), have indicated that changes in R_{eff} for M type cases as compared to PC type cases were sufficient to counteract the forcing due to the doubling of CO_2 [Menon and Saxena, 1998]. Earlier results from cloud microphysical and chemical measurements at the same experimental site indicated that varying sulfate contents in cloud water were related to changes in N which ultimately lead to changes in cloud optical depths and thereby, cloud albedos [Saxena *et al.*, 1996]. The non-linearity in CCN-sulfate implies a reduced sensitivity of cloud albedo to anthropogenic aerosols that is investigated in the following sections.

4.6 Cloud Albedo Susceptibility

Twomey [1991] defined cloud albedo susceptibility as the sensitivity of the cloud albedo to the change in the corresponding droplet concentration, assuming LWC does not change. Accordingly, cloud albedo susceptibility is given as;

$$\frac{dA}{dN} = \frac{\partial A}{\partial \tau} \frac{d\tau}{dN} + \frac{\partial A}{\partial \varpi_0} \frac{d\varpi_0}{dN} + \frac{\partial A}{\partial g} \frac{dg}{dN} \quad (4.7)$$

Here, g the asymmetry parameter for single scattering is taken as 0.85 for droplets with radii greater than the wavelength of visible light, $\varpi_0 = 1$ for the special case of conservative scattering and $\tau \propto N^{1/3}$ for an optically thin cloud. Eq. (4.7) can then be approximated as;

$$\frac{dA}{dN} = \frac{1}{3 \times N} [A(1 - A)] \quad (4.8)$$

where the two stream approximation for the cloud albedo was evaluated as;

$$A = \frac{\tau(1 - g)}{2 + \tau(1 - g)} \quad (4.9)$$

and τ is given as;

$$\tau = 2\pi \overline{r^2} NH \quad (4.10)$$

The cloud thickness (H) is obtained from the soundings using the HY-SPLIT model and is calculated as given in *Saxena et al.* [1996]. The sensitivity of cloud albedo to logarithmic changes in N for fixed LWC and cloud thickness can be approximated [*Schwartz and Slingo*, 1996] as;

$$\Delta A|_{LWC, H} = \frac{1}{3} [A(1 - A)] \Delta \ln(N) \quad (4.11)$$

Substituting, Eq.'s (4.9) and (4.10) in Eq. (4.11) and taking the derivative of A w.r.t. N results in the following equation;

$$\frac{dA}{dN} = C_1 \overline{r^2} \quad (4.12)$$

For field data, we used a functional relationship between $\overline{r^2}$ and N to relate changes that take place in cloud reflectivity as N changes. The resulting equation can be written as:

$$\frac{dA}{dN} = C_1 (A_1 N + B_1) \quad (4.13)$$

where $C_1 = \frac{4 \pi (1 - g) H}{(2 + (1 - g) \tau)^2},$

A_1 and B_1 are obtained empirically and are $6.0 \text{ E-}10$ and $-2.0 \text{ E-}8$, respectively.

Figure 4.3 illustrates the susceptibility of cloud albedo to changes in N as a function of the cloud albedo from field data. The cases were chosen such that the cloud thickness was not greater than 500 m to reduce effect of variable cloud depth, since the optical depth increases with increasing H and the variability in the microphysical properties increases for larger values of H. The range for susceptibility obtained from our data is within the range indicated by *Taylor and McHaffie*, [1993]. *Taylor and McHaffie* [1993] performed simulations to investigate the sensitivity of cloud albedo in warm stratocumulus clouds to changes in N, using observations as initial conditions for their simulations. Their results were obtained in the vicinity of Azores (between 35° and 37° N and 19° and 25° W) and are also shown in Fig. 4.3. The high value of susceptibility of $5.17\text{E-}03 \text{ cm}^3$ obtained by *Taylor and McHaffie* was for a marine air mass with a low

value of $N \sim 15 \text{ cm}^{-3}$. The marine air mass encountered at the Mt. Mitchell site must traverse over some land before being intercepted at the site. Therefore, we do not have such high values of cloud susceptibility. However, the general trend indicated in Fig. 4.3 suggests that cloud albedo susceptibility decreases with increasing cloud albedo.

Other studies of cloud susceptibility by *Platnick and Twomey* [1994] and *Schwartz and Slingo* [1996] have indicated that susceptibility decreases as the total cloud droplet concentration increased. *Pincus and Baker* [1994] suggested that changes in cloud thickness could modulate cloud albedo susceptibility for all values of N and cloud thickness, with largest enhancement occurring for the greatest variation in cloud thickness with N . Their calculated enhancement factors were between 0.5 to 2 when they accounted for the variations of cloud thickness with N for cloud albedo susceptibility calculations. Therefore, variations in cloud thickness with N need to be included in susceptibility calculations. Since both R_{eff} and LWC vary with cloud height, the location of the sampling site w.r.t. cloud base needs to be ascertained, as the fixed elevation of the sampling site implies that the cloud could be sampled at various vertical levels. The effect of vertical variations in R_{eff} , LWC and N may lead to differences in the magnitude of the susceptibility that have not been included in our analysis. Since we only include cases with cloud thickness less than 500 m the variability in N , R_{eff} and LWC might be slightly reduced. Orographic influences could also lead to additional complexity in determining the variability in N , R_{eff} , LWC with H .

4.7 Optical Depth Sensitivity

Cloud optical depth can be given as;

$$\tau = \frac{3}{2 \rho_w} \int_{\text{cloud base}}^{\text{cloud top}} \frac{LWC}{R_{\text{eff}}} dz \quad (4.14)$$

where LWC is in g m^{-3} , R_{eff} is in μm and ρ_w is the density of water [*Slingo and Schrecker, 1982*]. Here, we assume both LWC and R_{eff} to be constant within the cloud, since vertical variations in these quantities were not measured. Therefore, their values at cloud top will be underestimated since LWC is known to increase height within most clouds and R_{eff} is also expected to be the greatest at cloud top due to the increased LWC at cloud top. The sensitivity of cloud optical depth to some of the cloud microphysical parameters such as liquid water path (LWP, taken simply as the product of LWC and the cloud thickness, since we assume the LWC to be constant with cloud depth), N and R_{eff} was investigated. Two pH intervals ranging from $2.6 < \text{pH} < 3.3$ and $3.3 < \text{pH} < 3.9$ were chosen to represent a polluted air mass and a lesser polluted type air mass, since low values of pH usually correspond to higher sulfate content in cloud water and vice versa, as shown in Fig. 4.4. The dependence of cloud water pH on the air mass source has been determined previously [*Ulman and Saxena, 1997*].

The variations in τ arising from the variations in the cloud microphysical properties can then be expressed as;

$$\Delta\tau = \frac{\partial\tau}{\partial m} \Delta m \quad (4.15)$$

where m is one of the microphysical parameters (LWP, R_{eff} and N) and Δm is its increment [Kogan *et al.*, 1995]. By taking the derivative of Eq. (4.10) and Eq. (4.14) and holding two of the parameters fixed, one can obtain the derivative of the optical depth with respect to LWP, R_{eff} or N . The absolute values of the variation in τ due to the variations in the three microphysical parameters by their standard deviations are shown in Fig. 4.5. The largest contribution arises from R_{eff} and LWP. The contribution of both these quantities is more than twice the contribution from N . The variations in LWP between polluted and lesser polluted type air masses is not as strong as that for R_{eff} . Optical depth was more sensitive to changes in R_{eff} from polluted to lesser polluted type air masses. Due to the inherent variability of the LWP to cloud albedo, Han *et al.* [1994] found R_{eff} to be a more sensitive indicator of anthropogenic influence. Thus, analysis of observational data indicated that the optical depth was most sensitive to R_{eff} and LWP.

4.8 Influence of sulfates on cloud albedo

The sensitivity of cloud albedo to CCN is important in determining the magnitude of anthropogenic perturbation to climate. Changes in CCN concentrations that affect N lead to changes in the optical thickness of thin stratus clouds, thereby affecting its reflectivity [Twomey, 1977]. Brenguier *et al.* [1998] have found N to be more characteristic of pollution within a cloud and a more intrinsic parameter of a cloud than is the R_{eff} . Figure 4.6 shows the CCN concentration and N as a function of cloud water sulfate. A linear relationship between CCN-sulfate and N -sulfate is not obtained. Previous analyses have indicated quantitative non-linear relationships between aerosol

concentrations, CCN and N [Leaitch *et al.*, 1992; Martin *et al.*, 1994; Menon and Saxena, 1998]. Using data from previous years at Mt. Mitchell, Menon and Saxena [1998] have compared empirical relations between N and sulfate with those used by Boucher and Lohmann [1995] to quantify the indirect effect and found greater negative forcing for the Southeast than was indicated by modeling results.

Ghan *et al.* [1990] calculated that a factor of four increase in CCN concentrations in marine stratus clouds would lead to an increase in cloud albedo by 2%, thereby, counteracting the greenhouse warming due to doubling of CO₂. Hegg [1994] calculated the change in cloud albedo for a fractional change in sulfate mass and N using data from the four different locations and found a reduced sensitivity of cloud albedo to sulfate variability as compared to CCN variability. To evaluate the sensitivity of cloud albedo to cloud water sulfate, cloud albedo was calculated from in situ observations using the expression from Lacis and Hansen [1974] given as;

$$A = \frac{\tau}{\tau + 7.7} \quad (4.16)$$

where the optical depth of the cloud is obtained from Twomey [1977] as;

$$\tau = H \left\{ 4.5 \pi N (\text{LWC})^2 \rho_w^{-2} \right\}^{\frac{1}{3}} \quad (4.17)$$

All values for cloud albedo that were calculated from in situ observations are at various zenith angles and no corrections were made to account for variations in cloud albedo for different solar zenith angles. Figure 4.7 shows the albedo as a function of Reff. Due to the dependency of the cloud albedo on the macrophysical properties such as LWC and cloud thickness, the data set was categorized in terms of the product of LWC

and cloud thickness. Three intervals were chosen to divide the data in terms of the product of $LWC \cdot H$ with values ranging from 20 to 160 g m^{-2} . The figure indicates higher reflectivities for decreasing values of R_{eff} in conformance with theoretical expectations and satellite results as obtained by *Han et al.* [1994]. Comparison of cloud albedos calculated from in situ measurements was performed with satellite retrieved cloud albedos from the AVHRR data for cases which coincided with in situ observations. The AVHRR data retrieved from the NOAA -11, NOAA-12, and NOAA-14 satellites provide visible, near infrared and thermal infrared information for retrieval of cloud albedo. Details on the retrieval procedure are given in *Saxena et al.* [1996]. Five cases were utilized from the 1993-94 field season and four cases were utilized from the 1995 field season. The five cases from the 1993-94 field season are discussed in detail in *Saxena et al.* [1996]. The correlation coefficient between satellite retrieved cloud albedo and that calculated from in situ measurements was about 0.90 for the nine cases as indicated in Fig. 4.8. Table 4.2 lists the cases and the associated variables such as cloud water pH, cloud water sulfate, N, R_{eff} , LWC, cloud thickness and optical depth for which the comparison was performed.

Figure 4.9 shows the cloud albedo retrieved from the AVHRR data divided by the corresponding cloud thickness as a function of N, whereas, Fig.4.10 is that versus the cloud water sulfate. Due to the sensitivity of satellite retrieved cloud albedo to the microphysical variables near cloud top, we chose cases where cloud thickness was less than 300 m, to minimize the effect of vertical variations of cloud properties on cloud albedo. Since cloud albedo increases with increasing cloud thickness, the cloud albedo

retrieved from satellite data was divided by the corresponding cloud thickness. *Twomey* [1977] suggested that the rate of increase in reflectance will decrease with increasing optical depth such that all but the most polluted clouds would have increased reflectance for an increase in the pollution content. Higher optical depths usually imply greater N . Figures 4.9 and 4.10 indicate that as N and cloud water sulfate increase, the cloud albedo thickness ratio also increases. The sensitivity of the increase is greater for Fig. 4.9, though the distribution of the points suggests that at lower values of N , this increase will not be as significant. However, the wider distribution of points in Fig. 4.10 suggests that cloud albedo increases with sulfate but the increase is less sensitive than was obtained for the relationship between cloud albedo and N . *Wigley* [1991] had postulated that there could be an upper limit on the magnitude of forcing from sulfate. Our results suggest that there is a reduced sensitivity of cloud albedo to sulfate as compared to that between cloud albedo and N . This indicates that anthropogenic pollution over the continent plays a role in changing the reflectivity of clouds. However, this increase in cloud albedo is a strong function of the macro and microphysical properties of the cloud.

The lower value of the slope in the relationship between cloud water sulfate and the cloud albedo divided by the corresponding cloud thickness, suggests that there could be an upper limit to the cloud water sulfate concentration that affects albedo. These observations are based on data from nine cases that are from a three-year period. This is because cases for comparison of cloud albedo retrieved from satellite data and that calculated from in situ observations are difficult to obtain since a variety of conditions such as -- non-precipitating cloud events, variable sulfate content in the cloud forming air

mass, cloud thickness less than 300 m, coincidence of satellite passage with sampling period, etc -- need to be fulfilled. The conditions imposed for comparison are discussed in *Saxena et al.* [1996]. Therefore, a larger data set would be needed to analyze the sensitivity of cloud albedo to the sulfate content. In terms of the indirect forcing effect of sulfates, for the first time we have been able to demonstrate the increase in cloud albedo with sulfate for the southeastern U.S. using surface-based observations and satellite retrievals. More recently, *Brenguier et al.* [1998] have provided observational evidence of changes in cloud radiances in marine and polluted air masses for stratocumulus clouds in the Northeast Atlantic.

4.9 Conclusions

The sulfate-mass light scattering efficiency was evaluated as $6.0 \pm 0.6 \text{ m}^2 \text{ g}^{-1}$ at ambient relative humidity. The potential sulfate nucleation efficiency as determined from the CCN-sulfate regression equation was $\sim 60 \text{ cm}^{-3} \text{ m}^{-3} \mu\text{g}^{-1}$. The above estimates are for cases where we make the assumption that the sulfate concentration is conserved for the entire cloud event. This gives us a first order estimate of the modification in CCN concentration and light scattering that result from sulfates. Increased CCN concentrations corresponded to increased levels of sulfates obtained in cloud water. The air masses that traversed from the polluted sectors in the Ohio River Valley region to the southeastern U.S. were found to have higher sulfate levels and higher CCN concentrations.

Optical depth was more sensitive to R_{eff} than to N and LWP. The variations in optical depth for R_{eff} from polluted to lesser polluted air masses suggest that R_{eff} is a more sensitive indicator of anthropogenic influence on reflectivity. Cloud albedo susceptibility calculations indicated a maximum sensitivity of cloud albedo to changes in N at low values of cloud albedo. A good correlation was obtained between the cloud albedo retrieved from the AVHRR data and that computed from in situ measurements for nine cases from a three year period (1993-95). Thus, this leads to a “closure experiment”, wherein, we were able to verify the cloud albedo calculated from in situ measurements with that retrieved remotely. The relationship between cloud albedo divided by the corresponding cloud thickness and cloud water sulfate suggests that the reflectivity increases with sulfate concentration though the rate of this increase was found to be lower than that observed between cloud albedo and N . This suggests the existence of an upper limit for the cloud water sulfate concentration that affects reflectivity. These results will help set a limit to the indirect effect of sulfates on forcing that must be noted by climate models that quantify the indirect effect. This limit would however be dependent on the source of cloud forming air masses as well as on the cloud macrophysical properties.

The transport of anthropogenic emissions over the continent influenced the microphysical and optical properties of cloud forming air masses that arrived at our remote mountaintop site in the southeastern U.S. Measurements that relate the production and the transport of aerosols to cloud microphysical and optical properties should be made at a number of different locations due to the regional radiative forcing effect of aerosols. Appropriate parameterizations can then be employed by climate

models to fully assess and verify the role of anthropogenic aerosols in modifying global climate.

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Table 4.1. Average values and standard deviation of cloud condensation nuclei (CCN) concentration, cloud water sulfate content, cloud droplet number concentration (N) and the effective radii (R_{eff}) of cloud droplets for air masses that arrived from either polluted continental (PC) or continental (C) sectors for the 1995 field season for the number of observations listed below.

Sources	Continental (C)				Polluted continental (PC)			
Properties	CCN	SO ₄ ⁼	N	R _{eff}	CCN	SO ₄ ⁼	N	R _{eff}
	(cm ⁻³)	(μeq l ⁻¹)	(cm ⁻³)	(μm)	(cm ⁻³)	(μeq l ⁻¹)	(cm ⁻³)	(μm)
Average	306	607	228	4.10	1294	1018	286	3.90
Std. deviation	172	374	107	1.03	281	391	92	1.61
No of observations	10	13	15	15	5	14	15	15

Table 4.2. Comparison of cloud albedo calculated from in situ measurements to that retrieved from the Advanced Very High Resolution Radiometer (AVHRR) data along with the coincident measurements of cloud water pH, cloud water sulfate, cloud droplet number concentration (N), effective radii (R_{eff}), liquid water content (LWC), cloud thickness and cloud optical depth.

Dates	pH	[SO ₄ ⁼] ($\mu\text{eq l}^{-1}$)	N (cm^{-3})	R_{eff} (μm)	LWC (g m^{-3})	Cloud thickness (m)	Optical depth	In situ albedo (%)	AVHRR albedo $\lambda=0.65\mu\text{m}$ (%)
14 Jun 1993	2.84	664	823 ± 150	2.88 ± 0.57	0.180	148 ± 20	10.8 ± 1.5	58.1 ± 3.4	60.0 ± 10.0
19 Jun 1993	3.77	162	218 ± 160	4.51 ± 0.92	0.190	238 ± 51	11.5 ± 2.4	59.3 ± 5.2	70.0 ± 5.0
19 Aug 1993	2.97	1110	613 ± 100	3.36 ± 0.83	0.150	105 ± 5	6.1 ± 0.3	44.4 ± 1.1	35.0 ± 5.0
21 Jul 1994	3.47	420	54 ± 15	5.79 ± 0.44	0.260	276 ± 23	11.1 ± 0.9	59.0 ± 2.1	56.5 ± 6.5
24 Jul 1994	2.92	105	231 ± 91	3.33 ± 0.90	0.070	101 ± 10	2.5 ± 0.3	24.0 ± 2.0	22.0 ± 6.0
8 Aug 1995	4.08	695	76 ± 79	2.53 ± 1.33	0.261	259 ± 22	11.2 ± 0.9	59.2 ± 1.9	56.0 ± 2.0
9 Aug 1995	3.92	197	136 ± 80	5.19 ± 0.90	0.124	220 ± 17	7.1 ± 0.6	47.8 ± 1.9	35.0 ± 2.0
9 Aug 1995	3.64	382	198 ± 56	4.81 ± 0.93	0.166	268 ± 28	11.8 ± 1.2	60.5 ± 2.4	58.5 ± 3.5
10 Aug 1995	3.49	511	189 ± 44	4.39 ± 1.00	0.294	210 ± 14	13.3 ± 0.9	63.3 ± 1.6	57.5 ± 2.5

Figure 4.1. Light scattering extinction coefficient (bscat) as a function of sulfate mass concentration for the 1995 field season

Figure 4.2. Cloud condensation nuclei (CCN) concentrations at 1% supersaturation as a function of sulfate mass concentration for the 1995 field season.

Figure 4.3. Sensitivity of cloud albedo to changes in cloud droplet number concentration (N) as a function of cloud albedo. The solid circles are from Taylor and McHaffie (1994) and the open diamonds are calculated from Mt. Mitchell data.

Figure 4.4. Cloud water sulfate as a function of cloud water pH. A correlation coefficient of 0.91 is obtained for the relationship between cloud water sulfate and cloud water pH.

Figure 4.5. Variation in cloud optical depth ($\Delta \tau$) caused by variations in the liquid water path (LWP), cloud droplet number concentration (N) and effective radii (R_{eff}) of cloud droplets. Data set is categorized as acidic ($pH < 3.3$) and less acidic ($3.3 < pH < 3.9$).

Figure 4.6. Cloud condensation nuclei (CCN) concentrations at 1% supersaturation and cloud droplet number concentration (N) from the cloud-droplet size distributions as a function of cloud water sulfate.

Figure 4.7. Cloud albedo calculated from in situ measurements as a function of effective radii (R_{eff}) of cloud droplets for three different intervals for the product of liquid water content and cloud thickness ($\text{LWC} \cdot H$) ranging from 20 to 160 g m^{-2} .

Figure 4.8. Cloud albedo retrieved from the Advanced Very High Resolution Radiometer (AVHRR) data versus that calculated from in situ measurements.

Figure 4.9. Cloud albedo retrieved from the Advanced Very High Resolution Radiometer (AVHRR) data divided by the corresponding cloud thickness as a function of cloud droplet number concentration (N).

Figure 4.10. Cloud albedo retrieved from the Advanced Very High Resolution Radiometer (AVHRR) data divide• by the corresponding cloud thickness as a function of cloud water sulfate.

**5. OBSERVATIONS OF THE CHEMICAL HETEROGENEITY IN CLOUD
DROPLETS**

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5.1 ABSTRACT

Variations in the chemistry of cloud droplets of different sizes are predicted in models of cloud microphysics, however, measurements made in natural clouds to verify this are extremely limited. During the spring of 1995 and summers of 1995-96, a size-fractionating version of the California Institute of Technology active strand cloud water collector was operated on a mountain-top platform in Mt. Mitchell State Park, North Carolina ($35^{\circ} 44' 05''$ N $82^{\circ} 17' 15''$ W), USA, to examine differences in drop chemistry between large and small cloud droplets. The size fractionated measurements were also compared to the chemical composition collected from a passive string type collector that collects bulk samples. The differences in cloud drop acidity on cloud liquid water, cloud condensation nuclei, cloud droplet number concentration and cloud droplet effective radii were investigated. Back-trajectory analysis was used to categorize the source of cloud forming air masses that arrived at the site as polluted continental, continental and marine. On an average, smaller drops were more enriched in SO_4^{2-} , NO_3^- , NH_4^+ and H^+ ; whereas; larger droplets had higher values of Na^+ , Ca^{2+} , Mg^{2+} . However, samples were collected where the reverse was true. Higher solute concentrations for the larger droplet size range were found for events caused by orographic lifting, whereas, for cloud events influenced by frontal activity, higher solute concentrations were found for the smaller drop size range. In this study, cloud droplet chemical inhomogeneity between droplet sizes and the effect of air mass origin on the variations in the chemical composition are examined.

5.2 Introduction

Cloud water solute is significant because of its potential effect on the environment having both direct detrimental effects, such as adversely affecting forest growth through impaction (DeFelice and Saxena, 1991) and indirect effects by altering cloud properties such as albedo, thereby, affecting the climate (Twomey, 1974, 1977, 1991; Charlson et al., 1992; Saxena et al., 1996; Menon and Saxena, 1998). Atmospheric sulfate is thought to play an important role in affecting cloud albedo by varying the optical depth of the cloud through changes in the cloud droplet number concentration (N). A seemingly minor 2% change in the planetary albedo, in which cloud reflectance is a major contributor, would be roughly enough to offset greenhouse warming expected with a doubling of atmospheric CO_2 (Twomey, 1991). However, the forcing effect of aerosols on climate is more regional compared to that of greenhouse gases, which is more global. This is due to the residence time of tropospheric aerosols, which is of the order of a few weeks, whereas, that of greenhouse gases ranges from decades to centuries (IPCC, 1994).

An increase in sulfate production is thought to generate larger numbers of cloud condensation nuclei (CCN) (e.g., see for references: Radke and Hegg, 1972; Hegg, 1991; Langner et al., 1992; Lelieveld and Heintzenberg, 1992; Leaitch and Issac, 1993; Easter and Peters, 1994), though there is no agreement on the generation mechanism. Given the same amount of water available for the cloud, an increase in N would result in smaller average sizes of cloud droplets as more droplets compete for the same available water. This in turn would affect the reflectivity of the cloud produced (Lacis and Hansen, 1974; Twomey, 1977; Kaufman and Fraser, 1991; Leaitch and Issac, 1993). Surface

temperatures can also be affected by changes in cloud reflectance if there are no changes in the cloud amount (Twomey, 1991).

It has been suggested (Hegg and Hobbs, 1981; Lelieveld and Heintzenberg, 1992; Easter and Peters, 1994) that the majority of global atmospheric sulfate production occurs in clouds. In the presence of oxidants such as ozone, hydrogen peroxide, formaldehyde, oxygen, trace metal catalysts and carbonaceous particles, sulfur dioxide can be oxidized more rapidly in the aqueous than in the gaseous phase (Seinfeld, 1986). To estimate possible climatic effects, such as changes in N leading to changes in cloud albedo, sulfur dioxide oxidation rates are often determined using bulk cloud water properties, such as cloud water pH (e.g. Hegg and Hobbs, 1981; Daum, 1990; DeFelice and Saxena, 1990a; McHenry and Dennis, 1994). The "bulk water" approach not only assumes similar chemical compositions between different sizes of cloud droplets, but also between cloud droplets of the same size. This view, in part, originated with the theory that in warm clouds, particularly stratocumulus, droplets become monodispersed over time, and was also based on the analysis of cloud water collected from instruments with no means of fractionating droplet sizes. These collections contained polydispersed drop sizes mixed together. While it is easy and convenient to obtain cloud water samples in this manner, the mixing of cloud droplets into bulk samples tends to mask chemical differences between droplets of different sizes (Ogren and Charlson, 1992).

Ogren and Charlson (1992) proposed a number of reasons for cloud drop populations to be chemically heterogeneous, based on the nature and type of CCN, varying droplet growth rates and varying rates of soluble gas uptake by different sized

droplets. Models also predict large variations in acidity and chemical composition between large and small droplets (Seidl, 1989; Twohy et al., 1989; Hegg and Larson, 1990; Wurzler et al., 1995; to name a few). This heterogeneity within the population of cloud droplets can lead to sulfate production in clouds exceeding estimates made using bulk cloud water characteristics, especially for air originating in marine environment (Hegg and Larson, 1990). Hegg (1990) used drop-size dependent chemistry and explicit microphysics in a Lagrangian parcel model to estimate growth of activated CCN. He concluded that aqueous sulfate production was needed to activate newly created drops in marine stratus clouds. Collett et al. (1994), demonstrated that using bulk cloud water samples, sulfate production rates can be seriously under-predicted for clouds where the acidity varies between large and small droplets, particularly where the small droplets are more acidic. Yuen et al. (1994) indicated that this heterogeneity in chemistry across the cloud-droplet size distribution could have a significant impact on in-cloud sulfate production.

Some studies (Munger et al., 1989; Collett et al., 1993, Carter and Borys, 1993; Millet et al., 1995; Schell et al., 1997; Bator and Collett, 1997; Laj et al., 1998) have been conducted to determine experimentally if cloud droplet compositions vary between drop sizes as theory predicts and to ascertain whether this commonly occurs in nature. In this study, drop-size dependent chemistry and the effect of air mass origin on the variations in chemical composition are presented. Since cloud water pH depends on the origin of the cloud forming air masses (Saxena and Yeh, 1988; Saxena et al., 1989), variations in acidities between droplet size fractions may also be air mass dependent. The climatic

implications of droplet chemical inhomogeneity on CCN, N and cloud droplet effective radii (R_{eff}) from in situ observations for continental and marine air masses are discussed.

5.3 Experimental site and Instrumentation

The experimental site is located at Mt. Gibbs (2006 m MSL), approximately 2 km south of Mt. Mitchell Peak (35° 44' 05" N 82° 17' 15"W), North Carolina. The experimental site, referred to as the Mt. Mitchell site, is ideal for *in situ* cloud measurements as seven out of ten days during the summer have a cloud event (Saxena et al., 1989) and is influenced by varying air mass types: highly polluted air from the Ohio Valley region, clean maritime air from the ocean, and relatively clean continental air from the western parts of the U.S. (Saxena and Yeh, 1988). It is frequently located in the free troposphere. Additionally, there is no local source of pollution near the experimental site, thereby allowing for the study of the long range transport of natural and anthropogenic aerosols.

An observation tower, 17.1 m tall extending roughly 10 m above the forest canopy, was equipped with meteorological sensors for ambient temperature, relative humidity, barometric pressure and solar radiation. During the spring of 1995 and summer of 1996, two cloud water collectors were operated simultaneously at the field station. The collectors used were an Atmospheric Science Research Center passive cloud water collector (ASRC), (McLaren et al., 1985; Saxena et al., 1989; DeFelice and Saxena, 1990b) and a Size-Fractionating Caltech Active Strand Cloud Water Collector (SFAC) as described by Demoz et al. (1996) mounted side-by-side on a rotatable carriage

at the top of an observation tower, above the boundary layer of the forest canopy. Differences between active and passive type cloud water collectors can be found in DeFelice and Saxena (1990b).

The SFAC collects two drop size fractions by impaction on Teflon rods and strands. The Teflon rods and strands are inclined at 35° from the vertical to enhance droplet removal through aerodynamic drag and gravity. The first stage, comprised of 10 rows of eight Teflon rods (9.525 mm in diameter), collects large droplets (theoretically 50% size cut for droplets 9.05 μm in radius), while the second stage collects smaller droplets, (theoretically 50% size cut for droplets 2.75 μm in radius) via impaction on six rows of Teflon strands (0.508 mm in diameter). The flow rate of air for both stages is given as $15 \text{ m}^3 \text{ min}^{-1}$ with an average sampling velocity of 5.1 m s^{-1} . The total fraction of air sampled for the first stage is 0.98, with a fraction of 0.34 sampled for each row, whereas, for the second stage, the total fraction of air sampled is 0.86, with a fraction of 0.28 sampled for each row (Daube, personal communication). Details on the operational procedures of the SFAC can be obtained from Demoz et al. (1996). However, the SFAC operated by Demoz had four rows each containing eight rods (12.7 mm diameter) in the first stage (theoretically 50% size cut for droplets 11.5 μm in radius) and six rows of Teflon strands (0.508 mm in diameter) in the second stage (theoretically 50% size cut for droplets 2.0 μm in radius). The maximum collection efficiency and the sharpness of the size cut increases with the number of rows. Therefore, some differences will exist between the collection efficiencies in the SFAC used in this paper and the one used by Demoz et al. It should be noted that the size fractionating ability of the SFAC is not as

sharp as would be found using a device such as a cascade impactor and some mixing between small and large droplets does occur (Collett et al., 1994).

The cloud water collectors used in this experiment were manually operated on an hourly basis upon the occurrence of a cloud event. Before and after every cloud event, the collectors were cleaned by spraying distilled, deionized water on the collection surfaces to remove traces of chemicals that may have been present from previous sampling. A cloud event began when a stationary object at a distance of 1 km from the tower became immersed in clouds and stayed consistently obscured from view for a period of at least 15 minutes. The stationary object was conveniently chosen as a television tower, which also had an unfocused red light on it facilitating nocturnal observations. The pH of the collected cloud water was measured for two samples within minutes of collection and the remaining cloud water was refrigerated at 4 C for future chemical analysis using a Dionex 2010i ion chromatograph. The pH of a buffer solution (usually with a pH of 4.0) was determined immediately as a check to estimate the range of error in determining cloud water pH. The standard deviation associated with pH measurements on the field site are on an average $\sim \pm 0.02$ for all cases. Samples whose pH values were beyond this error limit were discarded. The error for the pH electrode probe instrument is within ± 0.01 . The pH of the solution was subsequently checked in the laboratory for replicate analysis to ensure that the measured pH in the field was not different from laboratory measurements. Measurements of pH in the laboratory were consistently higher than field measurements probably due to loss of acidity during storage as was also reported by Hering et al. (1987). The pH instrument was calibrated before

and after every cloud event using buffer solutions with pH's of 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0.

Eight ionic species namely SO_4^{2-} , NO_3^- , NH_4^+ , Ca^{2+} , K^+ , Mg^{2+} , Na^+ and Cl^- were analyzed from collected cloud water samples by means of ion chromatography (Cl^- , SO_4^{2-}), flow injection analysis (NO_3^- , NH_4^+) and ionically coupled plasma atomic emission spectroscopy (Ca^{2+} , K^+ , Mg^{2+} , Na^+). The instrument and method detection limits were determined using standard methods. The instrument detection limits were $2 \mu\text{eq l}^{-1}$ for NO_3^- and NH_4^+ , 0.5 and $1.0 \mu\text{eq l}^{-1}$ for Cl^- and SO_4^{2-} respectively, $5 \mu\text{eq l}^{-1}$ for Na^+ , $3 \mu\text{eq l}^{-1}$ for K^+ , $0.4 \mu\text{eq l}^{-1}$ for Ca^{2+} and $1 \mu\text{eq l}^{-1}$ for Mg^{2+} . Method detection limits were $10 \mu\text{eq l}^{-1}$ for NO_3^- and NH_4^+ , 2.5 and $5.0 \mu\text{eq l}^{-1}$ for Cl^- and SO_4^{2-} respectively, $25 \mu\text{eq l}^{-1}$ for Na^+ , $15 \mu\text{eq l}^{-1}$ for K^+ , $2.0 \mu\text{eq l}^{-1}$ for Ca^{2+} and $4 \mu\text{eq l}^{-1}$ for Mg^{2+} . After rinsing, the collectors were sprayed with distilled, deionized water, which were collected as blank samples. Blank samples were obtained usually after every fourth cloud event as a means of quality check to ensure that the collectors were not contaminated. The chemical analysis of the blank samples indicated very low values for the major ion concentrations and higher concentrations of chlorine. Contributions from collector rinse blanks were not used for the method detection limit values that may probably lead to some error in accurately determining the method detection values.

Bulk samples from the ASRC were used to estimate cloud liquid water content (ω) in g m^{-3} as given (Saxena et al., 1989) for wind speeds between 2 and 12 m s^{-1} ;

$$\omega = [a * (\text{mass of water collected}) / (\text{wind speed} * dt)] + b \quad (5.1)$$

For the above semi-empirical relationship the sampling area and collision efficiency are taken into account by 'a' given as $\sim 17.37 \text{ m}^{-2}$, 'b' a constant is 0.027 g m^{-3} and dt represents the time during which the cloud water is collected. At higher wind speeds ($> 12 \text{ m s}^{-1}$), droplets may fly off or get suspended in the upper or lower portions of the strings as was observed by DeFelice and Saxena (1990). Droplets that are collected usually range between 1 and $10 \text{ }\mu\text{m}$ in radius. Details on impaction efficiency, wind speed and droplet sizes for the ASRC are in McLaren et al. (1985).

A Particle Measuring System (PMS) Forward Scattering Spectrometer Probe (FSSP) (Knollenberg, 1981) was used to measure cloud droplet size distribution. The alignment was checked after every cloud event by recording the spectra that resulted when glass beads of varying sizes were introduced and was calibrated if the alignment was not proper. Before and after every field season, the FSSP was factory calibrated. The calibration between each of the field events is detailed in DeFelice and Saxena (1994). The FSSP was deployed on the same movable carriage as the ASRC and SFAC. The FSSP sizes particles from 1 to $16 \text{ }\mu\text{m}$ in radius. The FSSP data were obtained for three size ranges covering 0.25 to 4.0, 0.5 to 8 and 1 to $16 \text{ }\mu\text{m}$. Particles were resolved into 15 equally spaced intervals for each size range. For the data set reported in this paper, the large: $1 < r < 16 \text{ }\mu\text{m}$ and small: $0.5 < r < 8.0 \text{ }\mu\text{m}$ size ranges are used. Except for droplets between 0.5 and $1.0 \text{ }\mu\text{m}$, the larger size range includes all droplets measured by the smaller size range but in a coarser bin size resolution. The particle size interval for the large size range is $1 \text{ }\mu\text{m}$ and for the small size range is $0.5 \text{ }\mu\text{m}$. On an average, data was obtained mostly in the small size range except for the marine air masses that have

droplets in the larger size range. The data were obtained every 5 seconds and averaged to obtain hourly averages that correlate to the hourly averages for the chemical data and cloud water data. Note that the size cut for the radius of the large drops for the SFAC is $r > 9.05$ and that for the small drops is $2.75 < r < 9.05 \mu\text{m}$, whereas, that for the FSSP large drop radius is $1 < r < 16$ and for the small drops is $0.5 < r < 8.0 \mu\text{m}$. Measurements from the FSSP were used to estimate N as given;

$$N = \int n(r)dr \quad (5.2)$$

where $n(r)$ is the droplet size distribution and dr is the droplet range. The R_{eff} defined as the ratio of the moments of the drop size distribution is given as;

$$R_{\text{eff}} = \frac{\int_{-\infty}^{+\infty} r^3 n(r) dr}{\int_{-\infty}^{+\infty} r^2 n(r) dr} \quad (5.3)$$

The CCN spectrometer described by Fukuta and Saxena (1979 a,b) was operated from a shed located about 8 m to the north east of the tower. Its inlet is an inverted funnel (0.1 m diameter) that extends 0.5 m outwards and whose opening is 2 m above the top of the shed and is oriented perpendicular to the airflow past it. The spectrometer provides a continuous measurement of the CCN concentration as a function of the supersaturations and is described in DeFelice and Saxena (1994).

Air mass trajectories for all cloud events were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectories (HY-SPLIT) Model (Draxler, 1992, Mueller, 1994). During the 'Across North America Tracer Experiment' (ANATEX) period,

accuracy of trajectories calculated using HY-SPLIT was validated with aircraft observations of tracer plume position. Errors involved using these trajectories ranged from 20% to 30% of the travel distance (Draxler, 1991). Three sectors, identified as the polluted continental sector, from 290° to 65° azimuth relative to the site, the continental sector, 210° to 290° azimuth, and the marine sector, 65° to 210° azimuth, were used to classify the cloud forming air masses (Lin and Saxena, 1991). Characterization of air masses traversing the Mount Mitchell site was accomplished by utilizing anthropogenic emissions data of SO_x and NO_x available from the U.S. Environmental Protection Agency. Validation of the trajectories of the cloud forming air masses that arrived at the site have been previously performed by relating the ionic composition in cloud water (Deininger and Saxena, 1997) and pH of cloud water (Ulman and Saxena, 1997) with the source of the air mass.

5.4 Results and Discussion

5.4.1 Differences in chemical composition of cloud droplets

The period of observations for our study ran from early March intermittently through the middle of June 1995, covering 15 cloud events and 67 cloud water samples collected from non-precipitating clouds. During the summer of 1996, 12 cloud events and 47 cloud water samples were collected mainly from non-precipitating clouds. Differing contributions of acids and bases to individual cloud drops produce a distribution in drop acidities. Figure 5.1 compares the pH values of small and large cloud drops for the spring of 1995 and for the summer of 1996. The range of pH values

observed from less than 3 to nearly 5.5 depict a variation in drop sizes. The smaller droplets were usually more acidic than the larger ones, with some exceptions as can be noticed in Fig. 5.1. Differences between pH of larger and smaller drops were found to be less than one unit. The percentage difference between measured values of the cations and anions from the fractionated and bulk cloud water samples were found to be less than 6% on an average, indicating good ionic balance. The values that were beyond this error limit have not been reported and could represent errors in analyzing all the cations and anions or in determining the species concentrations.

Within the pH range observed (3.0 - 5.5), oxidation of SO_2 by H_2O_2 should be more important than that due to O_3 , which would be of greater importance for $\text{pH} > 5.0$. (Penkett et al., 1979). Measurements from previous field studies have indicated that the O_3 gas concentration (mean ~ 68 ppbv) is significantly higher than the H_2O_2 gas concentration (mean 0.63 ± 0.57 ppbv) for the summer months (DeFelice and Saxena, 1990b; Claiborn and Aneja, 1991). Since the oxidation of SO_2 to SO_4^{2-} is limited by the amount of available H_2O_2 (Daum, 1990), the fraction of SO_2 that would get converted to SO_4^{2-} would be lower if the H_2O_2 concentration were lower. Lower H_2O_2 concentrations indicates that the rate of S(IV) oxidation by ozone would be more important than that due to H_2O_2 (Penkett et al., 1979, Seinfeld, 1986). This in turn would probably affect sulfate production rates estimated from pH, if indeed oxidation by O_3 was more dominant. Since we did not measure any gaseous concentrations during 1995-96, a detailed analysis on the oxidation pathway either by O_3 , H_2O_2 or metal catalysts cannot be performed.

Five cases (June 8, June 13, July 13, July 15 and Aug 1) with different air mass origins and different chemical concentrations in the smaller and larger droplets were chosen from the 1996 data out of a total of fifteen cases. These cases were chosen because the periods of sampling during these cases were of sufficiently long duration and had coincident measurements of cloud droplet concentration and effective radii. Table 5.1 lists the average concentration of the ionic species both from fractionated and bulk cloud water samples. The ranges of measured values are reported as one standard deviation. The differences in pH between small and large droplets were found to be significant at the 95% confidence interval for a two-sided test, except for case 1 and case 5. The differences in pH for these cases were significant only at the 65% confidence level. The differences between sulfate concentrations in the large and small droplets were found to be significant at the 70% confidence interval on an average. Some exceptions were observed as in the case of the cloud event of June 13 and July 13 that did not have significant differences in the sulfate concentrations. However, the differences in average values of nitrates and sulfates between large and small drops were found to be significant at the 95% confidence level for cases 2, 3 and 4, at 80% confidence level for case 5 with no significant difference for case 1. For case 1, the difference between large and bulk for sulfates was more significant.

The mean values of the ionic species from the bulk samples usually lie between the concentrations reported for the large and small droplets. However, some exceptions as in Case 1 were found as indicated in Table 5.1. The strings of the ASRC collector have a diameter of 0.4 mm that is smaller than the strands of the SFAC that measured

0.508 mm in diameter. The two collectors will therefore collect different portions of the droplet size spectrum. DeFelice and Saxena (1990) found the amount of water collected by the ASRC was related to the string diameter and droplet spectra. Differences could also be a result of sampling artifact. Hering et al. (1987) have also noted differences in chemical concentrations in cloud water collected by five different collectors which they attributed to differences in collection.

Figures 5.2a, b, c, d and e depict the concentrations of the ionic composition of the small and large droplets as measured by the SFAC for the five cloud events. Case 1 is for a seven-hour cloud event observed on June 8, 1996. The synoptic charts for this event indicated that orographic lifting caused the cloud forming air mass. There were strong southerly wind flows from the Gulf Stream. Back trajectory analysis confirmed the marine influence for this event. The major contribution to the cloud water composition for this case was from SO_4^{2-} as well from NH_4^+ and NO_3^- . Due to the maritime nature of the cloud, this case had large amounts of Na^+ and Cl^- in the larger drops that were well correlated temporally. NaCl is usually found in the coarse aerosol mode and is found more preferentially in the larger droplets (Schell et al., 1997).

Case 2 is for a nine-hour cloud event that occurred on June 13, 1996. Synoptic charts for this event indicated the cloud formed due to orographic lifting with flow from the western sector. This case had higher NO_3^- , Mg^{2+} and Ca^{2+} concentrations for the larger droplets as compared to the smaller droplets as can be seen in Fig. 5.2b. Bulk measurements and smaller droplets from the SFAC indicated good agreement between the sulfate content and pH of the cloud water. However, there was a greater variation in

the pH and sulfate content of the larger droplets. The low H^+ for the larger drops as compared to the smaller drops was probably due to the high amounts of calcium salts in the large drops that seemed to be the dominant contributor to the chemical composition of the cloud water. This concentration was one of the highest recorded from all samples collected during 1996. This case also had one of the highest amounts of SO_4^{2-} , NO_3^- , NH_4^+ , Ca^{2+} and H^+ from all the five cases considered. The source of the cloud forming air mass was mostly from the continental sector for the first half of the event with some influence from the polluted continental sector during the latter half of the event. Previous analysis (Deininger and Saxena, 1997) has indicated that calcium concentrations were usually high for cloud events originating from the continental sector. Calcium from the continental sector is usually associated with cultivation and construction activities.

Case 3 is for a seven-hour cloud event that occurred on 13 July 1996. This was around the period of the passage of Hurricane Bertha. The air mass originated from the marine sector and passed through the polluted continental sector. The slight maritime influence in this air mass can be detected from the analysis of the chemical composition of the large and small cloud drops. The amounts of Na^+ and Cl^- as well as the SO_4^{2-} and NO_3^- in the large drops for case 3 were one of the highest recorded for most of the marine events observed. The temporal variations of Na^+ and Cl^- were also well correlated. Due to the influence of air mass from the polluted continental sector, this case also had high amounts of NO_3^- , Mg^{2+} and Ca^{2+} in the larger drops. The H^+ was much higher for the smaller drops than the larger drops similar to case 2, which again could be attributed to

the larger amounts of calcium salts in the large drops as compared to that found in the small drops. Bulk samples for both cases 2 and 3 indicated a fairly high amount of Ca^{2+} .

Case 4 is for an eleven-hour cloud event for July 15, 1996. The synoptic conditions for this event indicated a very strong front on the western part of the Mt. Mitchell site that influenced the cloud event. The entire eastern portion of the U.S. northwards of Florida was covered with clouds. The source of the cloud forming air mass was mainly from the continental sector with some influence from the polluted continental sector during the end of the cloud event as indicated by the back trajectory analysis. The smaller droplets had higher H^+ and sulfate as compared to the larger droplets. There were some contributions from nitrates and ammonium for the smaller droplets. Strong correlation between cloud water pH and sulfate content was exhibited both by bulk water samples and fractionated cloud water samples. The correlation coefficients between sulfate and cloud water pH were 0.87 for the large drops, 0.95 for the small drops and 0.96 for the bulk samples.

Case 5 is for an eleven-hour cloud event on August 1, 1996. Frontal conditions that were not as strong as the one for July 15 influenced the formation of the cloud event for this case. The 850 mb level which is the level closest to the site (at ~810 mb) indicated air flow coming from the south west from a high pressure system moving towards the low pressure system located in the north east. The larger droplets had lower sulfate, ammonium and nitrate contents compared to the smaller droplets. The cloud forming air mass was mainly from the continental sector with some influence from the polluted sector. There was more variability in the sulfate content and measured pH for

the smaller droplets as compared to the larger droplets and bulk water samples. There seemed to be a decrease in the NH_4^+ concentration as the cloud event progressed especially for the larger drops. The smaller droplets exhibited a greater variability in the H^+ concentration than did the larger droplets. The slight precipitation during 07:30 coincided with an increase in calcium, potassium and chlorine and a decrease in the concentration of the other ions in the smaller droplets. Variations in H^+ and NO_3^- were strongly correlated to each other especially for the larger drops. This suggests that HNO_3 was one of the contributors to the size-dependent acidification of the droplets for the large droplets. In contrast, the case of 13 June had strong correlation between temporal variations of H^+ and NO_3^- for the small drops, whereas, the case for 15 July had strong correlation between H^+ and NO_3^- for both large and small drops. Therefore, we do find cases where HNO_3 uptake influences the large or small drop acidity or in some cases both. Thus, although one would expect the smaller drops to acidify more than the larger drops through nitric acid uptake (higher relative surface areas), the stronger correlation between H^+ and NO_3^- seen for the larger drops suggest that large drops could also be influenced by HNO_3 uptake.

5.4.2 *Differences in microphysical properties of cloud droplets*

Changes in relative water volume for the two stages of the SFAC and R_{eff} and N obtained from FSSP measurements during the cloud events were investigated for the five cases. The temporal variability in relative water volumes collected for each stage by the SFAC is shown in Fig. 5.3. For case 1, the larger drops had greater amounts of water

collected relative to the smaller drops that increased as the cloud event progressed and then slowly decreased towards the end of the cloud event as can be observed. Figures 5.4a and b illustrate the drop size distribution as obtained from the FSSP measurements for case 1 for the large and small size range. The numbers on the curve represents the sequence of the time period of sampling. Due to the maritime nature of the cloud event, spectra were obtained in the large and small size ranges. The modal radii during the first three hours of the event is at $\sim 6 \mu\text{m}$ and shifts to $4 \mu\text{m}$ during the end of the event for the large size range. The number distribution $N(r)$ increases from $1100 \text{ cm}^{-3} \mu\text{m}^{-1}$ to $2300 \text{ cm}^{-3} \mu\text{m}^{-1}$ corresponding to the decrease in radii. This case also had the largest R_{eff} from all the five cases as can be noticed in Fig. 5.5 that illustrates the temporal variability in R_{eff} as measured by the FSSP for two size ranges; large size range: $1 < r < 16 \mu\text{m}$, and small size range: $0.5 < r < 8.0 \mu\text{m}$. Marine cases usually have larger R_{eff} as compared to continental cases. The R_{eff} gradually decreased from $\sim 6.5 \mu\text{m}$ at the beginning of the cloud event to $\sim 4.2 \mu\text{m}$ as the cloud event ended. Figure 5.6 depicts the temporal variability in N as measured by the FSSP in the large and small size ranges for all the five cases. For case 1, the value of N varied from $\sim 140 \text{ cm}^{-3}$ at the beginning of the cloud event to $\sim 170\text{-}190 \text{ cm}^{-3}$ for cloud droplets in the larger size range, whereas, droplets in the smaller size range varied from $\sim 80 \text{ cm}^{-3}$ to about 110 cm^{-3} . Thus, the higher number of droplets in the larger size range, larger droplet sizes and the chemical composition of the droplets that had higher concentrations of Na^+ and Cl^- in the larger drops exhibited the maritime nature of the cloud. This case also had the highest ω as determined from the bulk sampler of $\sim 0.38 (\pm 0.13) \text{ g m}^{-3}$ from all the five cases.

For case 2, more water was collected for the smaller droplets as indicated in Fig. 5.3. This was in exception to the other three cases (June 8, July 15 and August 1). The value of ω obtained from the bulk sampler was $\sim 0.23 (\pm 0.05) \text{ g m}^{-3}$. Figure 5.4c depicts the size distribution obtained for the smaller size range. For case 2, the number concentration decreased from $\sim 3200 \text{ cm}^{-3} \mu\text{m}^{-1}$ (in the larger size range, not shown) during the first three hours to $\sim 1350 \text{ cm}^{-3} \mu\text{m}^{-1}$ during the rest of the cloud event. A bimodal distribution can be noticed in Fig. 5.4c with the first peak located at $2 \mu\text{m}$. The second peak shifts from $4.0 \mu\text{m}$ for the first three hours to $3.5 \mu\text{m}$ for the rest of the event. From Fig. 5.5, the average R_{eff} for the first three hours was $\sim 4.36 \mu\text{m}$ which decreased to $3.86 \mu\text{m}$ for the next two hours and then increased to an average of $4.10 \mu\text{m}$ for the next four hours. Figure 5.6 indicates an average value of $\sim 294 \text{ cm}^{-3}$ for N in the large size range during the first three hours of the cloud event and an average value of $\sim 144 \text{ cm}^{-3}$ for N in the smaller size range after the first three hours of the cloud event. N decreased after the first three hours and was constant thereafter. The slight temporal variations in R_{eff} after the first three hours coincided with the variations in the water mass for the smaller drops and the values of ω from the bulk sampler.

The source of the cloud forming air mass was from the continental sector during 01:00 to 06:00. From 06:00 to 11:00, the air mass traversed through the polluted continental sector before passing through the continental sector and reaching the Mt. Mitchell site that coincided with an increase in the sulfate content in the smaller drops during 06:00. The decrease in N after 05:00 coincided with the decrease in the sulfate content in the larger drops, except towards the end of the event. The CCN concentration

at 0.7 % supersaturation measured during cloud are representative of interstitial particles. The CCN concentration showed a slight increase after the first four hours of the cloud event that corresponds with the increase in sulfate in the smaller drops. Thus, even though the CCN concentration increased, it quite probable that a lot of particles remained unactivated, thereby, accounting for the lower values of N . Some of these unactivated particles may get scavenged by cloud droplets. The drop-size dependency of solute concentrations was thus not clearly indicated for this event, since the presence of unactivated particles in the smaller size would not necessarily result in a faster dilution of solute concentrations for the small drops. Noone et al. (1988) found smaller droplets diluted faster than larger droplets only if nucleation was responsible for cloud solute concentration. Thus, even though the larger drops had higher solute concentrations, the differences in sulfates between large and small drops were not statistically significant.

For case 3, the smaller drops had a higher water mass than did the larger drops similar to case 2. The value of ω from the bulk sampler was $\sim 0.18 (\pm 0.03) \text{ g m}^{-3}$. This case was influenced by air masses that originated in the marine sector and then passed through the polluted continental sector. This was the time period that corresponded to the passage of Hurricane Bertha. The values for N were fairly low. The drop size distribution as shown in Fig. 5.4d decreases from $\sim 2000 \text{ cm}^{-3} \mu\text{m}^{-1}$ to $\sim 1200 \text{ cm}^{-3} \mu\text{m}^{-1}$ towards the end of the event. However, CCN measurements during cloud indicate a strong increase that corresponds to the increase in sulfate concentrations especially for the large drops. However, since the values for N did not increase, it is quite possible that all the droplet numbers were not accounted for and there was some loss of N . This case

indicated a sharp increase in the amount of CCN concentration from 165 cm^{-3} at the beginning of the event to $\sim 700 \text{ cm}^{-3}$ after 09:00 that corresponds to an increase in sulfate in the larger drops. Similar to case 2, the lower statistical significance for the differences between the large and small drop sulfate composition suggests the presence of large number of unactivated particles.

For case 4, the amount of water collected for both stages increased during the time precipitation occurred during the third, fourth and fifth hours of the event and towards the end of the cloud event. The value of ω from the bulk sampler was $\sim 0.23 (\pm 0.07) \text{ g m}^{-3}$ and some overflow was recorded during the occurrence of precipitation. The water collected for the larger drops also overflowed during the fourth and fifth hour of collection and hence could not be recorded. The occurrence of precipitation can be noticed in the shift of R_{eff} towards slightly larger sizes (Fig. 5.5) and a corresponding decrease in N (Fig. 5.6). Similar features can be observed for case 5, that also had slight precipitation during the second, third, seventh and eight hours of the cloud event. The occurrence of precipitation during this event coincided with a decrease in solute concentrations and also in variability in N and R_{eff} for both these events. The time during precipitation coincided with the droplet spectra exhibiting low N and larger R_{eff} suggesting the removal of droplets that were large enough to precipitate, thereby reducing the total cloud droplet number.

The smaller drops were usually, but not always, more enriched in sulfates, nitrates and ammonium relative to the larger ones. If droplets exhibit a size dependency on the condensation nucleus, then it is quite probable that the chemical composition of droplets

is also size dependent (Munger et al., 1989). Munger et al. (1989) investigated the chemical composition of coastal stratus clouds in California. They found that the concentration of Na^+ , Ca^{2+} and Mg^{2+} in the larger droplet was higher than in the smaller droplet and indicated that these large droplets formed on sea-salt and soil dust while smaller droplets which had higher SO_4^{2-} , NO_3^- , H^+ and NH_4^+ , usually formed on small secondary aerosols composed of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 . For marine stratus clouds, Noone et al. (1988), found the solute concentration within cloud droplets to be size dependent. They found that smaller droplets dilute faster than the larger droplets, which then results in an increase in solute concentration with size. The above phenomenon can only be observed if nucleation was primarily responsible for cloud solute production and cannot be observed if unactivated cloud droplets are scavenged by cloud droplets or in-cloud production of solute takes place (Noone et al. 1988). However, their observations were for one single cloud event and did not include the variability in marine stratus clouds.

The drop-size dependence of solute concentrations is dependent on whether drops are in stable equilibrium with the environment or are activated and are growing unstably. If the water vapor saturation ratio exceeds the equilibrium saturation ratio of the droplets, the droplets will grow until they reach a critical diameter. The critical diameter is usually between 0.2 and 2 μm for most droplets and depends on the solute and the temperature (Pruppacher and Klett, 1997). If sufficient water vapor is available they will exceed the critical diameter and get activated. The unactivated droplets can also have concentrations that get diluted as the droplet grows. Therefore, the dilution of the solute concentration

in the small drop fraction of the cloud drops that are sampled at the Mt. Mitchell site will depend on if the small drop fraction is influenced by drops that are either activated or that are large but not activated.

Schell et al. (1997) suggested that droplet growth time is an important factor for the size dependence of solute concentration and found higher solute concentrations in larger droplets for droplets that were relatively young and formed by orographic lifting. For clouds that are more aged, solute concentration decreased with an increase in diameter. Factors that are responsible for the changing pattern of solute concentrations with droplet age are the width of the CCN size distribution -- determined by the peak supersaturations and the number of particles in the coarse mode range -- and the solubility of the particle (Schell et al., 1997). Schell et al. also suggest that increased solute concentrations in smaller droplet size range could result from entrainment when new particles enter the cloud and form new droplets. From Table 5.1, it can be seen that slightly higher solute concentrations for the larger droplet size range found for the June 8, June 13 and July 13 cases were for events that were caused by orographic lifting as was indicated by synoptic charts. However, some of these orographic events (e.g. June 13) lasted for over seven hours and therefore, were not always shorter relative to the cloud events influenced by frontal activity that were typically of longer duration. For the cloud events of July 15 and August 1 that were influenced by frontal activity, higher solute concentrations were found for the smaller drop size range. However, it must be noted that orographic effects also affect clouds influenced by frontal systems. Therefore,

detailed cloud dynamics might be necessary to differentiate between cloud properties that result from either frontal or orographic influences.

The location of the sampling site relative to cloud base is an important factor since both drop size distribution and LWC are dependent on cloud thickness. This has not been accounted for in this paper and must be accounted for in future analysis. Fractionated measurements from the SFAC indicate the existence of a variability of chemical concentration with size of the cloud droplets. Estimation of the dependency of chemical heterogeneity on cloud droplet size can be realized more accurately if cloud water samples could be obtained with either a sampler with a sharper size cut off, or by using a device which would fractionate the droplets into more than two size ranges.

5.4.3 Influence of Air Mass Trajectory

Data sets from 1995-96 were used to tabulate the number of times the small and large droplets were within a particular pH range as a function of the source of the air mass as listed in Table 5.2. The origins of air masses are listed as marine, continental, polluted continental, and a mix of continental and marine. Three pH intervals (3.0-4.0, 4.0-5.0 and 5.0-6.0) were chosen to represent the range of acidity in the drops within the range of pH observed. For the 39 marine cases sampled, at least 33% of the small drops had pH in the 3.0 – 4.0 range as opposed to ~ 8% of the larger drops that were in the 3.0 – 4.0 pH range. For air masses originating in the continental regime, including a mixed continental/marine regime, there was no predictable relationship between acidity and droplet size. However, continental air masses do yield larger differences in the large and

small drop pH value, particularly in more acidic clouds. Out of the six polluted continental cases sampled, five of these were in the 3.0 – 4.0 pH range for the smaller drops, whereas, for the larger drops, all the cases had pH in the 4.0 – 5.0 range. Thus, smaller droplets were more acidic than the larger droplets for air masses which were polluted continental in origin, though due to fewer number of these cases, no strong inference was drawn. For the small drops, out of the total of 102 cases, 46% were in the 3.0 – 4.0 pH range and 49% were in the 4.0 – 5.0 pH range, whereas, for the large drops, 79% of the samples were in the 4.0 – 5.0 pH range. Thus, the smaller drops were more frequently in the low pH range than were the larger drops.

Table 5.3 lists the range and average values for the sulfate content in the larger and smaller cloud drops from the SFAC, bulk cloud water sulfate measurements from the ASRC and the averages and ranges of CCN, N and R_{eff} for different air masses for the 1996 data. Previous measurements at the experimental site indicated that clouds with high sulfate concentrations generally have higher average acidities, smaller average droplet sizes and higher N than clouds with lower sulfate concentrations (Saxena et al., 1996). Table 5.3 indicates that the highest sulfate content, highest CCN and lowest R_{eff} were usually for polluted continental type air masses. The polluted continental sector had the highest sulfate content recorded that was found in the small drops. The range for sulfate content from bulk samples is between the range obtained for the fractionated samples, although the average for the marine sector is skewed towards slightly lower values. The change in average values of N from the marine to the continental and the polluted continental sector for the smaller size resolution is offset by the high standard

deviations that were observed for the marine and continental cases. These high standard deviations in N could arise due to differences in dynamical situations of the air masses encountered during the sampling period that result in fluctuations in droplet concentrations. The occurrence of brief precipitation for a few events could also result in large fluctuations in N as some of the droplets that were large enough would precipitate, thereby, reducing the total droplet number. The size of the droplets decreased from an average of $\sim 5.76 \mu\text{m}$ for the marine cases for the large size resolution to $\sim 3.89 \mu\text{m}$ for the polluted cases. This reduction in droplet size of $\sim 32\%$ would be of significance if a larger data set could be obtained. Menon and Saxena (1998) analyzed four years of data at the Mt. Mitchell site and found sufficient evidence for a decrease in droplet size as the air mass source moves from the marine sector to the polluted continental sector. Slingo (1990) had suggested that a decrease in R_{eff} by $\sim 21\%$ for fixed vertical variations in the cloud liquid water content over the cloud thickness could offset the warming due to doubling of carbon dioxide based on his modeling study.

5.4.4 Climatic implications

Ghan et al. (1990), Charlson et al. (1991) and Lelieveld and Heintzenberg (1992) hypothesized that increased atmospheric sulfate production increases cloud albedo by increasing N . If N is dominated by chemical species that are different from those that dominate the volume weighted mean molarity in cloud droplets, the albedo effect would be related to the subset of droplets rather than the overall solute concentration (Ogren and Charlson, 1992). Since the initial solute in cloud droplets is usually provided by the

CCN, the pH of the cloud water during early stages of droplet growth is controlled to some extent by the CCN (Ogren and Charlson, 1992).

For clouds that have similar ω , the cloud would either have high values of N and small R_{eff} or low values of N and large R_{eff} . The optical depth of a cloud with high N and small R_{eff} would be greater than that of the cloud with low N and large R_{eff} since the optical depth is inversely proportional to R_{eff} (Slingo and Schrecker, 1982) and is proportional to $N^{1/3}$ (Twomey, 1991). A cloud with a large number of small drops with high sulfate content would have higher reflectivity than a cloud with a small number of large drops that have lower sulfate. Thus, difference in the solute concentrations between large and small droplets that is usually not accounted for in bulk sampling can affect the optical properties through the cloud drop size distribution. Since most climate models (e.g. Boucher and Lohmann, 1995) usually use empirical relations between N and the sulfate content from bulk samples to calculate the optical properties and the magnitude of the indirect radiative forcing effect, the effect of drop-size dependent chemistry on cloud droplet spectra will lead to either an underestimation or an overestimation of the forcing effect.

5.5 Conclusions

Sulfate production in clouds is a critical component of the global sulfur cycle. Traditionally, bulk water measurements of cloud water acidity have been used to estimate sulfate production within clouds. While it is easy and convenient to use bulk water measurements to infer in-cloud sulfate production rates, it tends to mask chemical

differences between droplets of different sizes, and also between droplets of the same size. Both models, and limited experimental data, suggest that cloud droplet populations are chemically heterogeneous. Field measurements of pH variations between large and small cloud droplets indicated that smaller droplets are often, but not always, more acidic than larger droplets. On an average, smaller drops were enriched in SO_4^{2-} , NO_3^- , NH_4^+ and H^+ ; whereas; larger droplets had higher values of Na^+ , Ca^{2+} , Mg^{2+} . However, samples were collected where the reverse was true. Smaller droplets were usually more acidic than the larger droplets for both marine and polluted air masses, whereas, for continental air masses no such inference could be drawn. Cloud forming air masses from the polluted continental sector had the highest sulfate content for both larger and smaller drops.

Higher solute concentrations for the larger droplet size range were found for events that were caused by orographic lifting as indicated by synoptic charts. However, the difference in sulfate concentration between large and small drops were not found to be statistically significant for some of the orographic cases sampled, possibly due to the presence of unactivated particles. However, for the same cases, differences between average values of sulfates and nitrates for small and large drops were found to be statistically significant. The dilution of the solute concentration in the small drop fraction of the cloud drops that were sampled at the Mt. Mitchell site were found to depend on if the small drop fraction was influenced by drops that were either activated or that were large but not activated. For the cloud events that were influenced by frontal activity, higher solute concentrations were found for the smaller drop size range. Thus, depending

on the CCN size distribution and the solubility of the aerosols, droplet growth time is an important factor for size dependence of solute concentrations in droplets (Schell et al. 1997). Climate models that use empirical relationships between droplet number and sulfate content from bulk samples to estimate the indirect effect will either overestimate or underestimate the indirect effect if drop-size dependent chemistry and its relation to droplet size distribution is not accounted for.

The results presented here are based on a small number of cases. A larger data set that also takes into account cloud dynamics, cloud base and location of sampling site relative to cloud base, would lead to a better understanding of the effect of drop-size dependent chemistry on cloud microphysical properties. Optimal division of droplets to account for chemical heterogeneity as a function of droplet size would aid in better understanding of the effect of chemical composition of droplets on cloud microphysical and radiative properties and must be accounted for in future modeling and experimental studies.

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Table 5.1. Average solute concentrations and standard errors (represented as one standard deviation) found in cloudwater collected from the size fractionated active string type cloud water collector (SFAC) for large and small cloud droplets and bulk measurements from the passive string type cloud water collector (ASRC) during the 1996 field season. Values that were below the method detection limit are reported as “too low”.

Date	Cases	pH	H ⁺ μeq l ⁻¹	Mg ²⁺ μeq l ⁻¹	Ca ²⁺ μeq l ⁻¹	Na ⁺ μeq l ⁻¹	NH ₄ ⁺ μeq l ⁻¹	NO ₃ ⁻ μeq l ⁻¹	Cl ⁻ μeq l ⁻¹	SO ₄ ²⁻ μeq l ⁻¹
8-June	Large drop (SFAC)	4.1 ± 0.1	76.7 ± 15.1	7.8 ± 1.5	24.2 ± 5.8	27.3 ± 6.2	79.0 ± 14.0	74.3 ± 18.0	20.8 ± 4.5	154 ± 19.4
	Small drop (SFAC)	4.2 ± 0.2	67.7 ± 24.7	Too low	9.4 ± 2.2	Too low	88.2 ± 29.0	67.5 ± 17.8	16.9 ± 7.8	142 ± 28.2
	Bulk (ASRC)	4.0 ± 0.1	102 ± 30.3	4.0 ± 2.0	9.3 ± 5.7	Too low	54.6 ± 29.8	65.8 ± 29.0	12.2 ± 5.9	118 ± 27.9
13-June	Large drop (SFAC)	4.0 ± 0.1	97.1 ± 11.8	31.1 ± 18.3	266 ± 169	Too low	257 ± 77.4	381 ± 197	18.0 ± 4.1	330 ± 97.3
	Small drop (SFAC)	3.7 ± 0.1	202 ± 46.1	Too low	32.3 ± 9.4	Too low	271 ± 70.4	189 ± 43.5	11.5 ± 1.6	297 ± 89.1
	Bulk (ASRC)	3.8 ± 0.1	177 ± 35.9	16.5 ± 7.6	138 ± 83.7	Too low	257 ± 90.2	275 ± 106	12.5 ± 4.8	303 ± 117
13-July	Large drop (SFAC)	4.2 ± 0.5	95.8 ± 69.9	82.5 ± 42.5	305 ± 148	189 ± 107	216 ± 113	437 ± 220	122 ± 56.3	536 ± 299
	Small drop (SFAC)	3.6 ± 0.4	340 ± 182	7.9 ± 5.7	22.7 ± 17.8	Too low	168 ± 157	136 ± 79	33.9 ± 12.8	363 ± 356
	Bulk (ASRC)	3.8 ± 0.5	268 ± 186	34.9 ± 14.2	122 ± 51.3	71.9 ± 32.9	188 ± 102	247 ± 114	68.1 ± 26.5	382 ± 252

15-July	Large drop (SFAC)	4.3 ± 0.2	53.6 ± 28.5	Too low	4.4 ± 2.5	Too low	34.3 ± 20.9	42.0 ± 22.0	5.8 ± 2.5	96.5 ± 47.8
	Small drop (SFAC)	4.1 ± 0.3	102 ± 48.5	Too low	7.9 ± 10.9	Too low	63.5 ± 24.5	63.5 ± 28.8	7.9 ± 3.3	168 ± 70
	Bulk (ASRC)	4.2 ± 0.3	72.1 ± 44.4	Too low	2.2 ± 1.6	Too low	37.2 ± 24.5	43.1 ± 22.1	4.97± 1.82	101 ± 61.3
1-Aug	Large drop (SFAC)	4.3 ± 0.3	66.4 ± 42.6	Too low	10.0 ± 5.7	Too low	41.4 ± 26.0	58.9 ± 33.0	13.7 ± 12.8	122 ± 78.4
	Small drop (SFAC)	4.4 ± 0.5	84.2 ± 92.0	Too low	7.8 ± 4.5	Too low	55.0 ± 37.0	66.8 ± 43.5	11.5 ± 8.1	184 ± 119
	Bulk (ASRC)	4.1 ± 0.3	109 ± 97.3	Too low	9.7 ± 6.8	Too low	41.7 ± 39.3	61.0 ± 42.2	5.3 ± 3.3	130 ± 118

Table 5.2. Number of times the small and large droplets from the SFAC measurements were within a particular pH range as a function of the source of the cloud forming air mass. M stands for marine, C for continental, P for polluted continental and C/M is an air mass that crossed from the continental sector to the marine sector. Data is for the 1995 and 1996 field season.

Time		Spring 1995 and summer 1996								
pH range	Small drop					Large drop				
	M	C	C/M	P	Total	M	C	C/M	P	Total
3.0-4.0	13	17	12	5	47	3	7	8	0	18
4.0-5.0	22	20	7	1	50	32	31	11	6	80
5.0-6.0	4	1	0	0	5	4	0	0	0	4
TOTAL	39	38	19	6	102	39	38	19	6	102

Table 5.3. Average sulfate contents from the size fractionated cloud water collector for large and small droplets and from bulk samples from the passive string type cloud water collector. Also listed are the effective radii (R_{eff}), droplet number concentration (N) and cloud condensation nuclei (CCN) concentration for polluted continental, continental and marine air masses for the 1996 field season. The number of samples and the range of values for each property are also given.

Air mass source	Marine			Continental			Polluted continental		
Properties	Range	Average	Samples	Range	Average	Samples	Range	Average	Samples
Sulfates ($\mu\text{eq l}^{-1}$) large drops	6 - 176	102	15	29 - 896	207	23	122 - 941	511	10
Sulfates ($\mu\text{eq l}^{-1}$) small drops	10 - 264	115	15	42 - 1209	260	22	70 - 1113	399	10
Sulfates ($\mu\text{eq l}^{-1}$) bulk	6 - 198	89	15	28 - 1047	225	23	108 - 794	393	10
CCN (cm^{-3})	154 - 286	216	7	145 - 639	264	20	136 - 853	373	10
N (cm^{-3}) ($2 < d < 32 \mu\text{m}$)	39 - 198	128	11	-		0	-		0
R_{eff} (μm) ($2 < d < 32 \mu\text{m}$)	3.9 - 8.8	5.76	11	-		0	-		0
N (cm^{-3}) ($1 < d < 16 \mu\text{m}$)	16 - 111	64	13	22 - 167	73	20	143 - 145	144	4
R_{eff} (μm) ($1 < d < 16 \mu\text{m}$)	2.0 - 5.5	3.76	13	1.3 - 5.2	3.41	20	3.3 - 4.1	3.89	4

Figure 5.1. Cloud water pH for smaller and larger drops from the 1995 and 1996 field season. Error bars for pH are between ± 0.02 . The solid line represents the one-to-one correspondence for pH for both size fractions.

Figure 5.2a. Time series of ionic composition of the sample for 8 June in the given size range.

Figure 5.2b. Time series of ionic composition of the sample for 13 June in the given size range.

$r > 9.05 \text{ (}\mu\text{m)}$

$2.75 < r < 9.05 \text{ (}\mu\text{m)}$

Figure 5.2c. Time series of ionic composition of the sample for 13 July in the given size range.

Figure 5.2d. Time series of ionic composition of the sample for 15 July in the given size range.

Figure 5.2e. Time series of ionic composition of the sample for 1 August in the given size range.

Figure 5.3. Time series of amount of cloud water collected from fractionated cloud water samples for large and small droplets.

Figure 5.4. The drop size distribution as obtained from the Forward Scattering Spectrometer Probe measurements in the given size range. (a) For 8 June in the larger size range, (b) For 8 June in the smaller size range, and (c) For 13 June. The numbers on the curves represent the sequence of the time period of sampling.

Figure 5.4. The drop size distribution as obtained from the Forward Scattering Spectrometer Probe measurements in the given size range. (d) For 13 July, (e) For 15 July, and (f) For 1 August. The numbers on the curves represent the sequence of the time period of sampling.

Figure 5.5. Time series of size of the droplets (R_{eff}) as obtained from the Forward Scattering Spectrometer Probe measurements. Two size ranges are given: Large size: for $1 < r < 16 \mu\text{m}$ and small size: for $0.5 < r < 8.0 \mu\text{m}$.

Figure 5.6. Time series of cloud droplet number concentration (N) as obtained from the Forward Scattering Spectrometer Probe measurements. Two size ranges are given, Large size: for $1 < r < 16 \mu\text{m}$ and small size: for $0.5 < r < 8.0 \mu\text{m}$.

**6. OBSERVATIONS OF CLOUD MICROPHYSICAL-CHEMICAL
PROPERTIES AND ITS EFFECT ON REGIONAL CLIMATE**

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6.1 Abstract

The effect of pollutants on microphysical and optical properties of clouds has been studied using data from a remote mountaintop location in the southeastern U.S. Sulfates are found to be the dominant chemical specie. The atmospheric sulfate concentrations at Mt. Gibbes were greater during 1993-97 than during 1986-89. Differences in cloud droplet sizes in going from marine to polluted air masses were greater during 1993-97, suggesting greater atmospheric cooling (smaller droplets scatter more efficiently). Cloud albedo retrieved from satellite data, and calculated from surface observations, does not indicate a continual increase in cloud albedo with increasing sulfate content in the air mass. Analyses of the direct and indirect radiative forcing effect of sulfates for the southeastern U.S. indicate that the negative forcing effect is of greater magnitude than is predicted by modeling results.

6.2 Introduction

It is widely recognized that anthropogenic aerosols perturb the atmospheric radiation field through direct and indirect interactions with solar radiation, thereby, influencing climate. Via the direct effect, aerosols can scatter and absorb solar radiation in cloud-free air (1). In terms of the indirect effect, aerosols composed of soluble substances such as sulfates can act as cloud condensation nuclei (CCN). Increases in CCN concentrations increase cloud droplet number (N), thereby, reducing cloud droplet size, assuming the liquid water content (LWC) stays the same (2). This enhances cloud albedo (3) and can also act to suppress drizzle production, which then increases fractional cloudiness and cloud lifetime (4).

The magnitude of the direct forcing usually relates linearly to aerosol loading for an optically “thin” atmosphere (5). Quantification of the indirect forcing remains debatable due to the large uncertainty in the relationship between aerosol number distribution and anthropogenic pollution (1). Previous studies estimate the contribution of sulfates to indirect forcing by relating the atmospheric sulfate mass concentration to aerosol concentration (N_a) and/or CCN concentration through empirical observations and coupled chemistry-climate models (e.g. 6 and 7). The global-average estimates of indirect forcing from these studies range from -1.0 to -1.3 W m^{-2} with greater negative forcing for eastern U.S., southeastern Europe and eastern China (8) where sulfate emissions are greater. This could lead to changes in surface temperature and cloud reflectivity in these areas (9). Empirical evidence of sulfate aerosol forcing on surface-air

temperature and optical depth has been found (10). Analysis of long-term surface-air temperature records indicates a cooling trend for the southeastern U.S. (11).

The amount of sulfate aerosols that can act as CCN still remains an unresolved issue (12). Few observations exist that confirm the enhancement in cloud albedo as CCN concentrations increase (13). Due to theoretical limitations in deducing these relationships without major uncertainty, models usually use some empirical relationships to predict climate change. Given the regional variability in aerosol properties, regional measurements in several parts of the globe will be necessary to reduce the uncertainty in developing appropriate empirical relationships.

To investigate the climatic impact of anthropogenic aerosols in the southeastern U.S., the direct and indirect effects of aerosols (primarily sulfates and to a lesser extent black carbon (BC)) were investigated using surface measurements, modeling results and remotely sensed data. Monitoring of the chemical characteristics of cloud water has been ongoing since 1986 at a remote mountain top location in the southeastern U.S. Additionally, cloud microphysical and radiative characteristics have been analyzed since 1993. In addition to these observations, a column radiative forcing model (CRM) was used to estimate the direct radiative forcing during four years for which relevant data are available. Empirical relations between sulfate and CCN, N and cloud droplet effective radii (R_{eff}) were used to investigate whether cloud albedo increases as pollution increases, as suggested (3). Since the observational site intercepts marine and continental air masses, it is possible to delineate the effect of pollution content on cloud properties in continental versus marine air masses.

6.3 Methodology

The field site is located on Mount Gibbs (2004 m MSL, 35°44'05"N and 82°17'15"W), in Mount Mitchell State Park in North Carolina, USA. Mt. Mitchell is the highest peak in eastern North America. The site is unique in that at least seven out of ten days have a cloud episode during the summer months. The types of clouds commonly encountered are those formed due to orographic lifting and those caused from frontal activity (14). The sources of the cloud forming air masses were analyzed from their back trajectories obtained from the Hybrid Single Particle Lagrangian Integrated Trajectory Model (HY-SPLIT) (15). The empirical data from the site is considered as regionally representative since the site is located far away from any known local pollution sources, frequently stays in the free troposphere and intercepts marine, continental and polluted continental air masses.

Continuous measurements of meteorological data such as wind speed, wind direction, pressure, temperature and relative humidity were obtained by instruments located atop a 17.1-m walk-up tower, above the top of the forest canopy. A passive string-type cloud water collector (16) mounted on a rotatable carriage atop the tower was used to estimate LWC (17). A forward scattering spectrometer probe (FSSP) was used to estimate cloud drop-size distribution and to determine drop sizes. The R_{eff} were estimated from the ratio of the third and second moments of the drop-size distribution. CCN activation spectra were measured by a Horizontal Thermal Gradient Cloud Condensation Nucleus Spectrometer (18). The pH of the cloud water was measured immediately after collection. Cloud water samples were analyzed via ion

chromatography for eight ionic species: SO_4^{2-} , NO_3^- , NH_4^+ , Ca^{2+} , K^+ , Mg^{2+} , Na^+ and Cl^- . Since the summer of 1996, BC mass concentrations have also been measured using a two-channel aethalometer developed at Lawrence Berkeley Laboratory (19).

6.4 Direct forcing

The direct radiative forcing was estimated by means of a CRM of the Climate Community Model (CCM III) that was coupled to a Mie code (20). The aerosol optical properties and the mass mixing ratios were used in the shortwave radiative transfer portion of the CRM to calculate forcing. The forcing due to aerosols is obtained as the difference in total solar absorbed when the model is run once with and without any aerosol mass loading (21). During May to August of 1993-96, a total of 55 daytime cases were obtained. The average values of forcing for each of the four years are -6.36 , -1.75 , -8.78 and -2.42 W m^{-2} , with an overall average of $\sim -4.80 \text{ W m}^{-2}$, and values of -1.29 , -3.60 and -10.04 W m^{-2} for marine, continental and polluted continental air masses, respectively. Since sulfate concentrations are well correlated with BC concentrations (suggesting the same source region), the change in forcing for BC aerosols internally mixed with sulfate aerosols was calculated for ten cases with coincident sulfate and BC concentrations. The direct forcing ranges from -5.3 to $+0.6 \text{ W m}^{-2}$ for an internally mixed BC-sulfate aerosol, with BC-sulfate mass ratios ranging from 0.7 to 10.0%. The only occurrence of positive forcing was for 10% BC-sulfate mass ratio. The direct forcing for sulfate aerosols (mass ranging from 1 to $8 \mu\text{g m}^{-3}$) ranges from -1.12 to -7.23 W m^{-2} , whereas, that for BC aerosols (mass ranging from 0.01 to $0.2 \mu\text{g m}^{-3}$) is from

+0.08 to +2.12 W m⁻². Thus, an internally mixed BC-sulfate aerosol results in an average reduction in forcing of ~1.12 W m⁻². Modeling studies (22) indicate that the direct forcing for sulfates is reduced by 0.034 W m⁻² for 1% of BC added to the sulfate mass mixing ratio. However, despite the reduction in forcing with the addition of BC aerosols, the values obtained for the direct forcing (minimum ~ -0.07 W m⁻² to a maximum of ~ -26.4 W m⁻²) due to sulfates are much higher than model predictions of ~ -2.0 W m⁻² (23) for the southeastern U.S. The above estimates for forcing are uncertain by a factor of two due to the various assumptions used in the calculation of aerosol optical properties and size distribution as well as in the aerosol mass concentrations that were calculated from sulfate concentrations in cloud water.

6.5 Indirect forcing

Since the incorporation of pollutants into clouds can affect drop-size distributions, the chemical characteristics of cloud water were investigated. Sulfates and nitrates are the two most important contributors to cloud water acidity, with average values of sulfate almost three times the average values of nitrates. Figure 6.1 indicates median values of cloud water sulfate for three intervals of cloud water pH: pH < 3.0, 3.0 < pH < 3.7 and pH > 3.7 to depict polluted continental, continental and marine air masses, respectively. The trends in cloud water sulfate depicted in Fig. 6.1 indicate that sulfate concentrations were higher during 1993-97 than during 1986-89. Previous analyses indicated a strong correlation between pH and wind direction of the air masses as well as cloud water

sulfate with the source of cloud forming air masses (24). Thus, the long-range transport of pollutants to the Southeast, of which sulfate is predominant, can be traced.

Table 6.1 gives regression relations between CCN, N, subcloud N_a , R_{eff} , LWC and sulfates for the southeastern and northeastern U.S. A quantitative relationship that determines the increase in CCN from an increase in N_a concentration is dependent on the chemical and dynamical characteristics of the cloud as well as on aerosol size distribution. Quantitative non-linear relationships between CCN-N were obtained from ground-based measurements for 1995-96 (25), similar to non-linear values from other investigations on N_a and N (26), as shown in Table 6.1. The change in cloud albedo (ΔAc) resulting from an enhancement in N or CCN, when N_a increases from 100 to 1000 cm^{-3} (values are chosen to represent cleaner and polluted air masses) was calculated (27) using a simple estimate as;

$$\Delta Ac = 0.057 \frac{\Delta N}{N} = 0.04 \frac{\Delta CCN}{CCN} \quad (6.1)$$

where ΔN and ΔCCN are the increases in N and CCN resulting from an increase in N_a . For the Southeast, ΔAc is ~ 0.33 , whereas, for the North Atlantic ΔAc is ~ 0.25 (using equations from Table 6.1).

Observations of marine stratus clouds in the North Pacific, by Vong and Covert, indicated a linear 1:1 correspondence between CCN and N for high LWC ($LWC > 0.25 \text{ g m}^{-3}$) (28). Stratifying data for the southeastern U.S. based on LWC results in a linear correlation for N-CCN (for all air masses). The slope was ~ 0.46 ($r^2 \sim 0.60$) as compared to a slope of 0.91 ($r^2 \sim 0.80$) found in the North Pacific. Considering only marine air

masses for the Southeast, results in a slope of 0.77 ($r^2 \sim 0.42$, for six M cases). CCN measurements from a CCN spectrometer were calculated at 1% supersaturation for the Southeast, whereas, that for the North Pacific was obtained by integrating aerosol size spectra for expected values of maximum supersaturation from 0.24 to 0.67%. A simple and consistent aerosol chemical composition in marine air masses was assumed for the North Pacific cases in contrast to the different air masses encountered at our site as well as possibly greater orographic influences than is encountered at the site in the North Pacific. The concentrations of CCN calculated at $\sim 0.7\%$ supersaturation resulted in a higher slope of 0.88 ($r^2 \sim 0.57$) for the CCN-N relationship as compared to that obtained at 1% supersaturation. Stratification of data based on LWC, N, chemical composition of the air mass and supersaturations encountered in clouds could be used to obtain meaningful estimates of N-CCN relationships from surface measurements.

For the Southeast for the 1995 data set, the range of sulfate mass was $\sim 1.5 - 10 \mu\text{g m}^{-3}$, with the exception of two cases that were between 20 to $30 \mu\text{g m}^{-3}$ and CCN concentrations were ~ 130 to 1700 cm^{-3} , whereas, that for the Northeast Atlantic was 0 to $10.5 \mu\text{g m}^{-3}$ for sulfates and $\sim 50 - 250 \text{ cm}^{-3}$ for CCN concentrations (29). The CCN concentrations for the Southeast and for the Northeast Atlantic were reported at 1% supersaturation. Using the regression relationship between CCN and sulfate given in Table 6.1, ΔCCN was calculated for an increase in sulfate mass from 2 to $5 \mu\text{g m}^{-3}$ (representative of average values of sulfate for cleaner and polluted air masses). The ΔAc calculated from Eq. (6.1) is ~ 0.03 for the Southeast and ~ 0.01 for the Northeast Atlantic.

Multivariate analysis was used to investigate changes in R_{eff} as functions of LWC and N . Values of $N=100 \text{ cm}^{-3}$ and 500 cm^{-3} are chosen to represent marine and continental air masses. Due to the smaller ranges in LWC in our results, the variation in R_{eff} is modelled for different N , keeping LWC constant at 0.3 g m^{-3} . The regression equation for marine cases for the entire data set (1993-96) is compared to that for the Northeast for marine stratus clouds (26) as indicated in Table 6.1. The values of R_{eff} are smaller by ~ 0.5 to $2 \text{ }\mu\text{m}$ for $300 < N < 1000 \text{ cm}^{-3}$ and 3 to $5 \text{ }\mu\text{m}$ smaller for $N < 300 \text{ cm}^{-3}$ for our results as compared to those for the Northeast. The R_{eff} of continental clouds usually are ~ 2 - $3 \text{ }\mu\text{m}$ smaller than the R_{eff} of marine clouds (30). The R_{eff} of marine stratus clouds in the Northeast exhibit a higher sensitivity to varying N than is found in the Southeast. This difference can be attributed to the modified marine air mass encountered at our site, as the marine air mass must traverse over some land before reaching our site in contrast to the marine stratiform clouds sampled at Nova Scotia in the Northeast. Vertical variations in LWC, R_{eff} and N must also be considered since surface measurements could be sampling at different levels in the cloud.

The differences in R_{eff} between marine and polluted continental air masses were found to be higher in the Southeast than in eastern North America for stratiform clouds. The differences in R_{eff} are sufficiently high to balance warming due to doubling of CO_2 (25), as suggested by model predictions (31) and indicated for eastern North America (32). The trend in R_{eff} from 1986-97 is calculated for median values of cloud water sulfate from Fig. 6.1 and representative values of N and LWC for polluted continental, continental and marine air masses. The trend indicates greater differences in R_{eff} between

marine and polluted continental air masses during 1993-97 (54%) than during 1986-89 (45%). Modeling studies (6) find larger cooling takes place for the largest change in R_{eff} . Therefore, greater cooling is inferred during 1993-97 as compared to that during 1986-89.

The apparent sensitivity of change in N to the corresponding change in sulfate concentration was estimated from the slope of the regression relationship between logarithm of N and sulfate (33). The higher sensitivity between N and sulfate obtained from our results compared to those at Puerto Rico for stratocumulus clouds (33) and in the Northeast (32) as indicated in Table 6.1, suggests that the indirect forcing is higher for the southeastern U.S. Previous analysis (25) of the N -sulfate mass relationship indicated that the indirect forcing for the Southeast is higher than the magnitude of -4.0 W m^{-2} indicated by the modeling study (6).

Cloud reflectivity was calculated from in situ observations and was retrieved from the Advanced Very High Resolution Radiometer (AVHRR) data. For in situ observations, the cloud optical depth (τ) is calculated (3) as;

$$\tau = H \{ 4.5 \pi N (LWC)^2 \rho^{-2} \}^{1/3} \quad (6.2)$$

where the density (ρ) of liquid water is 1000 kg m^{-3} and the cloud thickness, H , in meters is obtained from the HY-SPLIT sounding. The albedo (A) is evaluated (34) as;

$$A = \frac{\tau}{\tau + 7.7} \quad (6.3)$$

The radiances were retrieved from AVHRR data for the visible (Channel 1, $\lambda = 0.63 \text{ }\mu\text{m}$) and near-infrared (Channel 3, $\lambda = 3.7 \text{ }\mu\text{m}$).

Accordingly, cloud albedo calculated from in situ measurements for thin clouds was compared to that retrieved from the AVHRR data (35). During four years (1993-96), a total of 20 cases were obtained with r^2 of 0.71 for both comparisons. The regression relationship between sulfate content and cloud albedo indicate that as the sulfate content increases, the cloud albedo would increase until it would reach saturation and then indicated a decrease. Therefore, the data set was categorized in terms of the sulfate content. Ten cases with sulfate content $< 200 \mu\text{eq l}^{-1}$; seven cases with sulfate content between 200 and $700 \mu\text{eq l}^{-1}$ and three cases with sulfate contents between 700 and $1200 \mu\text{eq l}^{-1}$ were chosen. Figure 6.2a indicates average values of LWC, N, R_{eff} and cloud liquid water path (LWP) (taken as the product of LWC and H, since we assume constant LWC) for each category. Figure 6.2b indicates average values of cloud albedo calculated from in situ measurements and that from the AVHRR data for Channel 1 and 3.

The radiance in Channel 1 is chiefly composed of reflected solar radiation. This is dependent on N, H and to a smaller extent on LWC. Cloud reflectance at $3.7 \mu\text{m}$ is a combination of reflected and emitted radiant energy and is dependent on LWC and R_{eff} (36). With an increase in N_a , CCN and N increase and droplets get smaller if LWC remains unchanged. Thus, the reflectance in Channel 3 would increase due to an increase in backscattering and the change in the ratio of scattering to absorption. If LWC decreases, then the reflectance in Channel 3 would increase, whereas, the reflectance in Channel 1 would actually decrease (37).

In Fig.'s 6.2a and 6.2b, for an increase in average sulfate content by a factor of 2.5 (for sulfate $< 200 \mu\text{eq l}^{-1}$ to sulfate between 200 and $700 \mu\text{eq l}^{-1}$), N and LWC

increases (77% and 15%, respectively), but R_{eff} and LWP decreases (7%). The cloud albedos calculated from in situ measurements and that determined from AVHRR data at $0.63 \mu\text{m}$ are enhanced (23% and 9%, respectively). The increase in LWC and the small decrease in R_{eff} result in a decrease in Channel 3 reflectance (36%). An increase in average sulfate content by a factor of 1 (from sulfate between 200 and $700 \mu\text{eq l}^{-1}$ to sulfate between 700 and $1200 \mu\text{eq l}^{-1}$), decreases R_{eff} and LWC (20% and 52%, respectively), and leads to an increase in Channel 3 reflectance ($\sim 25\%$). The sharp decreases in LWP (64%) decrease cloud albedos, despite the increase in N (34%). Thus, a continual increase in cloud albedo with increasing cloud water sulfate is not indicated. Changes in the dynamical characteristics such as LWC and H and in cloud microphysical properties such as N and R_{eff} with varying sulfate content were found to be important in determining variations in cloud reflectance. Previous analysis indicated that susceptibility (defined as change in cloud albedo for a given change in N (38)) of cloud albedo was enhanced by a factor of two, when variations in N with cloud thickness are taken into account (39). Therefore, vertical variations in N, R_{eff} , LWC and ionic concentrations must be considered for analysis of variations in cloud reflectivity.

6.6 Conclusions

Time series observations of sulfate concentrations in cloud water since 1986 indicate higher sulfate concentrations for 1993-97 as compared to that during 1986-89. The calculated change in cloud albedo from differences in CCN and N in cleaner to polluted air masses was higher for the Southeast as compared to the Northeast. Varying

levels of sulfate in polluted and marine air masses, lead to changes in R_{eff} that are of sufficient magnitude to counteract warming expected due to doubling of CO_2 . Higher sensitivity of N to sulfate content is obtained for the southeastern U.S. as compared to that for eastern North America and Puerto Rico. The indirect forcing effect due to sulfates for the Southeast is greater than the -4.0 W m^{-2} estimated by modeling studies (7). A linear relationship between cloud albedo and cloud water sulfate was not found (both from satellite retrievals and calculations from in situ measurements). Variations in N and R_{eff} with varying sulfate content as well as in dynamical properties such as LWC and cloud thickness were found to be important in determining variations in cloud reflectivity. Vertical variations in LWC, N and R_{eff} must also be considered. An internal mixture of BC and sulfate reduces the sulfate forcing by $\sim 1.12 \text{ W m}^{-2}$. However, despite this reduction, the combination of both direct (average $\sim -4.8 \text{ W m}^{-2}$) and indirect (of greater magnitude than -4.0 W m^{-2}) radiative forcing for the sulfate aerosols for the past four years (1993-96) suggest that anthropogenic influences could balance any warming expected from the doubling of CO_2 for the southeastern U.S. On a regional scale, a cooling trend is underway for the eastern parts of U.S. Since regional climatic changes affect global climatic changes through the cloud-climate feedback mechanisms, possible consequences of the impact of reduced emissions on climate must be carefully investigated before measures are taken to control emissions and predict climate change.

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6.7 References and Notes

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Table 6.1. Comparisons of differences in the regression relation between cloud microphysical properties such as: cloud condensation nuclei concentration (CCN), cloud droplet number concentration (N), subcloud aerosol number concentration (N_a), cloud droplet effective radii (R_{eff}), cloud liquid water content (LWC) and sulfates for the southeastern and northeastern U.S.

Location	N and CCN/ N_a	CCN and sulfate	N and sulfate	R_{eff} , N and LWC (Marine cases)
Southeast U.S. (25)	$N = 183 \log(\text{CCN}) - 334$	$\text{CCN} = 60.4 (\pm 10.6) [\text{SO}_4^-] + 129.3 (\pm 95.8)$	$\log[N] = 0.66 (\pm 0.05) \log [\text{SO}_4^-]_{cw} + 0.67 (\pm 0.02)$	1993: $R_{eff} = 15.1 + 2.3 \log(\text{LWC}) - 3.8 \log N$ 1994: $R_{eff} = 16.1 + 2.9 \log(\text{LWC}) - 3.4 \log N$ 1996: $R_{eff} = 8.9 + 2.0 \log(\text{LWC}) - 1.5 \log N$
Northeast U.S. (32)	NA	NA	$\log[N] = 0.26 (\pm 0.05) \log [\text{SO}_4^-]_{cw} + 1.95 (\pm 0.21)$	NA
Puerto Rico (33)	NA	NA	$\log[N] = 0.09 (\pm 0.05) \log [\text{SO}_4^-] + 2.32 (\pm 0.15)$	NA
Northeast Atlantic (29)	NA	$\text{CCN} = 15.5 (\pm 3.3) [\text{SO}_4^-] + 94.5 (\pm 15.8)$	NA	NA
North Atlantic (26)	$N = 216 \log(N_a) - 382$	NA	NA	$R_{eff} = 14.8 + 11.5 \text{LWC} - 4.8 \log(N)$

Figure 6.1. Trend in median values of cloud water sulfate. Data are categorized in terms of cloud water pH to represent polluted continental, continental and marine type air masses.

Figure 6.2a. Average values of cloud liquid water content (LWC), cloud droplet number concentration (N), cloud droplet effective radii (R_{eff}) and cloud liquid water path (LWP) obtained for the three sulfate categories.

Figure 6.2b. Average values of cloud albedo calculated from in situ observations and cloud albedo retrieved from the Advanced Very High Resolution Radiometer (AVHRR) data at two wavelengths: $\lambda = 0.63 \mu\text{m}$ and $\lambda = 3.7 \mu\text{m}$ for the same three categories as Fig. 6.2a.

**7. DIRECT RADIATIVE FORCING OF SULFUR AND SOOT AEROSOLS
OVER A MOUNTAINTOP LOCATION IN THE SOUTHEASTERN U.S.**

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7.1 Abstract

The direct radiative forcing ability of aerosols, wherein, solar radiation is reflected back to space or absorbed, results in a cooling or warming effect on the earth's surface. The chemical properties of the aerosol particles are important in determining the ability of the aerosols to either absorb or reflect solar radiation. This in turn will affect the magnitude of the forcing. This paper considers the direct forcing effect of two kinds of aerosols: sulfate and soot. Since sulfate aerosols scatter radiation and soot aerosols absorb radiation, the effect of an internally mixed soot and sulfate aerosol can produce either a cooling or warming effect depending on their relative concentrations. Concurrent measurements of size segregated chemical samples, light scattering and absorption coefficients, aerosol size distribution and optical depth measurements are used to investigate the relationship between the chemical, physical and optical properties of aerosols. These measurements were conducted at a remote mountaintop location in the southeastern U.S. during winter. Modeling studies have identified the southeastern U.S. as the region most likely to be influenced by aerosols and predict greater negative forcing for the southeastern U.S. A column forcing model has been used in this study to determine the magnitude of the direct forcing due to sulfate, soot and an internal mixture of sulfate and soot. Based on the wintertime sulfate concentrations, the local direct forcing calculated for marine, continental and polluted continental air masses is -0.91 , -1.34 and -1.81 W m^{-2} , respectively. Similar calculations based on the soot concentrations yielded approximately $+0.1 \text{ W m}^{-2}$, for the three air masses. For an internal mixture of soot and sulfate aerosols the direct aerosol forcing values are -0.32 , $-$

0.55 and -0.66 W m^{-2} for marine, continental and polluted continental air masses. The sensitivity of forcing to aerosol physical and chemical properties is also investigated.

7.2 Introduction

Though highly uncertain, the role of anthropogenic aerosol particles in perturbing the radiation budget and affecting regional and global climate has become an increasingly important issue. The climatic effects aerosols are manifested through the back scattering or absorption of solar radiation which can reduce or increase the solar irradiance reaching the surface of the earth [Charlson, 1992]. This is usually referred to as the direct radiative forcing of aerosols. The indirect radiative forcing of aerosols refers to the enhancement in cloud albedo through an increase in the number concentration of cloud condensation nuclei (CCN) concentration. This results in an increase of both cloud lifetime and cloud cover [Twomey 1977; Albrecht, 1989]. This cloud-mediated effect is expected to be of greater magnitude than the direct effect though the exact magnitude has relatively large uncertainties. The combined direct and indirect effect of aerosol particles on radiative forcing must be considered in determining the role of anthropogenic aerosol particles and greenhouse gases on the perturbation of global climate.

The radiative effects of greenhouse gases have been well documented for many years. However, quantification of the aerosol forcing effect on climate is still a major uncertainty due to lack of coordinated observational and modeling studies in relating aerosol physical, chemical and radiative properties. Estimating the impact of the aerosols on the global warming caused by greenhouse gases is complicated by the spatial and temporal heterogeneity between aerosol and greenhouse-gas forcing. Since aerosol particles are comparatively short lived and spatially variant their impact on climate is more likely to be regional. Dettinger *et al.* [1995] and Saxena *et al.* [1997] have reported

that during the last fifty years a cooling trend has existed in the mean maximum surface temperature over the southeastern United States. This trend could either result from changes in circulation patterns, changes in cloud amount and/or the direct and cloud-mediated effects of increases in anthropogenic aerosol concentrations.

In order to improve climate change predictions, geographic and temporal variations in the distribution of aerosols have been represented in climate models [*Kiehl and Briegleb*, 1993]. The spatial and temporal heterogeneity results in varying chemical, physical and optical properties of aerosols on a regional basis. Due to the fundamental dependence of optical properties on aerosol size and chemistry, as well as lack of adequate representation in models, extensive measurements of aerosol optical properties are still necessary [*Boucher and Anderson*, 1995]. In this study, we use such measurements to estimate the optical properties and the total direct radiative forcing of sulfate and soot aerosols.

The box-model description of *Charlson et al.* [1992] can serve as a good first order estimate of the magnitude of forcing for an optically “thin” atmosphere. However, more reliable estimates of the forcing are attainable if variations in the microphysical factors (scattering efficiency and asymmetry parameter and the dependence on particle size and relative humidity) and atmospheric chemistry factors (production and residence time) are included [*Schwartz*, 1996].

In estimating the direct radiative forcing effect of aerosols, the aerosol optical depth, single scattering albedo (ω_0) and asymmetry parameter (g) are fundamental parameters. Recent literature [*Haywood and Shine*, 1995] has focussed on the direct

forcing ability of both anthropogenic sulfate (highly scattering) and soot (highly absorbing) aerosols. These are assumed to have similar sources and residence times (approximately one week). The absorption of radiation by soot particles results in a positive forcing. Thus the role of soot aerosols in counteracting the negative forcing of sulfates is an important factor that may change the cooling effect of sulfate aerosols to a warming effect in areas of high soot concentrations. Using the box model of *Charlson et al.* [1992], *Haywood and Shine* [1995] found an overall forcing of +0.03 to +0.24 W m⁻² for mixtures of soot and sulfate. One of the main impediments to the calculation of global forcing effects of soot is the lack of adequate data on the temporal and spatial distribution of soot aerosols.

Regional estimates of forcing from observational studies would help in reducing the uncertainty in the quantification of the forcing effect of aerosols on climate. The objective of this investigation is to use surface observations of the chemical and physical properties of aerosols, primarily sulfate and soot aerosols, in a column radiative forcing model (CRM) to determine the direct forcing due to these aerosols. Solar radiation extinction resulting from soot absorption and sulfate scattering is represented in the CRM by the optical properties and the mass mixing ratios of these species. The aerosols are identified with three air mass types: marine, continental and polluted continental.

The surface measurements used in this study are aerosol size distribution, size-segregated chemical samples, light scattering (total and hemispheric), light absorption and optical depth. These are complemented with model results of direct aerosol forcing. These surface measurements taken in the free troposphere (~ 2 km) provide an estimate

of the aerosol forcing effect above the boundary layer. Since the eastern U.S. has been identified as a region where the magnitude of the aerosol cooling effect can counteract the warming effect from greenhouse gases [Kiehl and Briegleb, 1993], our measurements and model estimates at this location can be used for comparison with other model predictions.

7.3 Methodology

7.3.1 Model description

The aerosol extinction efficiency (Ψ), single scattering albedo (ω_0), and asymmetry factor (g) were calculated using Mie theory for an assumed log-normal size-distribution of sulfate and soot. For the sulfate aerosols, the refractive indices used are those from *Palmer and Williams* [1975] for a mixture composed of 75% H_2SO_4 and 25% H_2O . The soot refractive indices are from *WCP* [1986]. The sulfate dry particle density was assumed to be 1.7 g m^{-3} [Kiehl and Briegleb, 1993] and a particle density of 1.0 g m^{-3} was assumed for soot aerosols. The aerosol size distribution was assumed to be log normal, with a geometric standard deviation of 2.1 and a geometric mean diameter of $0.1 \mu\text{m}$. The same size distributions were assumed for both sulfate and soot particles. The magnitude of the direct forcing is calculated for pure sulfate aerosols, pure soot aerosols and for an internal mixture of soot and sulfates (where the aerosol particle is composed of both soot and sulfate), to determine the critical value of the soot-sulfate ratio that would change the sign of the forcing from a negative to a positive value. The average density and refractive index for the internal mixture of soot and sulfate is calculated using a

volume averaging method [*Larson et al.* 1988; *Sloane* 1983]. The optical parameters are used in the CRM of the Climate Community Model (CCM3) of the National Center for Atmospheric Research. The model has 18 spectral intervals. The mass mixing ratios are calculated from the measured aerosol mass concentrations. The CCM3 Column Radiation Model uses a δ -Eddington approximation for the efficient calculation of solar radiation with altitude [*Briegleb*, 1992]. The δ -Eddington method involves solving for the reflectivity and transmissivity for each vertical layer. The CCM3 model atmosphere consists of a discrete vertical set of horizontally homogeneous layers within which radiative heating rates are to be specified. Each of the layers can be prescribed by a combination of radiatively active constituents. This method also simulates the effects of multiple scattering and uses a two-stream approximation rather than bulk expressions for gaseous absorption. It includes the properties of clouds when these are prescribed at each vertical level. The layers are then combined, accounting for multiple scattering between layers, which allows evaluation of upward and downward spectral fluxes at each interface boundary between layers.

Initial conditions used in the CRM are the mid-latitude winter McClatchey profiles of density, temperature, H₂O density and O₃ density [*McClatchey*, 1972].

7.3.2 Experimental setup

The experimental site is located on Mt. Gibbs (2038 m amsl, at 35°44'05"N and 82°17'15"W) in Mount Mitchell State Park, North Carolina. The site is at a remote location far away from any known local pollution sources. It frequently stays in the free

troposphere and intercepts continental and marine air masses. Meteorological variables such as temperature, pressure, wind speed, wind direction and humidity are measured continuously. Aerosol optical depths at visible wavelengths are obtained from the Multi-Filter Rotating Shadowband Radiometer (MFRSR) mounted on a rooftop platform. The MFRSR measures global, diffuse and direct irradiance at 415, 500, 615, 673, 870, and 940 nm with a channel bandwidth of approximately 10 nm. The cosine, spectral, and absolute response of each wavelength channel of the MFRSR is measured with National Institute of Standards and Technology (NIST)-traceable equipment by the manufacturer Yankee Environmental Systems before shipping. The calibration and intercomparison for the instrument occurs at the NOAA-SRRB (National Oceanic and Atmospheric Association - Solar Radiation Research Branch) Boulder, CO site using NIST traceable calibrations. The level of the MFRSR instrument and solar alignment of the shadowband is checked periodically to ensure accurate measurements.

The direct component from the MFRSR is used to calculate the aerosol optical thickness using the Beer-Lambert-Bouguer law. The aerosol optical depth is calculated at the 500 nm channel of the MFRSR. The Bouguer-Langley method was used to calculate an extraterrestrial constant. Details on the Bouguer-Langley method for determining aerosol optical depth from the MFRSR can be found in *Wenny et al.* [1998]. The value of the aerosol optical depth τ_λ , is calculated at each wavelength using the Beer's law:

$$\tau_\lambda = -\ln \left(\frac{V_\lambda}{V_{0\lambda}} \right) \cos(\theta), \quad (7.1)$$

where V is the instrument output or the direct radiance, V_0 is the extraterrestrial constant specified for a given day and adjusted to account for the earth-sun distance and θ is the zenith angle. The effect of Rayleigh scattering by air molecules was subtracted from the measurements.

Soot mass concentrations were continuously and remotely measured using a Magee Scientific Aethelometer since July 1996. While in operation the aethalometer performs internal system checks at regular intervals on the lamp intensity, photodetectors and air flow rates. A sample of the collected data and the internal system check report is sent monthly to the manufacturer, Magee Scientific, for inspection and to ensure the stability and proper operation of the instrument. Details on the operation of the instrument can be found in *Hansen et al.* [1984]. The operational definition of the soot measured by the Aethalometer is given as that fraction of the carbonaceous aerosol that will absorb light over a broad region of the visible spectrum, and is measured by determining the attenuation of light transmitted through the sample which is collected on a fibrous filter [*Hansen, 1996*].

During November 1997, an intensive field operation was carried out at the Mt. Mitchell site. The following measurements of aerosol physical, chemical and optical properties were obtained:

- Mass-particle size distributions of major submicrometer and supramicron particles.
- Spectrally-resolved measurements of aerosol absorption between 300 and 1100 nm.
- Integral total-scatter coefficient and backscatter at 450, 550 and 700 nm.
- Total particle number concentration from 3-1000 nm.

- Aerosol particle number size distribution from 13-850 nm.

Particle size-segregated aerosol samples were obtained from an 11-stage Multiple-Orifice cascade Impactor (MOI). The MOI flow rate is 30 L min^{-1} with 50% cut off diameters at 18, 9.9, 6.2, 3.1, 1.8, 1.0, 0.56, 0.32, 0.17 and $0.093 \mu\text{m}$. The samples on the filters were analyzed to determine ionic concentrations of SO_4^{2-} , NO_3^- , NH_4^+ and Cl^- species. Total aerosol mass concentrations were measured using a Tapered Element Oscillating Microbalance (TEOM) aerosol mass monitor. The TEOM measurements are based on the changing vibrational frequency of a long stem filter holder as a function of the mass loading of the filter. Total particle number concentrations were measured between 3 and 1000 nm range with a TSI Model 3010 Ultrafine Condensation Particle Counter (UFCPC). The aerosol particle size distributions were measured between 13 and 850 nm by means of a TSI Scanning Mobility Particle Sizer (SMPS). The uncertainty in the SMPS measurements usually arise from uncertainties in the flow ($\sim 3\%$) as well as from the counting of the number of particles. The Aerosol absorption coefficient was obtained by means of the Radiance Research Particle Soot Absorption Photometer (at 565 nm). Aerosol light scattering was measured using a TSI Integrating nephelometer at three wavelengths: 450, 550 and 700 nm. The integral total scattering coefficient and the backscatter were measured by means of a built-in rotating shutter. Rayleigh scattering is calculated from measured temperature and pressure and was subtracted from the scattering due to particles.

In addition to the TEOM measurements, ambient aerosol samples were collected during the summer of 1994 using an Anderson dichotomous sampler before and after

non-precipitating low-level cloud events. The aerosol content of the cloud forming air mass was analyzed for size and morphology by electron microscopy and an x-ray energy spectrometer. These data are used to obtain a first order estimate of seasonal forcing since summertime sulfate mass concentrations are much higher than during winter.

The sources of the air masses for all cases are analyzed from their back trajectories obtained from the Hybrid Single Particle Lagrangian Integrated Trajectory (HY-SPLIT) model. The trajectories are dependent on the wind field resolution, the type of computational scheme used and the associated synoptic-scale meteorological conditions. The accuracy of these trajectories, like all computed trajectories, is limited as observed by *Draxler* [1987]. Errors involved using these trajectories ranged from 20% to 30% of the travel distance [*Draxler*, 1991]. Classification of the air masses as polluted continental, continental and marine are based on the SO_x and NO_x emission inventories obtained from the U.S. Environmental Protection Agency [1993]. In this classification method, the continental U.S. is divided into three sectors with the polluted continental sector located between 290° and 65° azimuth relative to Mt. Mitchell, the marine sector between 65° and 210° and the continental sector between 210° and 290°.

Validation of the sources of the air masses with the cloud water pH [*Ulman and Saxena*, 1997] and with the ionic concentrations found in cloud water [*Deininger and Saxena*, 1997] have been conducted at the site. *Bahrman and Saxena* [1998] have also found higher average soot concentrations of $216.6 \pm 47.8 \text{ ng m}^{-3}$ in polluted continental air masses and lower concentrations of $65.6 \pm 23.5 \text{ ng m}^{-3}$ in marine air masses.

7.4 Results

7.4.1 Sulfur aerosols

The Ψ , ω_0 , and g for sulfate aerosol were calculated using a Mie code for 97 spectral intervals ranging from 200 to 5000 nm with an interval of 50 nm. These optical properties are dependent on the size distribution and the refractive index of the aerosol mixture. Since sulfate aerosols are non-absorbing in the visible part of the spectrum, the value of ω_0 is 1.0 in this region. The value obtained for g decreased from 0.71 to 0.68 (350 to 700 nm). Ψ is wavelength-dependent and usually decreases as $\lambda^{-1.1}$. For the Mt. Mitchell sulfate aerosol, Ψ decreased from $6.84 \text{ m}^2 \text{ g}^{-1}$ at 350 nm to $3.15 \text{ m}^2 \text{ g}^{-1}$ at 700 nm, with a value of $5.15 \text{ m}^2 \text{ g}^{-1}$ at 550 nm. The trends in the daily average values of sulfate mass concentration and the light scattering coefficient (B_{scat}) indicated in Fig. 7.1 are in fairly good agreement. These values are obtained for samples of air that have been heated to reduce the relative humidity to below 25%. The ambient relative humidity at the site ranged from 20 to 96%. Strong geographic patterns between sulfate aerosol concentration and extinction coefficient have previously been shown in the eastern U.S. [Husar *et al.* 1981]. The sulfate-scattering efficiency is usually obtained from the slope of the regression relationship between B_{scat} and sulfate mass. The value obtained for the sulfate-scattering efficiency was $7.0 \pm 1.2 \text{ m}^2 \text{ g}^{-1}$ with $r^2 \sim 0.71$ for sulfate mass in the range 0.01 to $1.65 \mu\text{g m}^{-3}$. B_{scat} values ranged from 0.37 to $12.0 (\times 10^{-6}) \text{ m}^{-1}$. Nitrates are also known to be as important as sulfates in visibility reduction. The nitrate-scattering efficiency was $\sim 20.0 \pm 3.2 \text{ m}^2 \text{ g}^{-1}$ ($r^2 = 0.69$) for nitrate mass in the range 0.01 to $0.64 \mu\text{g m}^{-3}$. However, due to the volatility of nitrate as HNO_3 , wherein, the material is returned

to the gas phase after dilution by atmospheric dispersion processes, the contribution of nitrates to radiative forcing is relatively low [Schwartz, 1996].

The mass concentrations of sulfates were significantly higher than that of nitrates, ammonium and soot. However, comparison of the sulfate mass with the total aerosol mass obtained from the TEOM measurements indicated that a substantial portion of the mass was composed of aerosols that were not sulfates, nitrates, ammonium or soot, as can be seen in Figure 7.2. The mass that was not chemically identified is referred to as the residual mass. The low value of the intercept obtained in the regression relationship between sulfates and nitrates with light scattering seem to suggest that most of this residual mass (with the exception of organics) do not contribute significantly to light scattering. Measurements taken at a mid-latitude, rural mid-western section in the U.S. have indicated B_{scat} values of 1.78 to 5.78 $\text{m}^2 \text{g}^{-1}$ for ranges of relative humidity between 30 and 90% for sulfates, whereas, that for organic carbon aerosol was between 3.81 to 6.90 $\text{m}^2 \text{g}^{-1}$. Organic carbon aerosols were found to dominate scattering at low relative humidities, whereas, sulfates dominated scattering at high relative humidities [Omar *et al.*, 1998].

The forcing as determined from the CRM for pure sulfate aerosols ranges from – 0.06 to – 3.26 W m^{-2} for the entire data set. The highest average value of forcing of – 1.81 W m^{-2} was obtained for polluted continental air masses, whereas, the lowest average value of forcing of – 0.91 W m^{-2} was found for marine air masses. For the continental air masses, the average value of forcing was – 1.34 W m^{-2} . Boucher and Anderson [1995] in their modeling study on direct forcing obtained values for forcing over a region

located in the southeastern U.S., that were between -1.0 and -1.5 W m^{-2} during January. These values were obtained for 11 aerosol types composed of $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 and H_2SO_4 . In comparison, the forcing that was calculated from data obtained during the summer of 1994 ranged from -2.0 W m^{-2} to -20 W m^{-2} for sulfate mass in the range 2 to $18 \mu\text{g m}^{-3}$. Similar values for forcing during July obtained by *Boucher and Anderson* [1995], were between -1.3 and -2.0 W m^{-2} . The summer values of the direct aerosol forcing are much higher compared to the winter values for our results, which is not surprising since sulfate concentrations usually approach a maximum during daytime summer conditions [*Kiehl and Briegleb*, 1993]. This change in the magnitude of forcing due to lowered sulfate concentrations in winter could be of consequence in forcing calculations if the concentrations of other aerosols namely organics and soot do not have seasonal variations. Here, both summer-time and winter-time forcing estimates are higher than model estimates.

7.4.2 Soot aerosols

The Ψ , ω_0 and g for pure soot aerosols were obtained from the Mie code for 97 spectral intervals. For the visible part of the spectrum (350 – 700 nm), ω_0 decreased from 0.46 to 0.42, g decreased from 0.73 to 0.62 and Ψ decreased from 9.42 at 350 nm to 7.31 $\text{m}^2 \text{ g}^{-1}$ at 700 nm, with a value of $\sim 8.26 \text{ m}^2 \text{ g}^{-1}$ at 550 nm.

The trend in the daily average values of soot mass concentration and light absorption coefficient (B_{ap}) were very similar as indicated in Fig. 7.3. The regression relationship between B_{ap} and the soot mass concentration resulted in a soot-absorption

efficiency of $20 \pm 3.6 \text{ m}^2 \text{ g}^{-1}$ ($r^2 = 0.53$). The soot-absorption efficiency is higher than modeling results. *Chýlek et al.* [1995] found that the specific absorption of soot is dependent on if the soot particle is internally or externally mixed with other chemical species and the specific absorption increases if it is internally mixed. Thus, the high absorption efficiency of soot aerosols suggests that it is present more as an internal mixture than as an external mixture. The soot mass concentrations ranged between 3 ng m^{-3} and 140 ng m^{-3} corresponding to a B_{ap} between 0.16 and 2.86 E-06 m^{-1} . These are lower than the value of 4.8 E-06 m^{-1} measured in the polluted boundary layer in the Mexico City basin [*Raga et al.* 1998]. The forcing obtained from the CRM for pure soot aerosols ranges from $+0.01$ to $+0.25 \text{ W m}^{-2}$ for the entire data set, for the same range of soot mass concentrations. Average values of $+0.13$, $+0.09$ and $+0.08 \text{ W m}^{-2}$ were obtained for polluted continental, continental, and marine air masses, respectively.

7.4.3 Mixture of sulfur and soot aerosols:

For an internal mixture of soot and sulfur ('internal' is used to imply that the soot particle is incorporated in the sulfate particle), the direct forcing ranged from $+0.25 \text{ W m}^{-2}$ to -1.07 W m^{-2} , with an average value of -0.32 W m^{-2} for soot-sulfate ratios between 0.01 and 1.12. The positive values of forcing were obtained for soot-sulfate ratios greater than 0.165. Average values of forcing of -0.41 , -0.33 and -0.20 W m^{-2} were obtained for polluted continental, continental and marine air masses, respectively. The soot-sulfate mass ratios for the summer months (May-August, 1997) at Mt. Gibbs were calculated to be between 0.01 and 0.06 [*Bahrmann and Saxena*, 1998]. These values are lower than

the soot-sulfate ratios for winter due to the higher sulfate concentrations during the summer months. The soot concentrations during summer were in the range of 0 to 200 ng m^{-3} and were not significantly higher than that during winter. Figure 7.4 represents a comparison of the forcing and aerosol mass concentrations for summer data and winter data. For the summer, the average negative forcing due to sulfates reduced by 1.2 W m^{-2} for an internal mixture of soot and sulfate for average soot-sulfate ratios of 0.03. For the winter cases, the reduction in forcing was 1.0 W m^{-2} for average soot-sulfate ratios of 0.19. Thus, wintertime reductions in sulfate forcing due to an internal mixture of soot and sulfate are higher than in summer, on account of lowered values of sulfate mass concentrations. Therefore, the soot-sulfate ratios during summer are well below the values needed to change the sign of the forcing.

Since ω_0 is usually indicative of the amount of scattering versus absorption, it is possible to calculate a critical value of ω_0 , such that, an increase in ω_0 beyond this value would result in an aerosol cooling effect and if ω_0 is less than this critical value a heating effect is produced. Depending on various assumptions, e.g., those for the mean surface albedo, the critical value for ω_0 is assumed to be between 0.70 and 0.90 [Bohren and Huffman, 1983]. Hansen *et al.* [1980] have estimated a critical ω_0 value of ~ 0.85 . Figure 7.5 indicates ω_0 obtained from measurements and that calculated using the Mie theory as a function of the direct forcing. For modeling results, the value for ω_0 at which the forcing changes sign is ~ 0.64 . Measurements reveal that for $\omega_0 > 0.59$, the forcing is negative with the exception of three cases where the forcing was positive for values of ω_0 of 0.70, 0.75 and 0.85. These values occurred during days 318, 319 and 320. While

the forcing was lower for days 318 and 319 (0.02 and 0.05 W m^{-2} , respectively), day 320 had a higher value of 0.25 W m^{-2} . The B_{scat} value for Day 320 from the nephelometer was much higher than the B_{ap} . The total particle concentration measured by the UFCPC was 1651 cm^{-3} . The ratio of the mass concentration of nitrates to sulfates was one of the highest for Day 320 as can be estimated from Fig. 7.2. Therefore, since nitrates are efficient scatterers of light, the B_{scat} value for this day was high even though the sulfate concentrations were not as high. Thus, this results in a higher value of ω_0 from observations. However, ω_0 calculated from the Mie code was $\sim 30\%$ lower since only the soot-sulfate ratio was accounted for in calculating the mass mixing ratio. This would imply that the direct forcing computed from the CRM does not adequately represent the forcing that would be obtained had all the identified chemical species been included in the estimation of the mass mixing ratio. *Chýlek et al.* [1988] have suggested that ω_0 and specific absorption for a particle composed of soot and sulfate is a very strong function of the location of soot within the sulfate particle. Since the volume averaging method used in this study did not account for the location of the soot particles within the sulfate particle, this could lead to the observed differences between calculated and measured values of ω_0 . The optical properties for a nonhomogeneous particle containing soot particle incorporated in a sulfate particle can be better approximated by means of modeling studies based on a layered sphere or on the effective medium approximations [Chýlek et al., 1995].

The hemispheric backscatter fraction (b) is defined as the fraction of scattered intensity that is redirected into the backward hemisphere. b can be found as a ratio of the

backscattering coefficient (B_{bscat}) to the scattering coefficient (B_{scat}), both measured by nephelometer at a given wavelength. Figure 7.6 shows the comparison of the measured and calculated values of b . An average value of 0.18 ± 0.04 was obtained from measurements with ranges between 0.13 and 0.29. A mean value of 0.12 ± 0.02 was obtained from the Mie code calculations with ranges between 0.10 and 0.20. The values are comparable to a mean value of 0.15 obtained at a rural location in eastern North America [Vanderpol, 1975]. Higher values are correlated to periods of fog or clouds. The largest differences in the values between model and experimental data occurs for days 311 through 316 and day 322, which did have some episodes of fog. Since the presence of fog was not accounted for in the Mie code calculations, a change in the refractive index of the soot-sulfate ratio (due to changes in the water content of the aerosols) may result in changes in b . The effect of non-sphericity of aerosols may also account for differences in values obtained by the Mie code that assumes particles are spherical. Backscattering is more affected by particle sphericity than is the total scattering as shown by *Mishchenko and Travis*, [1994]. The incorporation of chemical species, other than soot and sulfate in the calculation of the refractive index of the mixture may also cause the ratio to vary.

7.4.4 Influence of air masses on aerosol chemical, physical and optical properties

Table 7.1 lists average values of the chemical species such as sulfates, nitrates, ammonium and soot, the total particle number concentration and optical properties such as ω , B_{scat} , B_{ap} , B_{bscat} for polluted continental, continental and marine type air masses.

The direct forcing for sulfate, soot and an internal and external mixture of soot and sulfate are also listed. Highest values of forcing is obtained for the polluted continental air mass, that also had higher amounts of sulfate and lowest values were for the cleaner marine air masses that also had lower sulfates and lower values of soot.

Figure 7.7 represents the average aerosol size distribution for the three different air mass types, polluted continental, continental and marine, for the Julian days indicated. Highest values of $dN/d\log D$ are obtained for polluted continental air masses and lowest values are for marine air masses. The peak of the size distribution shifts from smaller diameters to larger diameters as the air masses changes from polluted continental to marine. Bimodal size distributions are exhibited by the continental and polluted continental air masses.

Due to the observed variations in the size-distribution for the marine, continental and polluted continental air masses, the average values for forcing that were obtained for these different air masses from the assumed log-normal size-distribution would be modified. e.g. The change in the magnitude of forcing caused by variations in the geometric diameter and the geometric standard deviation was calculated by varying the mean diameter by $\pm 40\%$ of the central value (i.e., between 0.06 and 0.14 μm) and the standard deviation by $\pm 30\%$ of the central value (i.e., between 1.5 and 2.6). The forcing increases by 18% for a 40% decrease in geometric diameter and decreases by $\sim 10\%$ for a 40% increase in geometric diameter. For a 30% decrease in the standard deviation, the forcing increases by 58% and a 30% increase in the standard deviation lowers the forcing by 20%. Thus, forcing estimates that are reported in this paper for the polluted

continental and continental air masses are probably lower than the forcing that would be obtained due to the much lower observed values of the geometric mean diameters than the assumed value of 0.1 μm and also due to the decrease in the geometric standard deviation. *Nemesure et al.* [1995] analyzed the effect of different size distributions on the direct forcing of sulfates and found dry particle size (determined by size distribution) to be one of the key quantities that influences forcing.

7.4.5 Effect of aerosol optical depth on forcing

The aerosol optical depth calculated from the MFRSR measurements were obtained for seven days for clear-sky afternoon and morning periods. Values ranged from 0.02 to 0.09 with an average value of 0.04. An analysis of the seasonal variability of optical depth made by *Flowers et al.* [1969] shows that the wintertime optical depth values are generally lower during winter than summertime. Table 7.2 lists values of optical depth, scattering and absorption optical depths (τ_{sc} and τ_{abs} respectively), and the magnitude of direct forcing. The forcing was calculated for an internal and external mixture of sulfate and soot aerosols using both the CRM and a first-order approximation suggested by *Chýlek and Wong* [1995], i.e.,

$$\Delta F = -\frac{S_o}{4} T^2 (1 - N)[(1 - a)^2 2 \beta \tau_{\text{sc}} - 4a\tau_{\text{abs}}], \quad (7.2)$$

where ΔF is the direct forcing of an optically thin aerosol layer, S_o is the solar constant, T is the transmittance of the atmosphere, N is the fraction of the sky covered by clouds, a is the surface albedo, and β is the upscatter fraction. The upscatter fraction is defined as the fraction of radiation that is scattered by the aerosol in the upward direction and is a

function of the asymmetry parameter. For an aerosol that only scatters the last term is zero and the equation reduces to *Charlson et al.*'s [1992] reference box model. The reflectance (R), transmittance and absorptance (A) of an optically thin aerosol layer over all angles of incoming radiation can be obtained as given in *Chýlek et al.* [1995] as;

$$R = 2 \tau \omega_0 \beta \quad (7.3)$$

$$T = 1 - 2(\beta \tau_{sc} - 2 \tau_{abs}) \quad (7.4)$$

$$A = 2 \tau_{abs} \quad (7.5)$$

The average values of τ_{sc} and τ_{abs} as given in Table 7.2 are 0.033 and 0.009. The values chosen for N and a are 0.4 and 0.15, respectively. Optical depth measurements are obtained at 550nm and are usually calculated during cloud-free skies. The value used for β is obtained from the Mie code and is ~ 0.19 . The absorption term in Eq. (7.2) is multiplied by a factor of 0.6 as only about 60% of solar radiation is within visible spectral range and soot particles affect the sulfate optical properties only in the visible part of the spectrum [*Chýlek et al.*, 1995].

The range of forcing obtained using the above values was -0.52 to -1.17 W m^{-2} with a value of $\sim -0.77 \text{ W m}^{-2}$ on an average. *Chýlek et al.* [1995] used values of 0.76 for T, 0.6 for N, 0.29 for β and values of 0.04 and 0.0006 for τ_{sc} and τ_{abs} . The values for forcing obtained by *Chýlek et al.* [1995] are -1.31 W m^{-2} and that by *Charlson et al.* [1992] is -1.22 Wm^{-2} . However, *Charlson et al.* [1992] did not consider the absorption term. Neglecting the absorption term in Eq. (7.2) results in an increase in the negative forcing by 17%. The above estimate for forcing is sensitive to the value of upscatter fraction. Increasing β from 0.19 to 0.29 increases the negative forcing from -0.77 to $-$

2.07 W m^{-2} . Higher values of forcing are also obtained for lower cloud fractions. A 20% decrease in transmission resulted in only a 2% change in forcing from -0.77 to -0.75 W m^{-2} . Using the first-order approximation as given in Eq. (7.2), the average value of forcing was overestimated by 70% from the average obtained using the CRM.

7.5. Conclusions

The magnitudes of direct forcing at a rural mountaintop location in the southeastern U.S for wintertime sulfate aerosol concentrations are -0.91 , -1.34 and -1.81 W m^{-2} and $+0.08$, $+0.09$ and $+0.13 \text{ W m}^{-2}$ for soot aerosols for marine, continental and polluted continental air masses, respectively. For an internal mixture of soot and sulfate aerosols the forcing values are -0.32 , -0.55 and -0.66 W m^{-2} for marine, continental and polluted continental air masses. A positive forcing was obtained when the soot-sulfate ratio exceeded 0.165. The single scattering albedo calculated from measurements as well as from modeling results indicated that the forcing changed signs from a positive value to a negative value when the single scattering albedo exceeded 0.64 for the modeling results and 0.59 for measurements at $\lambda = 550 \text{ nm}$. The differences in the measured and calculated single scattering albedo may be due to errors in determining the composite refractive indices of the soot and sulfate mixtures. Since the refractive index used in the Mie code was for an internal mixture of soot and sulfate, the change in refractive index due to the presence of other chemical species that were not identified could cause the differences observed between measurements and modeling results.

A reasonably good correlation was obtained between daily trends of average values of light scattering coefficient and sulfate mass concentrations as well as with light absorption coefficient and soot mass concentrations. The value of sulfate-scattering efficiency obtained was $7 \text{ m}^2 \text{ g}^{-1}$ and that for soot-absorption was $20 \text{ m}^2 \text{ g}^{-1}$. The high value of the soot-absorption efficiency suggests that the soot particles are present as internal mixtures along with other aerosols. The values of the hemispheric backscattered fraction were found to be between 0.13 to 0.29 from measurements and that from the Mie code calculations was found to be between 0.1 and 0.2. This fraction was found to be correlated to periods of fog or cloud.

Aerosol optical depth calculated from measurements for the atmospheric column was found to be between 0.02 to 0.09. These values were used to obtain an estimate of the forcing using a simple first-order approximation as given in *Chýlek et al.* [1995]. The magnitude of direct forcing as calculated using the first order approximation overestimated the forcing by 70%. Higher values of forcing are obtained for lower cloud fractions and an increase in the upscatter fraction.

Analyses of results obtained from measurements and modeling suggest that the presence of soot and sulfate alone cannot account for the optical properties of the atmosphere as was observed. The interaction of these particles with other accumulation-mode particles would probably lead to a better comparison of modeling and measurements. Comparison of the hemispheric backscattering efficiency as obtained from the Mie code and from measurements suggests that the assumption of a spherical particle used in the Mie code may also lead to unsatisfactory results. The values of the

forcing obtained indicate higher magnitudes both for summer and for winter than was obtained from previous modeling results. Since most modeling studies assume that aerosols are usually confined to the 1 km boundary layer, the high values of forcing that were obtained for aerosols at a vertical elevation of ~ 2 km suggest that the overall influence of aerosols on radiative forcing for the southeastern US is much higher than previous estimates. The decreased sulfate concentrations in winter and the lack of any strong seasonal variations in soot concentrations led to greater reductions in the winter-time sulfate forcing due to an internal mixture of soot and sulfate as compared to summer-time results. The direct effect in areas where either sulfate or soot are present above clouds cannot be ignored. However, we have not been able to take this into account in the present study. Using observed values of the aerosol size distributions for the different air masses will lead to more realistic values of forcing.

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Table 7.1. Average values of the identified chemical species, light scatter and light absorption coefficients (B_{ap} and B_{scat}), total particle number concentration (Na), single scatter albedo (ω_o) and the direct forcing for sulfate, soot and an internal mixture of sulfate and soot. The average values are obtained for three different air mass types, identified as marine, continental and polluted continental.

Source	NO_3^-	$SO_4^{=}$	NH_4^+	Soot	B_{ap}	B_{scat}	ω_o	Total Na	Forcing sulfate	Forcing soot	Forcing Internal mixture	Forcing External mixture
	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	m^{-1}	m^{-1}		cm^{-3}	$W\ m^{-2}$	$W\ m^{-2}$	$W\ m^{-2}$	$W\ m^{-2}$
Marine (6 cases)	0.13	0.56	0.22	0.044	1.29E-06	5.11E-06	0.70	1109	-0.91	0.08	-0.19	-0.83
Continental (4 cases)	0.18	0.78	0.31	0.051	1.26E-06	5.27E-06	0.78	1857	-1.34	0.09	-0.33	-1.25
Polluted Continental (8 cases)	0.26	0.91	0.28	0.078	1.57E-06	7.23E-06	0.81	2219	-1.81	0.13	-0.42	-1.68

Table 7.2. Average values of total particle concentration (Na), single scatter albedo (ω_o) from the Mie code and from measurements, total aerosol optical depth, scattering and absorption optical depths (τ_a , τ_{sca} and τ_{abs}) and forcing as obtained from the column forcing model and using the approximation as given by *Chýlek et al.* [1995]. The time period is for the indicated Julian days, M stands for morning averages and A stands for afternoon averages. Indicated time periods coincide with the time period of available optical depth measurements.

Julian day	Particle Conc. N(a) cm ⁻³	ω_o (B _{scat} /B _{ap})	ω_o (Mie code)	τ_a	τ_{abs}	τ_{sca}	Direct forcing Internal mixture W m ⁻²	Direct forcing External Mixture W m ⁻²	Direct forcing using <i>Chýlek et al.</i> [1995] approx. W m ⁻²
308 M	601	0.68	0.80	0.029	0.013	0.027	-0.38	-1.12	-0.52
308 A	854			0.051					
309 A	2285	0.79	0.72	0.047	0.010	0.037	-0.18	-1.08	-0.84
314 M	594	0.78	0.66	0.035	0.008	0.027	-0.02	-0.43	-0.61
321 M	321	0.87	0.81	0.023	0.005	0.032	-1.07	-2.44	-0.92
321 A	770			0.051					
322 M	1048	0.79	0.64	0.029	0.013	0.046	0.00	-0.97	-0.99
322 A	681			0.088					
323 A	1874	0.82	0.78	0.059	0.011	0.048	-0.97	-2.62	-1.17
324 M	2519	0.83	0.74	0.016	0.003	0.013	-0.50	-1.91	-0.35

Figure 7.1. Average values of sulfate mass concentration measured from the Multiple-orifice cascade impactor and the light scattering coefficient (B_{scat}) at 550 nm measured from the nephelometer for the indicated Julian days.

Figure 7.2. Average values of soot mass concentration measured from the Aethalometer and light absorption coefficient (Bap) at 565 nm measured by a Soot absorption photometer for the indicated Julian days.

Figure 7.3. Average values of the mass concentration of indicated chemical specie and soot measured from the Multiple-orifice cascade impactor and the total aerosol mass concentration obtained from a tapered element oscillating microbalance aerosol mass monitor for the indicated Julian days.

Figure 7.4. Average values of sulfate and soot mass concentrations for the summer and winter. Summer values were obtained from 1996. Winter values are for 1997. The magnitude of forcing as obtained from the column forcing model for sulfate, soot and an internal mixture of sulfate and soot are indicated.

Figure 7.5. The hemispheric back scattered fraction (b) defined as the ratio of the back scattering efficiency (B_{bscat}) and the light scattering coefficient (B_{scat}) for the different Julian days. The values of b are obtained from both the Mie code and from measurements.

Figure 7.6. The hemispheric back scattered fraction (b) defined as the ratio of the back scattering efficiency (B_{bscat}) and the light scattering coefficient (B_{scat}) for the different Julian days. The values of b are obtained from both the Mie code and from measurements.

Figure 7.7. The log-normal size distribution as obtained from the Scanning mobility particle sizer for the different air masses for the indicated Julian days.

8. DIRECTIONS FOR FUTURE WORK

8.1 Recommendations

Increases in cloud cover are known to impact changes in minimum and maximum temperatures (Jones, 1994). Changes in cloud lifetimes in sulfate enriched atmosphere could account for part of the increase in cloud cover. To analyze the impact of sulfate aerosols on cloud amount, changes in cloud cover and cloud optical depth from the International Satellite Cloud Climatology Project (ISCCP) satellite data needs to be investigated for the Southeast. Quantitative comparisons of observed changes in surface temperature with estimated forcing would indicate the presence or absence of spatial coherence between calculated forcing patterns and observed temperature changes (Kiehl and Rodhe, 1995). Karl et al. (1995) found empirical evidence of sulfate aerosol forcing on surface-air temperature from the analysis of time rates of change of SO_x emissions and maximum and minimum temperature stratified by cloud amount. The decrease in maximum daily temperature with increasing SO_x emissions would possibly lead to a change in the optical thickness of the atmospheric column (Karl et al., 1995). Therefore, they suggest that the indirect effect of sulfate aerosols on CCN could be found by analyzing the temperature change on cloudy days. However, Karl et al. (1995) found that the apparent sulfate aerosol impact for overcast conditions was not substantially larger than in the clear-sky case. They did not include the probable impact of sulfate aerosols on cloud amount. Thus, they were not able to provide evidence from their analysis to support the indirect role of aerosols via CCN. Since the aerosol-forcing signal could be

masked by the presence of low clouds, changes in the low cloud cover from 1986 through 1996 can be used to estimate if there is a correlation between variations in temperature changes, sulfate amount, cloud cover and cloud optical depth.

Preliminary calculations from our experimental results have suggested that the aerosol negative forcing effect for the Southeast is of greater magnitude than predicted by modeling studies. In order to obtain a more detailed understanding on the cloud-aerosol interaction processes and its climatic effect, it would be desirable to:

1. Obtain a quantitative estimate of the magnitude of indirect aerosol forcing from 1986 onwards using a regional climate model. With the projected increase in sulfate as was observed from the 11-year trend (1986-97), what changes can one anticipate in regional radiative forcing for the Southeast?
2. Derive changes in indirect aerosol forcing for the Southeast during the last decade (1986-97) using a climate model that will have as input in situ data and the empirical relationships that have been developed. This can be used to detect climate change signal on the scale of a decade,
3. Establish a climatology of trends in the droplet number concentration as a function of sulfate content of cloud forming air masses and cloud liquid water from 1986 onwards. The values of droplet number concentration obtained can be used in the estimation of changes in cloud reflectivity since 1986 for the Southeast. Climate change signals for the Southeast can be deciphered from trends in cloud reflectivity. Model predictions for climate change can then be validated using these observational values,

4. Examine the effect of sulfates and other non-sulfate species such as organics and black carbon on cloud albedo and their contribution to the indirect effect for the Southeast. Since it appears that organics could be a major contributor to the chemical species, the role of organics in aerosol radiative forcing must be considered,
5. Obtain a better estimate of the vertical variations in cloud liquid water content and cloud microphysical properties within the cloud. Since cloud optical depth and reflectivity are very sensitive to cloud thickness, the cloud thickness needs to be determined more accurately. This would aid in better comparison of cloud albedo calculated from in situ measurements and that retrieved from satellite data. Since satellite retrieved cloud albedo takes into account reflectance from the cloud top, cloud microphysical variables at the cloud top needs to be determined more accurately.

The observed changes in the drop size distribution and cloud amount due to sulfates should be used to infer changes in the radiative forcing for the regional site by using a chemistry model coupled with a climate model. Since, the results and empirical relationships presented in this study are dependent on the sulfate concentrations, changes in sulfate concentrations can cause differences in the radiative forcing estimates. Thus, monitoring of cloud chemical and microphysical properties would have to be continued in view of the expected decline in sulfate emissions projected for the southeastern U.S. This would enable better climate change predictions.

8.2 References

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APPENDICES

APPENDIX A

LIST OF PUBLICATIONS AND PRESENTATIONS

Refereed Journal Articles

1. Menon, S. and V.K Saxena, 1998: Role of sulfates in regional cloud-climate interactions, *Atmospheric Research*, 47-48, 299-315.
2. Menon, S., V.K Saxena, P.A. Durkee, W.P. Robarge, B.N. Wenny, and K. Nielsen, 1998: Observed effects of sulfates on light scattering, cloud reflectivity and cloud susceptibility, *Journal of Geophysical Research*, (in submission).
3. Menon, S., V.K. Saxena and B.D. Logie, 1998: Observations of the chemical heterogeneity within cloud droplets, *Journal of Applied Meteorology*, (in revision).
4. V.K. Saxena and S. Menon, 1998: Observations of cloud microphysical-chemical properties and its counteracting effect on regional warming, *Science*, (in submission).
5. Menon, S., V.K. Saxena and A.H. Omar, 1998: Wintertime direct radiative forcing effects of sulfate and soot aerosols over a mountaintop location, *Journal of Geophysical Research*, (in submission).
6. Saxena, V.K., P.A. Durkee, S. Menon, J. Anderson, K.L. Burns and K.E. Nielsen, 1996: Physico-chemical measurements to investigate regional cloud-climate feedback mechanisms, *Atmospheric Environment*, 30, 1573-1579.

Conference Proceedings

1. Menon, S. and V.K. Saxena, 1998. Trends in sulfate aerosols in the southeastern U.S. prior to and after the implementation of the clean air act amendment, *Proceedings of 18th symposium of the Air and Waste Management Association*, Sep 1-3, 1998, Cary, NC.
2. Saxena, V.K., P. Durkee, W.P. Robarge, S. Menon and K. Nielsen, 1998. Susceptibility of cloud albedo to sulfate content of cloud forming air masses. *Proceedings of 1998 AMS Conf. on Cloud Physics*, Aug 17-21, Everett, WA.
3. Menon, S. and V.K. Saxena, 1998. Observational study on the cloud-mediated effect of sulfates in the southeastern U.S. *Joint Symposium on Global Atmospheric Chemistry*, Aug 19-25, Seattle, WA.
4. Saxena, V.K. and S. Menon, 1998. Collection of mountaintop clouds by a size-segregated sampler: Implications on regional climate. *Proceedings of 1st Intl. Conf. on Fog and Fog Collection*, July 20-24 1998, Vancouver, Canada.
5. Menon, S. and V.K. Saxena, 1998. Effects of the chemical and microphysical properties of aerosols on cloud radiative properties for the southeastern U.S. *Proceedings of AGU 1998 Spring Meeting*, May 26-29, Boston, MA.
6. Menon, S., V.K. Saxena, P. Durkee, W.P. Robarge, B.N. Wenny and K. Nielsen, 1997. Effect of sulfates on light scattering and cloud reflectivity. *Proceedings of 3rd AMS Conf. on Atmospheric Chemistry*, Feb 2-7, Long Beach, CA, 107-113.
7. Menon, S. and V.K. Saxena, 1997. Role of sulfates in cloud-climate feedback mechanisms. *Proceedings of AGU 1997 Spring Meeting*, May 27-30, Baltimore, MD, S69.
8. Saxena, V.K. and S. Menon, 1996. Regional climate change: Cloud-mediated effect of aerosols, *Proceedings of 4th Intl. Conf. of the Israeli Society for Ecology and Environmental Quality Sciences*, June 30-July 4, Jerusalem, Israel, 29-32.

9. Saxena, V.K., P. Durkee, S. Menon, J. Anderson and K. Nielsen, 1996. Cloud-climate feedback mechanisms: results from a ground-based closure experiment. *Proceedings of 12th Intl. Conf. on Cloud and Precipitation*, 19-23 August, Zurich, Switzerland.
10. Saxena, V.K., S. Menon, J. Anderson, B.N. Wenny, C.K. Deninger, B.D. Logie, S.J. Schafer, J.C. Ulman, C. Bahrmann, W.P. Robarge and P.A. Durkee, 1996. Impact of changes in cloud microstructure on cloud albedo. *Proceedings of AGU 1996 Spring Meeting*, Baltimore, MD.
11. Saxena, V. K and S. Menon, 1996. Impact of sulfate aerosols on short-wave albedo of clouds: A field study. *Proceeding of 4th Intl. Conf. on Nucleation and Atmospheric Aerosols*, 26-30 August, Helsinki, Finland.

Reports submitted to the National Institute for Global Environmental Change

1. Saxena, V.K., S. Menon, S.-C. Yu and C. Petrusac, 1998. Direct and cloud-mediated effects of aerosols in counteracting greenhouse warming in the southeastern US. In: *Annual Report Fiscal Year 1997*, National Institute of Global Environmental Change (NIGEC), Univ. of CA, Davis.
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4. Saxena, V.K., S. Menon, P.A. Durkee, W.P. Robarge, J. Anderson, B.N. Wenny, C.K. Deninger, B.D. Logie, J.S. Schafer, J.C. Ulman, S.-C. Yu and C. Bahrmann, 1995. Cloud-Climate Feedback Mechanisms: Impact of Reduction in Fossil-Fuel Emissions. Final Technical Report for 1993-95, SRC – NIGEC, Environmental Institute Publication No 51, Univ. of Alabama, Tuscaloosa, 1-44.