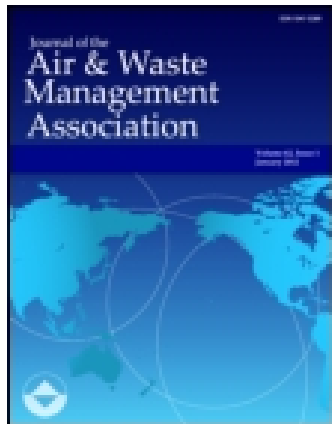


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Microphysical Effects on Cloud Water Acidity: A Case Study in a Nonprecipitating Cloud Event Observed at Mt. Mitchell, North Carolina

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NOTE-BOOK

Microphysical Effects on Cloud Water Acidity: A Case Study in a Nonprecipitating Cloud Event Observed at Mt. Mitchell, North Carolina

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There is increasing recognition that deposition of cloudwater may significantly contribute to the decline of forest, particularly at elevated sites where immersion in clouds occurs frequently.¹⁻⁵ Concentrations of major ions in nonprecipitating clouds and fogs have been reported to be significantly higher than those commonly observed in acidic precipitation.⁶⁻⁹ Lower dilutions and higher scavenging efficiencies due to reduced mass transfer limitations of gas phase absorption and longer residence times may explain, in part, the higher concentrations found in fog and cloud (droplet characteristic diameter: 1–100 μm) than in rain (droplet characteristic diameter: 0.1–3.0 mm).¹⁰ Fog and cloud water deposited on surfaces exposed to the atmosphere by wind-driven interception or settlement of the largest drops can enhance the damaging effects of substances previously deposited by dry deposition.³ This is especially true at the high elevation locations, while acidic exposure due to clouds may be about five fold due to rain over the same time period.⁵ Temporal variation of cloud water acidity during a cloud event is affected by cloud microphysical processes such as condensational growth and evaporative dissipation of cloud droplets.^{1,5} In warm clouds, wet deposition operates via the removal of aerosol particles by condensation (nucleation scavenging). This is done by transforming some of the aerosol particles into cloud droplets as a result of heterogeneous nucleation from the vapor, and via the removal of aerosol particles by impaction (impaction scavenging). Another method is by attaching aerosol particles to cloud and rain drops through the mechanism of Brownian diffusion, inertia and hydrodynamic forces, and via the transport of the scavenged materials to the ground.¹¹

In this paper, chemical and microphysical data obtained at Mt. Mitchell, North Carolina during one orographic cloud event (nonprecipitating) are examined to investigate the relationship between temporal variation of cloud acidity and cloud microphysics.

Sampling Site and Measurements

The sampling site is located in the Mt. Mitchell State Park, North Carolina. Mt. Mitchell is the highest peak (35°44'03" N, 82°17'15" W; 2,038 m MSL) in the eastern United States, and it is about 600 km west of the Atlantic coast. The topographical map of Mt. Mitchell area is shown in Figure 1.

All measurements, to characterize the chemical climatology, were taken on or near a 16.5 m tall aluminum walk-up tower installed near Mt. Gibbs (2,006 m MSL) which is located approximately 2.5 km southwest of Mt. Mitchell. The tower is equipped^{12,13} with the standard meteorological instrumentations (temperature, relative humidity, wind speed and direction, solar radiation and ambient pressure), a passive and an active cloud water collector, a Forward Scattering Spectrometer Probe (FSSP) and gas pollutant sensors (O_3 , SO_2 and NO_x). The cloud water was sampled with cloud and rain acidity/conductivity (CRAC) real time automated system, and it was analyzed chemically in the laboratory (major anions; SO_4^{2-} , NO_3^- , Cl^- , and major cations; H^+ , NH_4^+ , Ca^{2+} , Mg^{2+} , Na^+ , K^+).¹² The cloud pH and conductivity were measured directly by the CRAC system in the field. The liquid water content (LWC) of the cloud water was measured by a gravimetric technique.¹⁴

Results and Discussion

It was found that cloud water acidity was lower in mixed cloud (precipitating cloud) events ($\text{pH} = 3.57 - 4.05$) than in short cloud (≤ 8 hours nonprecipitating cloud) events ($\text{pH} = 3.03 - 3.23$), while the liquid water content was higher in mixed events ($0.32 - 0.71 \text{ g m}^{-3}$) than in short cloud event ($0.15 - 0.24 \text{ g m}^{-3}$).¹⁵ In cases of nonprecipitating cloud events, the average cloud pH for short events ($\text{pH} = 3.03 - 3.23$) were much lower than those for long events ($\text{pH} = 3.40 - 3.59$) as the average liquid water content increases from short events ($0.15 - 0.24 \text{ g m}^{-3}$) to long events ($0.22 - 0.54 \text{ g m}^{-3}$). This could be the result of dilution effect of airborne materials (particles and gases) in cloud drops due to abundant moisture in the long cloud events (> 8 hours duration) rather than the short cloud events.

A short cloud event occurred on August 19, 1987. It was chosen to examine the role of microphysical effects on the cloud water acidity. A total of 13 cloud water samples were collected during this event lasting about 3 hours. These samples were chemically analyzed for major cations and anions in the laboratory. Sequential variation of the concentration of four principal ions, and total concentration of major ions in cloud water with time interval are presented in Figure 2. It shows that the principal ions are hydrogen, ammonium, sulfate and nitrate; and their combined contribution is almost 98% of the total analyzed fraction of equivalents of all ionic constituents expressed as a percent

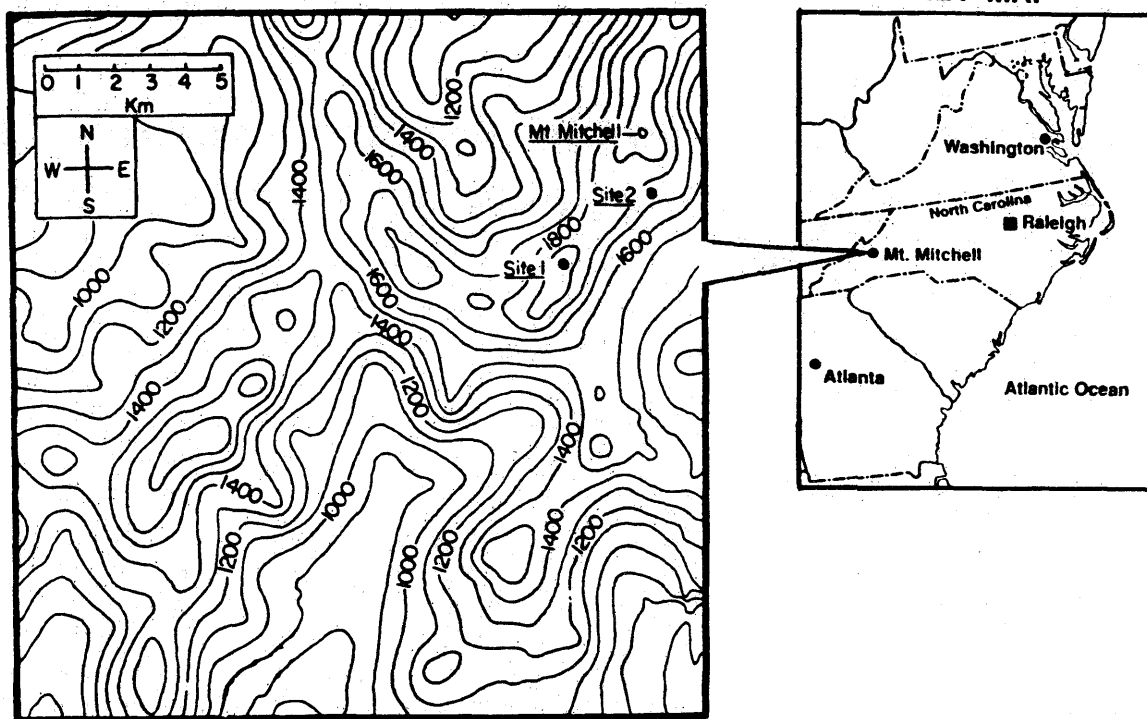


Figure 1. Topographical map of Mt. Mitchell site (Mt. Gibbs, NC) area.

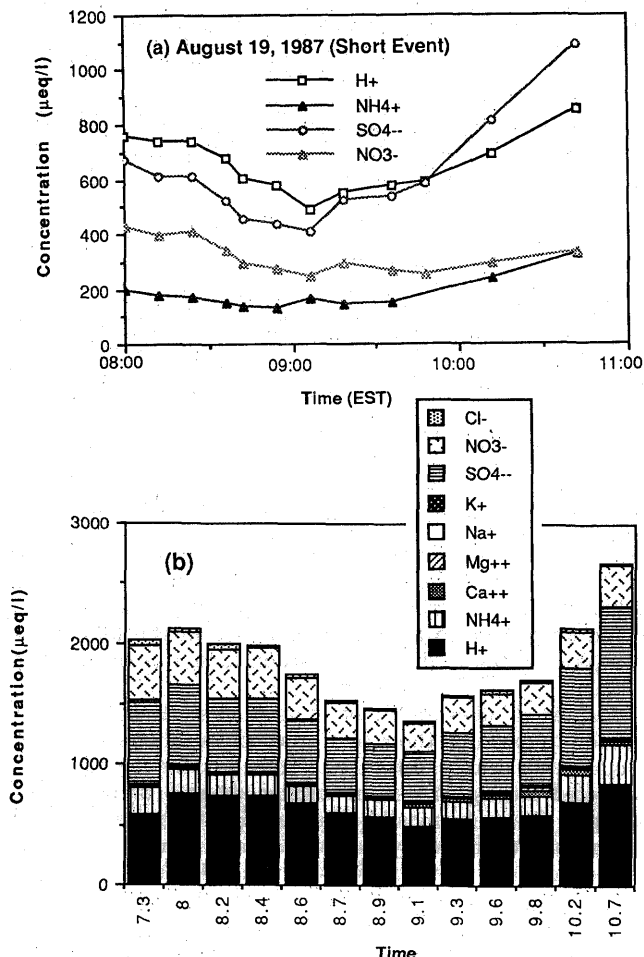


Figure 2. Total concentration of cloud water for (a) four principal ions and (b) all major ions during August 19, 1987 event.

in the cloud event. A concave trend in the profile of cloud water pollutant concentration versus time was observed, i.e., total concentration decreasing from the leading edge of the cloud to about 1 hour after, then rising toward the trailing edge of the cloud event. We also frequently observed that the pH increases during the beginning hours and decreases during the final hours of cloud event. These types of temporal variations in cloud water ionic concentrations and acidity have also been observed earlier.^{1,5,9,15,16} These observations suggest that water vapor condensation and evaporation of cloud droplets are the primary dominant processes in determining the total ionic concentration and acidity of the cloud water.

Figure 3 shows the temporal variations of the physico-chemical changes of the system (i.e., cloud water pH, solar radiation, temperature and relative humidity) during the cloud event of August 19, 1987. The pH of the cloud water increases during the beginning hour and decreases during the final hours of the cloud event. Sharp increase of cloud water pH during the first hour of event is attributed to initial droplet deliquescence on pre-existing aerosols. Similarly, decrease in pH during the final hours of the cloud event may be due to evaporation and/or regeneration of fine aerosol particles resulting from a host of heterogeneous chemical reactions induced by increasing temperature and/or due to enhanced photochemical production of HNO₃ and H₂SO₄ due to increased light intensity. During the final hours of the cloud event, an increase in temperature and solar radiation and a decrease in relative humidity were observed (Figure 3). Figure 4 shows the corresponding trend of the average microphysical parameters (liquid water content, average droplet size and droplet concentration) and the pH variation with time during the cloud event. We observed that liquid water content, average droplet size and droplet concentration decreased during the final hours of the cloud event while temperature increased and the relative humidity decreased during the corresponding time

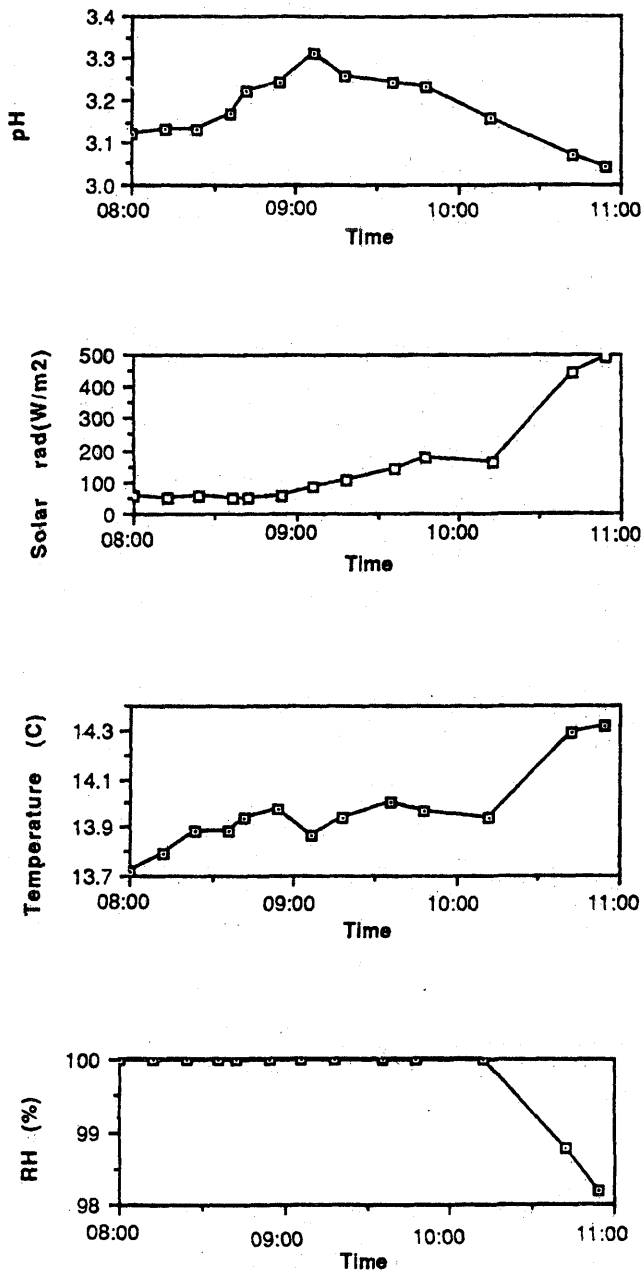


Figure 3. Cloud water pH, solar radiation, temperature and relative humidity with respect to time for August 19, 1987 cloud event.

period. These observations may suggest that evaporative dissipation of cloud droplets leads to the acidification of cloud water during the final hours of the cloud event.

Figure 5 shows the mean drop size distributions using Khrgian-Mazin¹⁷ empirical size distribution for the short cloud event of August 19, 1987. Most, but not all, drop size distributions measured in many different types of clouds under a variety of meteorological conditions exhibit this characteristic shape. Generally, the concentration rises sharply from low to a maximum, and then decreases gently towards the larger sizes, causing the distribution to be positively skewed with a long tail toward the larger sizes.¹⁸ Such a characteristic shape can be approximated well by either the lognormal or gamma distribution function. Khrgian and Mazin developed empirically mean drop size distribution, and their empirical size distribution can be expressed as

$$n(r) = Ar^2 \exp(-Br), \quad (1)$$

where $n(r)dr$ represents the number concentration of drops

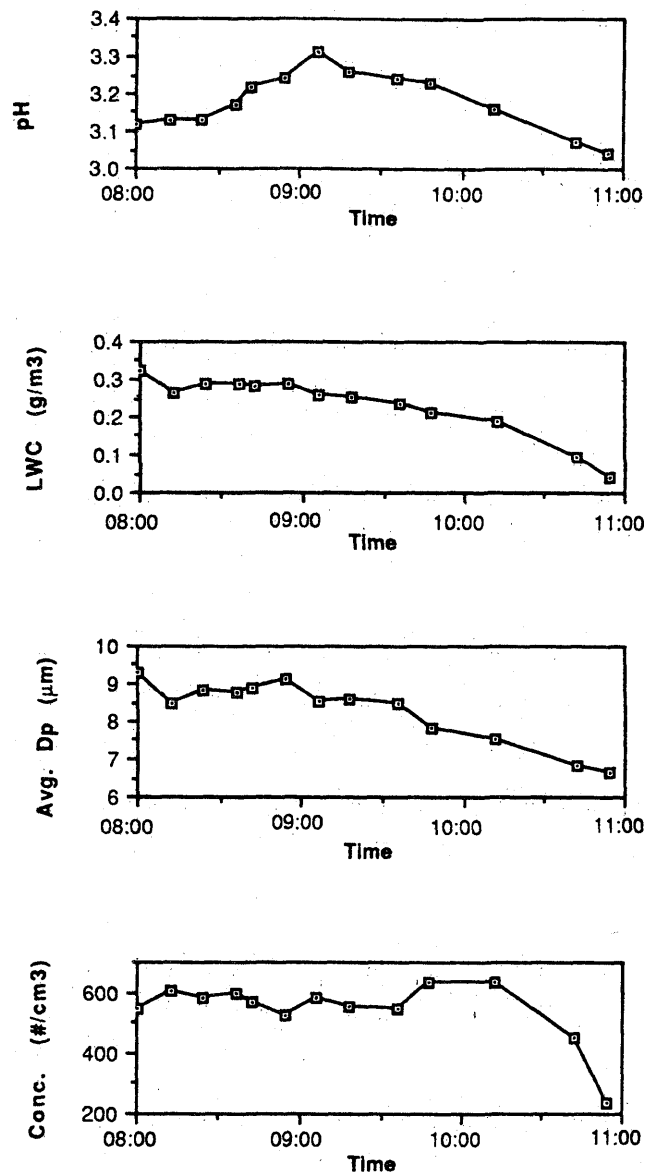


Figure 4. Cloud water pH, liquid water content, average droplet size and total concentration with respect to time for August 19, 1987 cloud event.

(cm^{-3}) in the radius range $(r, r + dr)$. The parameters A and B can be related to any two moments of the distribution. In terms of the total concentration N , and the average radius \bar{r} , then

$$N = \int_0^\infty n(r) dr = \frac{2A}{B^3}, \quad (2)$$

and

$$\bar{r} = \frac{1}{N} \int_0^\infty rn(r) dr = \frac{3}{B}. \quad (3)$$

To fit the empirical distribution function to mean drop size distribution with total concentration, equation (2) can be integrated on a specified range of droplet size (r_1, r_2) , and then it becomes

$$N(r_1, r_2) = \frac{A}{B} \left[e^{-Br} \left(r^2 + \frac{2}{B}r + \frac{2}{B^2} \right) \right]_{r=r_1}^{r=r_2}. \quad (4)$$

The corresponding equation for cloud liquid water content, LWC, is

$$\text{LWC}(\text{g/m}^3) = 10^6 \left(\frac{4\pi}{3} \right) \rho_w \int_0^\infty r^3 n(r) dr \quad (5)$$

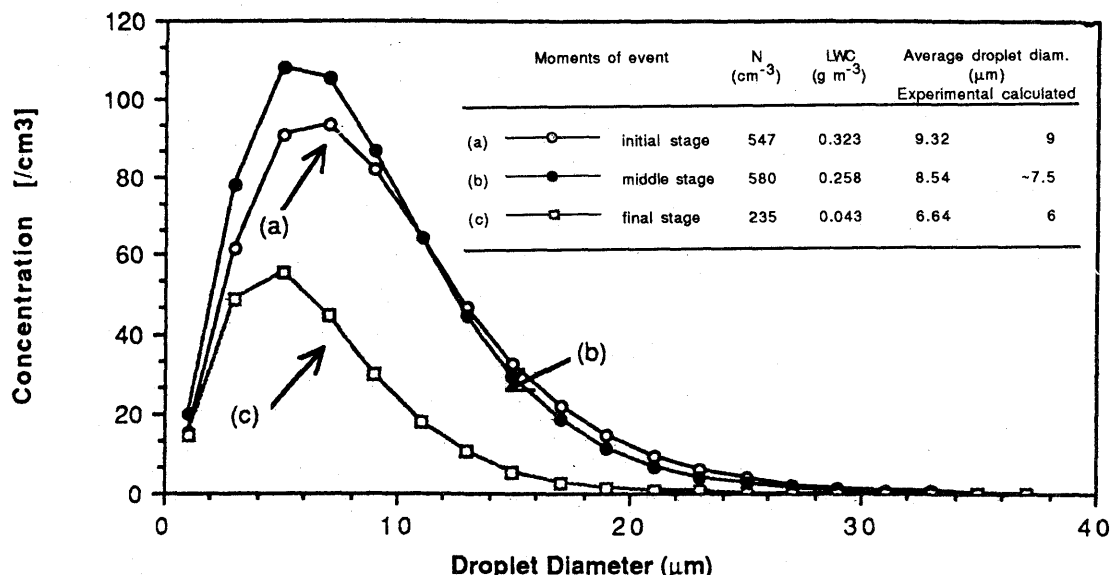


Figure 5. The fitted curves using Khrgian-Mazin drop size distribution at three different moments of the event; (a) initial, (b) middle, and (c) final stage of the event, during a cloud event lasting about 3 hours on August 19, 1987. The data in table are five minutes averaged total cloud droplet number concentrations, LWC, and averaged droplet diameters—experimental and calculated.

where ρ_w is the density of water in $g\ cm^{-3}$, and r is in cm.

These analytical expressions represent only average distributions. In this analysis five minutes averaged values were used to ascertain mean drop size distributions (equation 4), and/or LWC (equation 5).

Mean drop size distributions at three different moments of the cloud event; (a) initial stage (first five minutes of the event) (b) middle of the event (cloud water acidity is a minimum) and (c) final stage of the event (cloud water acidity is a maximum), are presented in Figure 5. The distributions show that an expected feature in which the modal droplet sizes (initial stage; $\sim 9\ \mu m$ characteristic diameter) smoothly shifts leftward as cloud dissipates (final stage; $\sim 6\ \mu m$). The highest droplet concentration appears at the middle stage ($580\ cm^{-3}$) of the event, and the lowest droplet concentration appears at the final stage ($235\ cm^{-3}$) of the event (Figures 4 and 5). The spread of drop size distribution in the final stage (average droplet size range; $1\text{--}25\ \mu m$) of the event is narrow compared to the other two stages (average droplet size range; $1\text{--}38\ \mu m$). These results

may also suggest that the evaporative dissipation of cloud droplets is a dominant process to acidify the cloud water in the final stage of the short orographic cloud event.

Figure 6 shows the plots of measured LWC versus LWC calculated by Khrgian-Mazin model equation for different cloud droplet size ranges. A linear relationship (at a correlation coefficient ~ 0.95) is observed in all the size ranges. However, the best fit (i.e. about one-to-one correlation) for measured LWC is obtained when the cloud droplet size range is in $0\text{--}20\ \mu m$ characteristic diameter. For the other size ranges considered the slope is ~ 0.7 (Figure 6). This further suggests that the droplet size measurement, using the Forward Scattering Spectrometer Probe (FSSP) in the particular cloud event, is in the range of about $0\text{--}20\ \mu m$ droplet size, as determined earlier.

Summary

Cloud chemical composition and acidity, sampled during one nonprecipitating cloud event, were analyzed based on nearly real-time cloud composition data to examine its relationship to cloud microphysics. The cloud acidity in nonprecipitating cloud events were substantially higher than those in precipitating cloud events. Sulfate, nitrate, ammonium and hydrogen ions were found to be the major constituents of the cloud water, and they accounted for $\sim 98\%$ of the total analyzed fraction of equivalents of all ionic constituents expressed as a percent in the cloud event. The profile of cloudwater ionic concentration versus time was observed to show decrease at the beginning and rising toward the end during the orographic cloud event. It suggests that water vapor condensation and evaporation of cloud droplets are the dominant processes in determining the total concentration of cloud water. Temporal variation of pH was investigated with respect to the microphysical parameters (liquid water content, average droplet size and droplet concentration) and meteorological parameters (temperature, solar radiation and relative humidity). During the final hours of the cloud event, decrease of cloud water pH was found, while temperature and solar radiation increased and relative humidity decreased. These observations may suggest that evaporative dissipation of cloud droplets leads

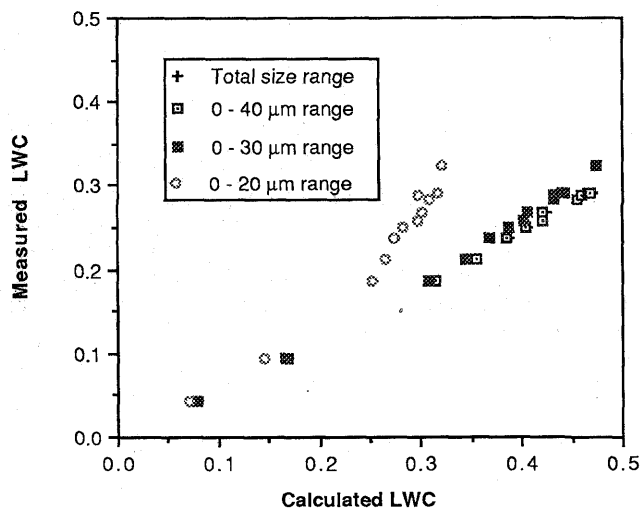


Figure 6. Plots of measured LWC vs. calculated LWC for different droplet size ranges (LWC in $g\ m^{-3}$).

to acidification of cloud water during the final hours of cloud event.

Acknowledgments

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