Chemical Heterogeneity across Cloud Droplet Size Spectra in Continental and Marine Air Masses

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ABSTRACT

Variations in the chemical composition of cloud droplets of different sizes are predicted in models. Measurements made in natural clouds to verify this prediction are extremely limited, however. During the spring of 1995 and the summers of 1995 and 1996, a size-fractionating version of the California Institute of Technology active-strand cloud water collector was operated on a mountaintop platform in Mount Mitchell State Park, North Carolina (35°44′05″N, 82°17′15″W), to examine differences in drop chemistry between large and small cloud droplets. The size-fractionated measurements also were compared with the chemical composition collected from a passive string–type collector that collects bulk samples. 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. The differences in cloud drop acidity and chemical constituents were investigated for these different air masses. On average, smaller drops were more enriched in SO_4^{2-}, NO_3^-, NH_4^+, and H^+; larger droplets had higher values of Na^+, Ca^{2+}, and Mg^{2+}. Samples were collected for which the reverse was true, however. In this study, cloud droplet chemical inhomogeneity between droplet sizes and the effect of airmass origin on variations in the chemical composition were examined. Smaller droplets were found to be more acidic than were larger droplets for both marine and polluted continental air masses. The sodium content was the highest in the larger drops for marine events. The sulfate content in both the larger and smaller droplets was the highest for air masses that were from the polluted continental sector. Slightly higher solute concentrations for the larger droplet size range were found for events caused by orographic lifting; for cloud events influenced by frontal activity, higher solute concentrations were found for the smaller drop size range.

1. Introduction

Cloud water chemical behavior is significant because of its potential effect on the environment through 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 and thereby affecting the climate (Twomey 1974, 1977, 1991; Charlson et al. 1992; Saxena et al. 1996; Menon and Saxena 1998). It has been suggested (Hegg and Hobbs 1981; Lelieveld and Heintzenberg 1992; Easter and Peters 1994) that the majority

of global atmospheric sulfate (SO_4^{2-}) 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 phase than in the gas phase (Seinfeld 1986).

Increases in sulfate production are thought to generate larger numbers of cloud condensation nuclei (CCN) (e.g., see Radke and Hegg 1972; Hegg 1991; Langner et al. 1992; Lelieveld and Heintzenberg 1992; Leaitch and Isaac 1994; Easter and Peters 1994), though there is no agreement on the generation mechanism. To estimate possible climatic effects such as increases in CCN and consequently the cloud droplet number concentration (N) that lead to changes in cloud albedo, sulfur dioxide oxidation rates often are 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 assumes not only homogeneous chemical compositions between differing size cloud droplets but

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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 also was based on the analysis of cloud water collected from instruments with no means of fractionating droplet sizes. These single collections contained polydispersed drop sizes mixed together. Although 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 may lead to increased sulfate production in clouds, exceeding estimates made using bulk cloud water characteristics, especially for air that originates in marine environments (Hegg and Larson 1990). If droplets exhibit a size dependency on the condensation nucleus, then it is probable that the chemical composition of droplets also is size dependent (Munger et al. 1989). Hegg (1990) used drop size–dependent chemical behavior and explicit microphysics in a Lagrangian parcel model to estimate growth of activated CCN and found that aqueous sulfate production was needed to activate newly created particles in marine stratus clouds. Collett et al. (1994) demonstrated that, using bulk cloud water samples, sulfate production rates can be underpredicted seriously for clouds in which the acidity varies between large and small droplets, particularly when the small droplets are more acidic. Yuen et al. (1994) indicated that this heterogeneity in chemical composition across the cloud droplet size distribution could have a significant effect 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; Ogawa et al. 1999) have been conducted to determine experimentally whether cloud droplet compositions vary between drop sizes as theory predicts and to ascertain whether this variation commonly occurs in nature. In this study, drop size–dependent chemical composition and the effect of airmass origin on the variations in chemical composition are presented. Because 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 also may be airmass dependent. Observations of droplet chemical inhomogeneity, CCN, N, and cloud droplet effective radii (R_{eff}) for continental and marine air masses are discussed.

2. Experimental site and instrumentation

The experimental site is located at Mount Gibbes (2006 m above mean sea level), approximately 2 km south of Mount Mitchell Peak (35°44′05″N, 82°17′15″W) in North Carolina. The experimental site, referred to as the Mount Mitchell site, is ideal for in situ cloud measurements because 7 out of 10 days during the summer have a cloud event (Saxena et al. 1989) and is influenced by varying airmass types: highly polluted air from the Ohio Valley region, clean maritime air from the ocean, and relatively clean continental air from the Great Plains (Saxena and Yeh 1988). It frequently is 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 and 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 Sciences Research Center passive cloud water collector (ASRC), (McLaren et al. 1985; Saxena et al. 1989; DeFelice and Saxena 1990b) and a size-fractionating California Institute of Technology 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 instrument 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, composed of 10 rows of eight Teflon rods (9.525-mm diameter), collects large droplets (theoretically, a 50% size cut for droplets of 18.1-μm diameter), and the second stage collects smaller droplets (theoretically, a 50% size cut for droplets of 5.5-μm diameter) via impaction on six rows of Teflon strands (0.508-mm diameter). The flow rate of air for both stages is given as 15 m³ 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 1997, personal communication). Details on the operational procedures of SFAC can be obtained from Demoz et al. (1996). The SFAC instrument operated by Demoz, however, had four rows, each containing eight rods (12.7-mm diameter) in

the first stage and six rows of Teflon strands (0.508-mm diameter) in the second stage. Therefore, differences will exist between the collection efficiencies in the instrument used in this paper and in the one used by Demoz et al. The maximum collection efficiency increases with the number of rows. It should be noted that the size fractionating ability of 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 operated manually 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. The water then was collected as blank samples. Blank samples usually were obtained after every fourth cloud event as a means of quality checking 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 chloride. A cloud event began when a stationary object at a distance of 1 km from the tower was immersed in clouds and consistently stayed obscured from view for a period of at least 15 min. The stationary object conveniently was chosen to be 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 with a Dionex Corporation 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 deviations associated with pH measurements on the field site are on the average of $\sim \pm 0.02$ for all cases. Samples whose pH values were beyond this error limit were discarded. The precision for the pH electrode-probe instrument is within ± 0.01. The pH of the solution subsequently was 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 consistently were higher than field measurements, probably because of loss of acidity during storage as was reported also by Hering et al. (1987). The pH instrument was calibrated before and after every cloud event using buffer solutions with pHs 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^- and SO_4^{2-}), flow injection analysis (NO_3^- and NH_4^+), and induced, coupled, plasma atomic emission spectroscopy (Ca^{2+}, K^+, Mg^{2+}, and Na^+). The instrument detection limit (IDL) and method detection

limit (MDL) were determined using standard methods. To determine the IDL value, distilled and deionized water was used as a blank. Contributions from collector rinse blanks were not used as blanks for determining IDL values. This fact probably may lead to some error in accurately determining IDL values. The blank is analyzed as a sample (at least 20 times) in order to have an average concentration value for the instrument baseline. The IDL value is the mean value measured plus three times the standard deviation and the MDL value is the mean value measured plus five times the standard deviation. The IDL values were 2 μeq L^{-1} for NO_3^- and NH_4^+, 0.5 and 1.0 μeq L^{-1} for Cl^- and SO_4^{2-}, respectively, 5 μeq L^{-1} for Na^+, 3 μeq L^{-1} for K^+, 0.4 μeq L^{-1} for Ca^{2+}, and 1 μeq L^{-1} for Mg^{2+}. MDL values were 10 μeq L^{-1} for NO_3^- and NH_4^+, 2.5 and 5.0 μeq L^{-1} for Cl^- and SO_4^{2-}, respectively, 25 μeq L^{-1} for Na^+, 15 μeq L^{-1} for K^+, 2.0 μeq L^{-1} for Ca^{2+}, and 4 μeq L^{-1} for Mg^{2+}. The errors in ion concentrations are calculated using the quality-control samples that are analyzed as samples, along with the cloud water samples. For concentrations between 1 and 20 times the MDL values, errors are usually 10%–15%, between 20 and 200 times the MDL values errors are 5%–10%, and for values greater than 200 times the MDL values, errors are 2%–5%.

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

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

(1)

The sampling area and collision efficiency are taken into account by a, given as $\sim$17.37 m^{-2}, b is 0.027 g m^{-3}, and dt represents the time during which the cloud water is collected. At higher wind speeds ($>$12 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 (1990b). Droplets that are collected usually range between 2 and 20 μm in diameter. For all cases reported in this paper, the wind speeds were high enough (between 2 and 12 m s^{-1}) to collect most of the measured spectra. It can be expected that at lower wind speeds all the measured spectra would not be collected, however. Details on the impaction efficiency, wind speed, and droplet sizes for the ASRC collector are in McLaren et al. (1985).

A Particle Measuring System 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 instrument was factory calibrated. The calibration between each of the field events is detailed

TABLE 1. 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 are for the spring 1995 and summer 1996 field seasons.

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

in DeFelice and Saxena (1994). FSSP was deployed on the same moveable carriage as ASRC and SFAC. FSSP sizes particles from 2 to 32 μm. The FSSP data were obtained for three size ranges that cover 0.5–8.0, 1–16, and 2–32 μm. Particles are resolved into 15 equally spaced intervals for each size range. For the dataset reported in this paper, the large ($2 < d < 32$ μm) and small ($1 < d < 16$ μm) size ranges are used, where d is particle diameter. The larger size range includes all droplets measured by the smaller size range in a coarser bin size resolution, except for those between 1 and 2 μm. The particle size interval for the large size range is 2 μm and for the small size range is 1 μm. The data are obtained every 5 s and then are averaged to obtain hourly averages that correlate to the hourly averages for the chemical and cloud water data. Measurements from FSSP were used to estimate N:

$$N = \int n(r) \, dr, \qquad (2)$$

where $n(r)$ is the droplet size distribution and dr is the droplet range. The cloud droplet effective radius, defined as the ratio of the moments of the drop size distribution, is given as

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

In this paper, the values for N and R_{eff} are reported in the large or small size range only if the size distribution stayed in the given size range for most of the time period during averaging.

The CCN spectrometer described by Fukuta and Saxena (1979a,b) was operated from a shed located about 8 m to the northeast of the tower. Its inlet is an inverted funnel (0.1-m diameter) that extends 0.5 m outward 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). Measurements of CCN reported in this paper are at 0.7% supersaturation. CCN measurements that were made in cloud represent the interstitial CCN.

Airmass 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 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°–290° azimuth, and the marine sector, 65°–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 sulfur oxides and nitrogen oxides available from the U.S. Environmental Protection Agency. Validation of the trajectories of the cloud-forming air masses that arrived at the site previously has been 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. The types of clouds formed for cloud events that are less than 8 h in duration are usually those due to orographic lifting, whereas cloud events that last for more than 8 h usually have clouds that are influenced by frontal passages (Saxena and Lin 1990).

3. Results and discussion

a. Influence of airmass trajectory

The period of observations for the study ran from early March intermittently through the middle of June 1995, covering 15 cloud events and 67 cloud water samples collected from nonprecipitating clouds. During the summer of 1996, 12 cloud events and 47 cloud water samples were collected, mainly from nonprecipitating clouds. Datasets from 1995 and 1996 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 1. Only cases that had their airmass sources identified were used in Table 1. 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

TABLE 2. 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 calculated at 0.7% supersaturation 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 also are given.

Airmass source	Marine			Continental			Polluted continental		
Properties	Range	Average	Samples	Range	Average	Samples	Range	Average	Samples
Sulfates (μeq L^{-1}) large drops	6–176	102	15	29–896	207	23	122–941	511	10
Sulfates (μeq L^{-1}) small drops	10–264	115	15	42–1209	260	22	70–1313	399	10
Sulfates (μeq 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 μm)	39–198	128	11	—		0	—		0
R_{eff} (μm)(2 < d < 32 μm)	3.9–8.8	5.76	11	—		0	—		0
N (cm^{-3})(1 < d < 16 μm)	—		0	22–167	73	20	143–145	144	4
R_{eff} (μm)(1 < d < 16 μm)	—		0	1.3–5.2	3.41	20	3.3–4.1	3.89	4

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 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. Continental air masses, however, 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 range of pH 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 were the larger droplets for air masses that were polluted continental in origin, though, because of 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 range of pH and 49% were in the 4.0–5.0 range, whereas, for the large drops, 79% of the samples were in the 4.0–5.0 range of pH. Thus, the smaller drops were more frequently in the low-pH range than were the larger drops.

Table 2 lists the range and average values for the sulfate content in fractionated and bulk samples, CCN concentrations at 0.7% supersaturation, 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 do clouds with lower sulfate concentrations (Saxena et al. 1996). Table 2 indicates that the highest sulfate content, highest CCN, and lowest R_{eff} were usually for polluted continental–type air masses. The average R_{eff} for the continental sector is slightly lower than that of the polluted continental sector, probably because of the influence of some polluted air mass on the continental sector as indicated by the high sulfate values that also were observed. 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 inside of the range obtained for the fractionated samples, although the average for the

marine sector is skewed toward slightly lower values (possibly a result of a rain artifact). For marine cases, the drop size distribution is usually in the larger size range, whereas those for continental and polluted continental cases are usually in the smaller size range.

The change in average values of N from the marine to the continental and the polluted continental sector is offset by the high standard deviations that were observed for the marine and continental cases. Also, the average values of ω, as calculated for bulk samples, are slightly higher for the marine sector (~0.36 $\pm$ 0.11 g m^{-3}) as compared with those for the continental and polluted continental sectors (~0.23 $\pm$ 0.10 g m^{-3}). The high standard deviations in N could arise because of these differences in ω as well as 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 also could result in large fluctuations in N as some of the droplets that were large enough would precipitate, thereby reducing the total droplet number. The effective radius of the droplets decreased from an average of about 5.76 μm for the marine cases to about 3.89 μm for the polluted cases. Menon and Saxena (1998) analyzed four years of data at the Mount Mitchell site and found sufficient evidence for a decrease in droplet size as the airmass source moves from the marine sector to the polluted continental sector. Slingo (1990) had suggested that a decrease in R_{eff} of about 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.

b. Differences in chemical composition of cloud droplets

Differing contributions of acids and bases to individual cloud drops produce a distribution in drop acidities. Figure 1 compares the pH values of small and large cloud drops for the spring of 1995 and the summer of 1996. The range of pH values observed, from less than 3 to nearly 5.5, depicts a variation with drop size. The
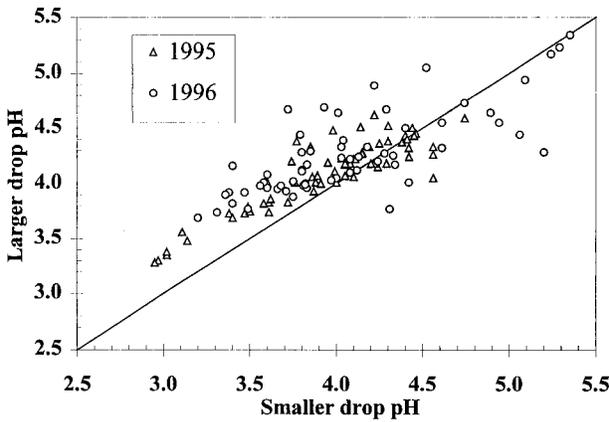
FIG. 1. Cloud water pH for smaller and larger droplets from the 1995 and 1996 field seasons. Samples selected are for nonprecipitating clouds with pH values ranging from 3.0 to 5.5. Standard deviations for pH are usually ±0.02. The solid line represents the 1:1 line where the pH from both size fractions is the same.

smaller droplets usually were more acidic than were the larger ones, with some exceptions, as can be noticed in Fig. 1. Differences between the 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 was found to be less than 6%, on 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.

Five cases (8 June, 13 June, 13 July, 15 July, and 1 August) with different airmass origins and different chemical concentrations in the smaller and larger droplets were chosen from the 1996 data, out of a total of 15 cases. These cases were chosen because the time periods of sampling during these cases were of sufficiently long duration and had coincident measurements of N and R_{eff}. Table 3 lists the average values and the standard deviation of the ionic concentrations during the time period of sampling for each of the five cases, both for fractionated and bulk cloud water samples. The correlation coefficient between the cations and anions was 0.99 for both fractionated and bulk samples. The differences in pH between small and large droplets were found to be significant at the 95% confidence interval, except for cases 1 and 5. The differences in pH for these cases were significant only at the 65% confidence level. Differences between sulfate concentrations in the large and small droplets were found to be significant at the 70% confidence interval, on average. Some exceptions were observed, as in the case of the cloud events of 13 June and 13 July, that did not have significant differences in the sulfate concentrations. The differences in average values of nitrates and sulfates between large and small drops, however, were found to be significant at the 95% confidence

TABLE 3. Average values and standard deviations of solute concentrations found in cloud water collected from the size-fractionated active string–type cloud water collector (SFAC) for large and small cloud droplets and from 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)	Mg²⁺ (μeq L⁻¹)	Ca²⁺ (μeq L⁻¹)	Na⁺ (μeq L⁻¹)	NH₄⁺ (μeq L⁻¹)	NO₃⁻ (μeq L⁻¹)	Cl⁻ (μeq L⁻¹)	SO₄²⁻ (μeq L⁻¹)
8 Jun	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 Jun	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 Jul	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 Jul	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

level for cases 2, 3, and 4 and the 80% confidence level for case 5, with no significant difference for case 1 at the 80% confidence level.

The mean values of the ionic species from the bulk samples usually lie between the concentrations reported for the large and small droplets. Some exceptions, as in case 1, were found, as indicated in Table 3. These exceptions could result from different collection efficiencies resulting from mechanical differences between the passive- and active-type collectors. The strings of the ASRC collector have a diameter (of 0.4 mm) that is smaller than the strands of the SFAC, which measured 0.508 millimeters in diameter. The two collectors therefore will collect different portions of the droplet size spectrum. Because collection strand diameter and drop velocity both contribute to the collector's cutoff size, these factors also could lead to the bulk samples not having ionic concentrations that are between large and small drop size fractions. DeFelice and Saxena (1990b) found the string diameter and droplet spectra to be related to the amount of water collected by the ASRC instrument. Differences also could be a result of sampling artifacts. Hering et al. (1987) also have noted differences in chemical concentrations in cloud water collected by five different collectors, which they attributed to differences in collection.

The slightly higher solute concentrations for the larger droplet size range observed for the 8 June, 13 June, and 13 July cases were for orographically influenced events as indicated by synoptic charts. Some of these orographic events (e.g., 13 June) lasted for over 8 h, however, and were not always shorter relative to events influenced by frontal activity, which typically were of longer duration. For the cloud events of 15 July and 1 August that were influenced by frontal activity, higher solute concentrations were found for the smaller drop size range. It must be noted, however, that orographic effects also affect clouds influenced by frontal systems. Differences in the chemical and microphysical properties for these cases are discussed.

c. Cloud events of 8 June, 13 June, and 13 July

Figures 2a, b, and c depict the concentrations of the ionic composition of the small and large droplets for the above-mentioned cloud events. Case 1 is for a 7-h cloud event observed on 8 June 1996. 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-}, with important contributions from ammonium (from NH_4^+) and nitrate (NO_3^-). Because of the maritime nature of the cloud, this case had large amounts of sodium (Na^+) and chloride (Cl^-) in the larger drops that were well-correlated temporally. NaCl usually is found in the coarse aerosol mode and is found more preferentially in the larger droplets (Schell et al. 1997).

Case 2 is for 9-h cloud event that occurred on 13 June 1996. Synoptic charts indicated flow from the western sector. The source of the cloud-forming air mass was mostly the continental sector for the first half with some influence from the polluted continental sector during the latter half. This case had higher NO_3^-, magnesium (Mg^{2+}), and calcium (Ca^{2+}) concentrations for the larger droplets as compared with the smaller droplets, as can be seen in Fig. 2b. Bulk measurements and smaller droplets from SFAC indicated good correlation between the sulfate content and hydronium ion (H^+) of the cloud water, with correlation coefficients of 0.70 and 0.95, respectively. There was, however, a greater variation in the pH and sulfate content of the larger droplets. The low H^+ for the larger drops as compared with the smaller drops probably was 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. Deininger and Saxena (1997) used principal component analysis to investigate cloud water data collected at the same experimental site for 1993 and 1994, and found calcium to have the highest concentration for cloud events originating from the continental sector. Calcium is a component of carbonate and silicate soil minerals that are blown into the atmosphere after cultivation and also could come from construction sites (Gorham et al. 1984). This case also had some of the highest amounts of SO_4^{2-}, NO_3^-, NH_4^+, Ca^{2+}, and H^+ of all the five cases considered.

Case 3 is for a 7-h cloud event that occurred on 13 July 1996. The synoptic charts indicated 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 some of the highest recorded for most of the marine events observed. The temporal variations of Na^+ and Cl^- also were well correlated. Because of the influence from the polluted continental sector, this case 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 for the larger drops, similar to case 2, which again could be attributed to the larger amount of calcium salts in the large drops as compared with that found in the small drops.

Changes in the relative water volume for the two stages of the SFAC instrument, ω as estimated for bulk samples, R_{eff}, and N were investigated for the five cases. The temporal variability in relative water volumes collected for each stage by the SFAC instrument is shown in Fig. 3. For case 1, the large fraction had greater amounts of water collected, relative to the small fraction, that increased as the cloud event progressed and then slowly decreased toward the end of the cloud event.
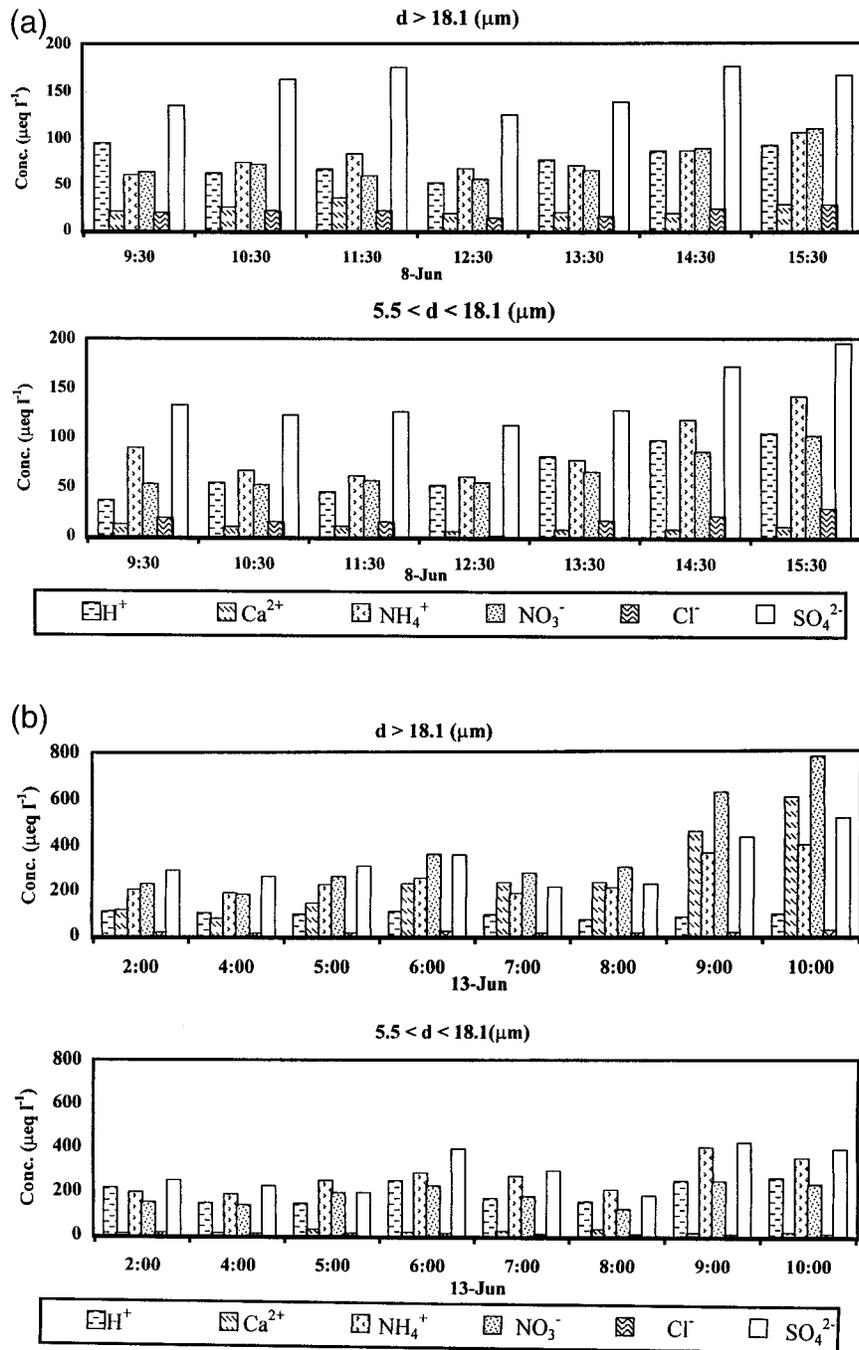
Fig. 2. Time series (UTC) of ionic composition in cloud water from fractionated cloud water samples for the given size ranges (d = particle diameter) for (a) 8 Jun, (b) 13 Jun, (c) 13 Jul, (d) 15 Jul, and (e) 1 Aug.

Figure 4a illustrates the drop size distribution as obtained from the FSSP measurements for case 1 for the larger size range. The numbers on the curve represent the sequence of the time period of sampling. Because of the maritime nature of the cloud event, spectra were obtained in the large size range. As can be seen, the modal radius during the first half of the event is at ~6 μm and shifts to 4 μm during the end of the event. The peak of the number distribution increases from 110 cm^{-3} μm^{-1} to 230 cm^{-3} μm^{-1} corresponding to the decrease in radii. This case also had the largest R_{eff} of all the five cases as can be noticed in Fig. 5, which illustrates the
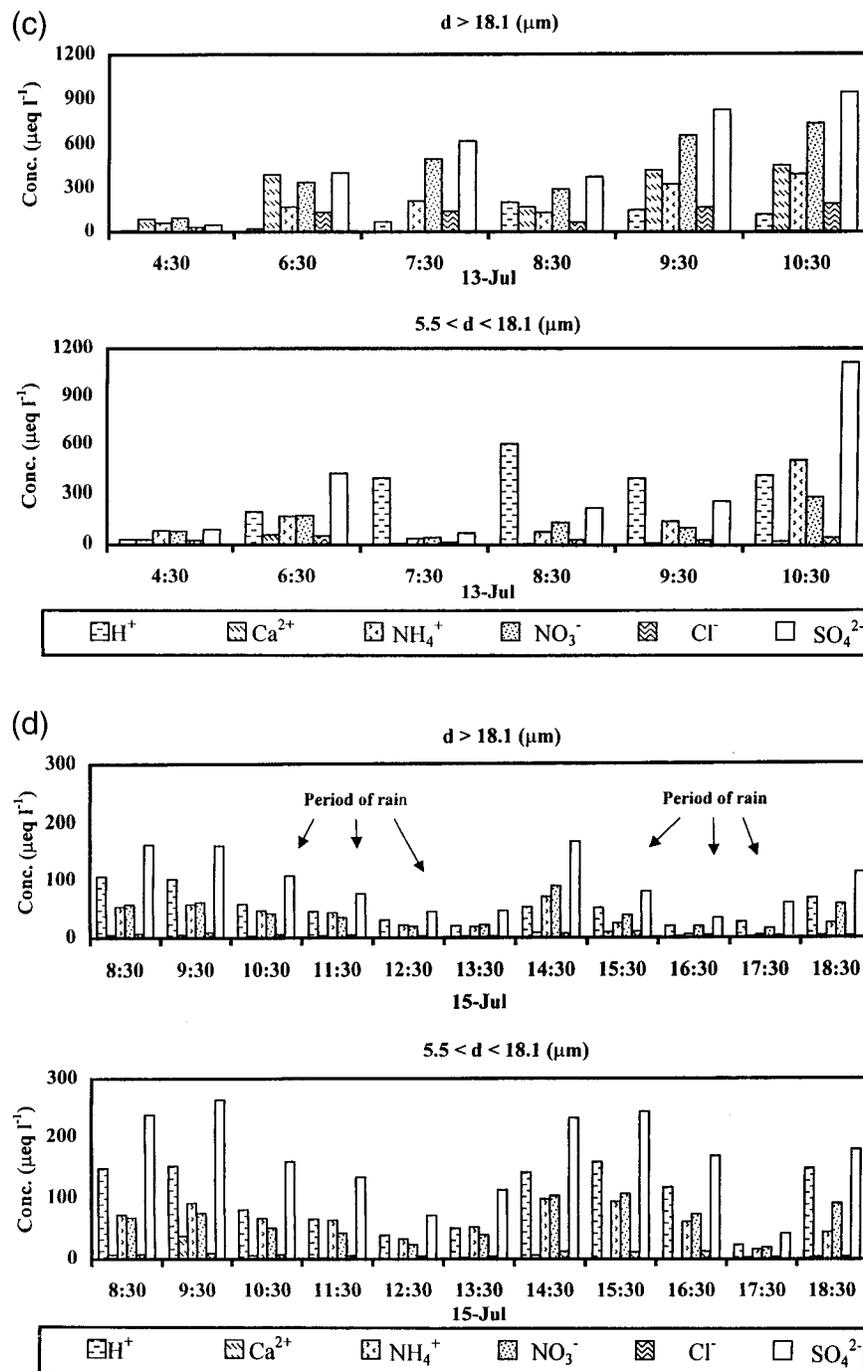
FIG. 2. (*Continued*)

temporal variability in R_{eff} for the large size range ($2 < d < 32$ μm) for case 1. Marine cases usually have larger R_{eff} in comparison with continental cases. For case 1, the value of N varied from $\sim$140 cm^{-3} at the beginning of the cloud event to $\sim$170–190 cm^{-3} as seen in Fig. 6, which depicts the temporal variability in N. Figure 7 depicts the time series of ω estimated for bulk samples for all five cases. For case 1, the temporal variations in

ω, R_{eff}, and N indicated that, as ω decreases and N increases, R_{eff} decreases, which can be noticed especially during the third, fourth, and fifth hours of the cloud event. Toward the end of the event, for similar values of ω, the slight increase in N corresponds to the slight decrease in R_{eff} as more droplets compete for the same water, thereby reducing cloud droplet size. The larger droplet sizes and the higher concentrations of Na$^+$ and
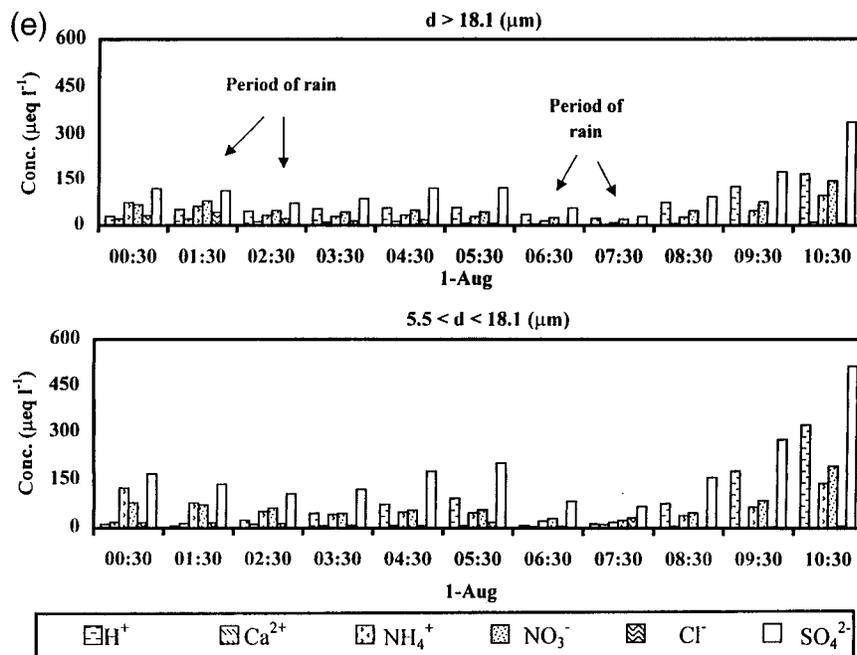
FIG. 2. (*Continued*)

Cl^- in the larger drops demonstrated the maritime nature of the cloud.

For cases 2 and 3, more water was collected for the smaller fraction, as indicated in Fig. 3. This increase was in exception to the other three cases (8 June, 15 July, and 1 August). Figures 4b,c depict the size distribution obtained for the smaller size range for both these cases. For the first 3 h of the 13 June cloud event, however, the size distribution was obtained for the larger size range (not shown), with the peak number concentration at ~320 cm^{-3} μm^{-1}. For the rest of the event, the peak number concentration was at ~135 cm^{-3} μm^{-1}. A bimodal distribution can be noticed in Fig. 4b with the first peak located at 2 μm. The second peak shifts from 4.0 μm for the first 3 h to 3.5 μm for the rest of the event. For case 2, from Fig. 5, the slight temporal variations in R_{eff} after the first 3 h coincided with the variations in the water mass for the smaller drops as well as ω from the bulk sampler. Figure 6 indicates an average value of ~294 cm^{-3} for N in the large size range during the first 3 h and an average value of ~144 cm^{-3} for N in the smaller size range after the first 3 h of the cloud event.

The possible reasons for the change in the droplet spectrum from the larger to the smaller size range for case 2 perhaps could be analyzed by investigating the CCN spectrum and the sulfate content of the large and small drops. The source of the cloud-forming air mass was from the continental sector during 0100–0600 UTC. From 0600 to 1100 UTC, the passage of the air mass through the polluted continental sector coincided with an increase in the sulfate content in the smaller drops

as well as with the interstitial CCN concentrations (increase from 142 cm^{-3} at 0500 UTC to 361 cm^{-3} at 0600 UTC). The shift in the droplet spectra toward smaller size ranges after 0500 UTC coincided with the decrease in the sulfate content in the larger drops, except toward the end of the event. Thus, even though the interstitial CCN concentrations increased, it is probable that many of the particles remained unactivated because N was almost constant since 0500 UTC (as seen in Fig. 6). It also is probable that cloud droplets would scavenge some of these unactivated particles.

The activation of an aerosol particle at a given supersaturation is controlled by its mass and chemical composition. 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. If sufficient water vapor is available they will exceed the critical diameter and get activated. This growth behavior is described by the Köhler equations that are a result of the balance between the solute effect and the curvature effect. Details on the equilibrium growth curves for typical marine and continental aerosol particles are in Pruppacher and Klett (1978). For droplets that are unactivated, the concentrations could get diluted as the droplet grows. The dilution of the solute concentration in the small drop fraction of the cloud drops that were sampled could be dependent on whether the small drop fraction contains drops that are activated or contains drops that are large but not activated. Noone
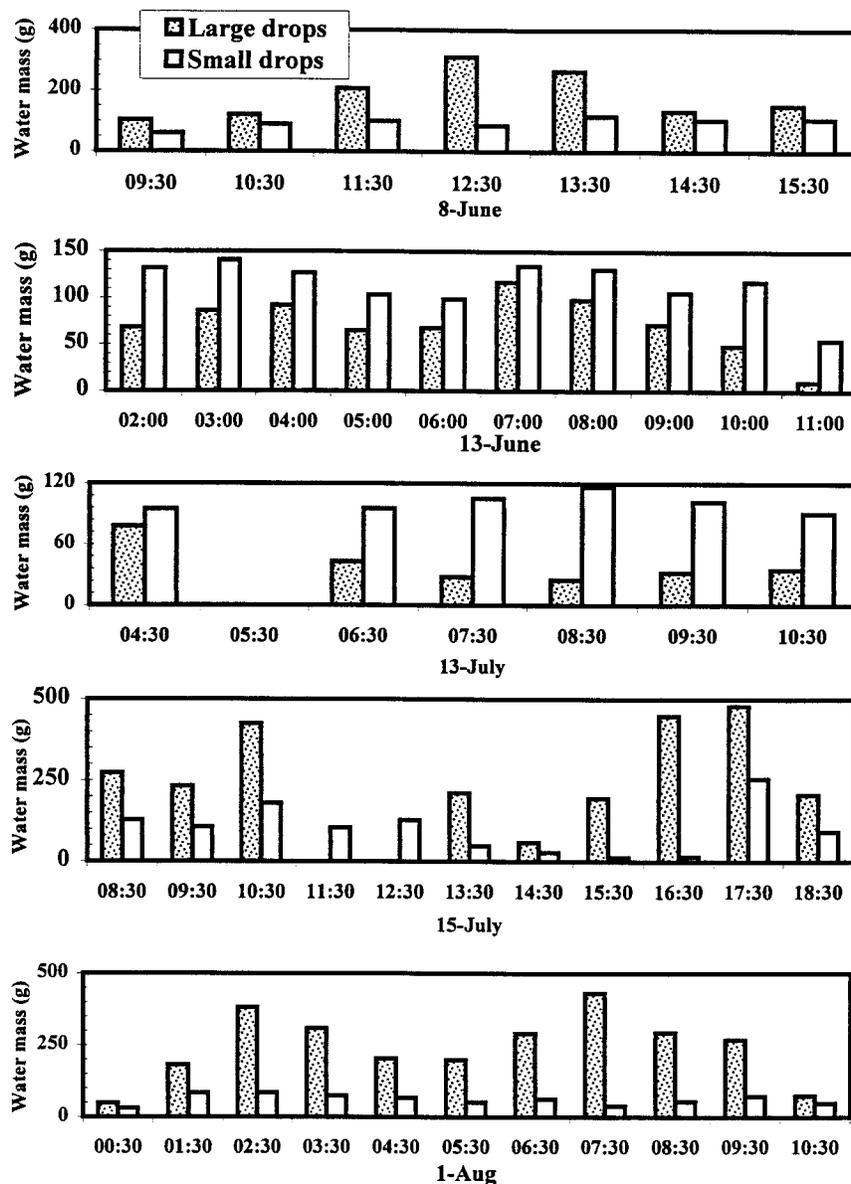
FIG. 3. Time series (UTC) of amount of cloud water collected from fractionated cloud water samples for large ($d > 18.1$ μm) and small droplets ($5.5 < d < 18.1$ μm).

et al. (1988) suggest that smaller droplets diluted faster than larger droplets only if nucleation was responsible for cloud solute concentration and not if unactivated aerosol particles were scavenged by cloud droplets or if in-cloud production of solute took place. Even though the larger drops had higher solute concentrations for the 13 June case, the nonstatistical significance of the difference in sulfates between large and small drops suggests that in-cloud scavenging of unactivated aerosol particles by cloud droplets could be a factor that influences solute concentration. Other factors include collection of unactivated sulfate haze drops by SFAC and the formation of large and small drops on chemically distinct CCN.

For case 3, a sharp increase in the CCN concentration from 165 cm^{-3} at the beginning of the event to ~700 cm^{-3} after 0900 UTC corresponded to an increase in sulfate in the larger and smaller drops. However, the values for N did not increase. Similar to case 2, the lower statistical significance for the differences between the large and small drop sulfate content suggests that the scavenging of unactivated aerosol particles by cloud droplets could have influenced solute concentration. The low values of R_{eff} and N at the end of the cloud event (~1030 UTC) for case 3 should be ignored because they probably arise from there not being enough 5-s FSSP data as the cloud dissipates to calculate the hourly average values of R_{eff} and N.
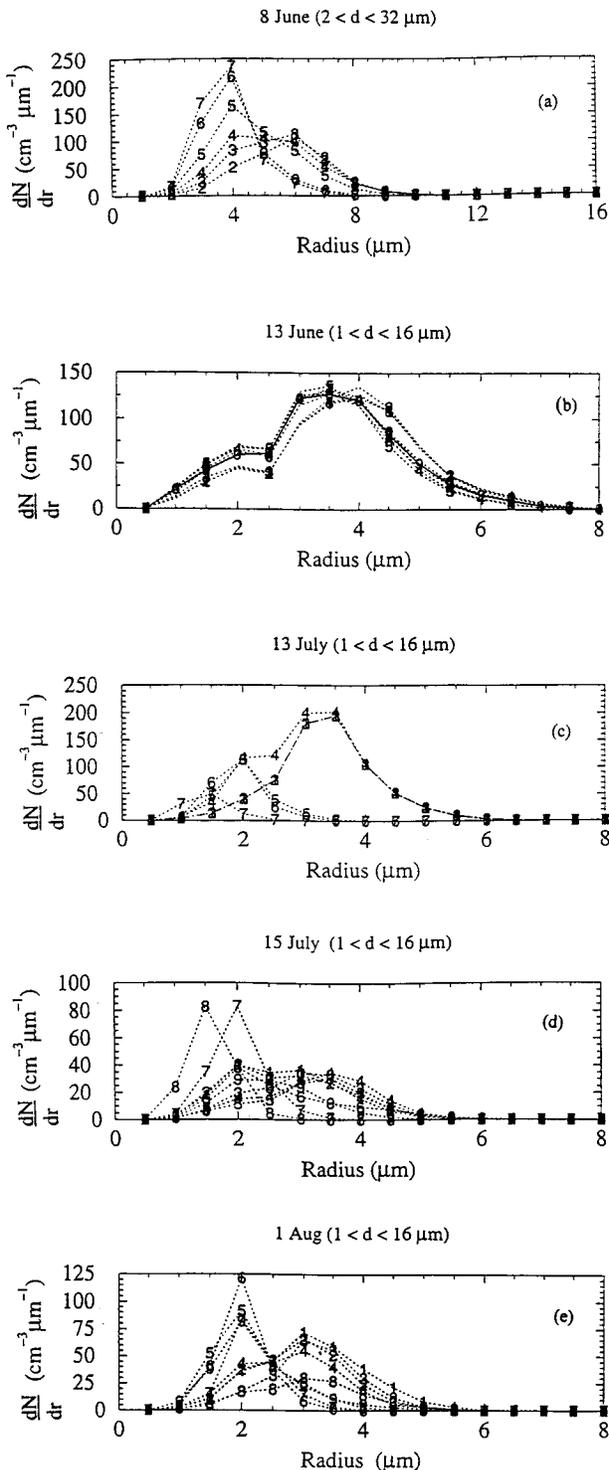
FIG. 4. Drop size distribution as obtained from the FSSP measurements for (a) 8 Jun for the large size range, (b) 13 Jun for the small size range, (c) 13 Jul for the small size range, (d) 15 Jul for the small size range, and (e) 1 Aug for the small size range.

d. Cloud events of 15 July and 1 August

Case 4 is for an 11-h cloud event for 15 July 1996. The synoptic conditions indicated a very strong front on the western part of the Mount Mitchell site that influenced the cloud event. The entire eastern portion of the United States northward 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. The smaller droplets had higher H^+, SO_4^{2-}, NO_3^-, and NH_4^+ in comparison with the larger droplets, as seen in Fig. 2d. Strong correlation between cloud water pH and sulfate content was exhibited both by bulk and fractionated cloud water samples. The correlation coefficients between sulfate and cloud water H^+ 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 11-h cloud event on 1 August 1996. Frontal conditions that were not as strong as for the one for 15 July influenced the formation of the cloud event. The 850-h Pa level that is the level closest to the site (which is at ~810 hPa) indicated airflow coming from the southwest from a high pressure system moving toward the low pressure system located in the northeast. The cloud-forming air mass was mainly from the continental sector with some influence from the polluted sector. The larger droplets had lower sulfate, ammonium, and nitrate contents in comparison with the smaller droplets, as seen in Fig. 2e. There was more variability in the sulfate content and measured pH for the smaller droplets in comparison with the larger droplets and bulk water samples.

For cases 4 and 5, the amount of water collected for both stages increased during the occurrence of precipitation, indicated in Figs. 2d,e. During the time of precipitation, some overflow was recorded for the bulk sampler as well as for the water collected for the larger fraction, and no values were recorded for that time. The occurrence of precipitation can be noticed in the shift of R_{eff} toward slightly larger sizes (Fig. 5) and a corresponding decrease in N (Fig. 6), suggesting the collision/coalescence and removal of droplets that were large enough to precipitate, thereby reducing the total cloud droplet number. There was also a decrease in the solute concentrations and more variability in N and R_{eff} for both these events during precipitation.

Observations of the chemical and microphysical properties of the cloud events discussed above indicated that the smaller drops were usually, but not always, more enriched in sulfates, nitrates, and ammonium relative to the larger ones. Munger et al. (1989) investigated the chemical composition of coastal stratus clouds in California. They found that the concentrations of Na^+, Ca^{2+}, and Mg^{2+} in the larger droplets were higher than in the smaller droplets and indicated that these large droplets formed on sea salt and soil dust, and smaller droplets, which had higher SO_4^{2-}, NO_3^-, H^+, and NH_4^+,
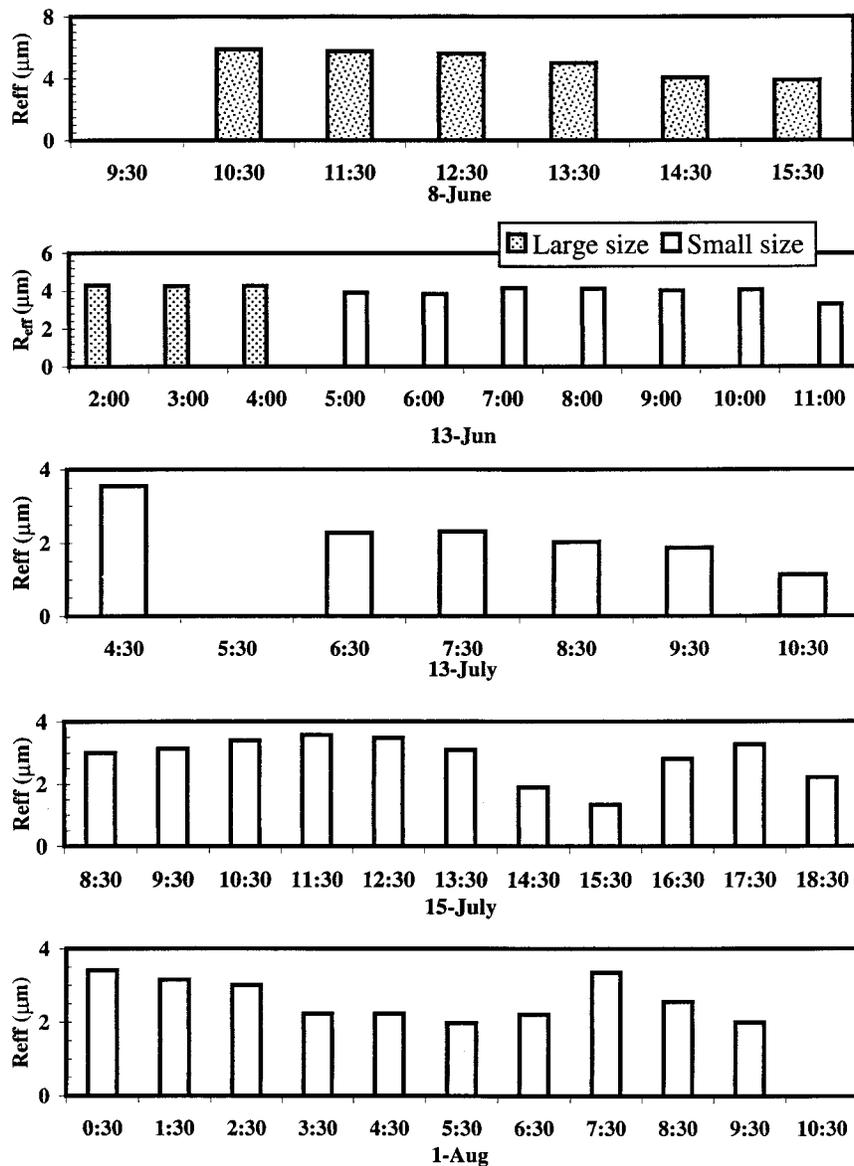
FIG. 5. Time series (UTC) of size of the droplets (R_{eff}) as obtained from the FSSP measurements. Two size ranges are given: large size, $2 < d < 32$ μm, and small size, $1 < d < 16$ μm.

usually formed on small secondary aerosols composed of ammonium sulfate [$(NH_4)_2SO_4$] and ammonium nitrate (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 do the larger droplets, which then results in an increase in solute concentration with size only if nucleation was responsible for cloud solute production. Their observations, however, were for one single cloud event and did not include the variability in marine stratus clouds.

Because higher solute concentrations were observed in larger droplets for cloud events influenced by orographic lifting, and events influenced by frontal systems had higher solute concentrations in smaller droplets, it would be necessary to determine if cloud drop lifetimes prior to sampling differed between cloud events. Therefore, determination of cloud base relative to sampling location as well as detailed cloud drop trajectories and cloud dynamics (that have not been presented here) would be necessary to differentiate between cloud properties that result from either frontal or orographic influences. Schell et al. (1997) found higher solute concentrations in larger droplets for droplets that were relatively young and formed by orographic lifting and suggested that droplet growth time is an important factor for the size dependence of solute concentration. For more aged clouds, solute concentration decreased with
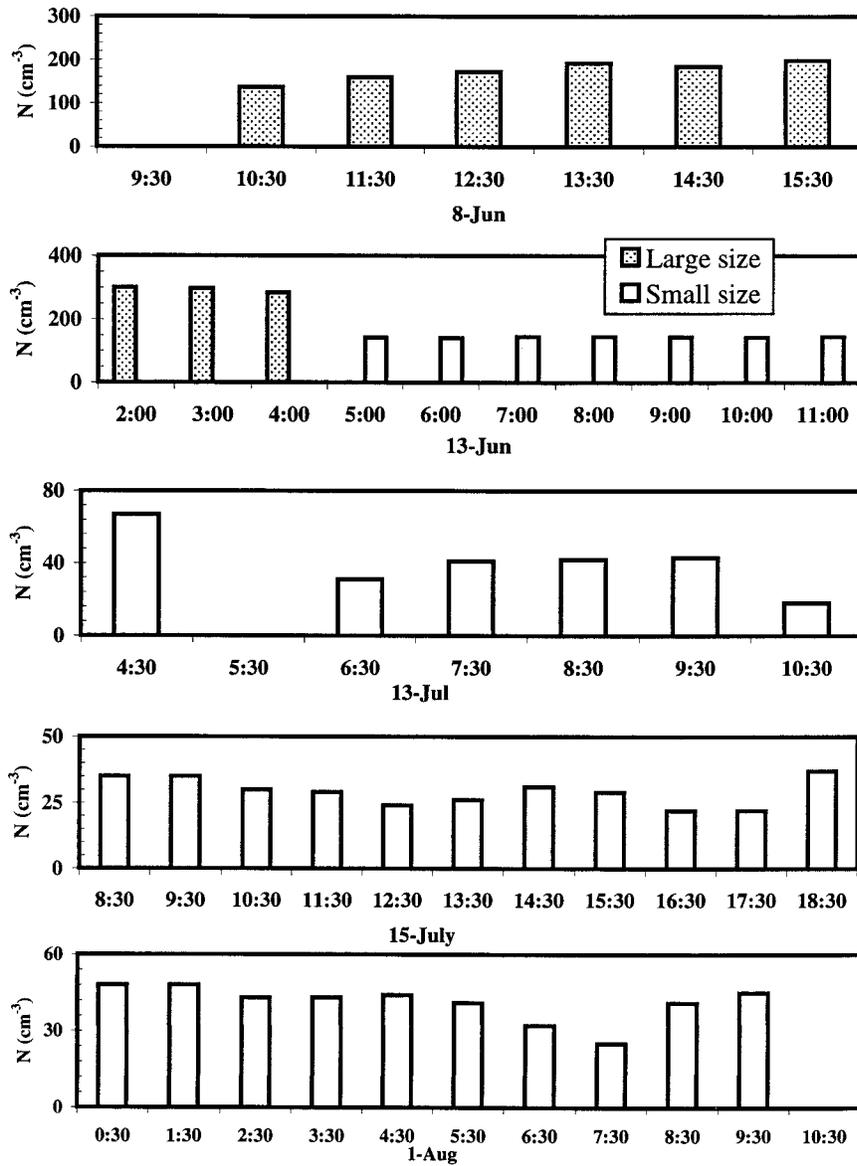
FIG. 6. Time series (UTC) of cloud droplet number concentration (*N*) as obtained from the FSSP measurements. Two size ranges are given: large size, $2 < d < 32$ μm, and small size, $1 < d < 16$ μm.

an increase in diameter. Schell et al. also suggested that the increased solute concentrations found in smaller droplets could result from entrainment when new particles enter the cloud and form new droplets.

Fractionated measurements from 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 that would fractionate the droplets into more than two size ranges, such as that used by Laj et al. (1998).

4. Conclusions

Sulfate production in clouds is a critical component of the global sulfur cycle. Bulk water measurements of cloud water acidity traditionally have been used to estimate sulfate production within clouds. Although 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 chemically are heterogeneous. Investigation of the pH variations between large and small cloud drop-
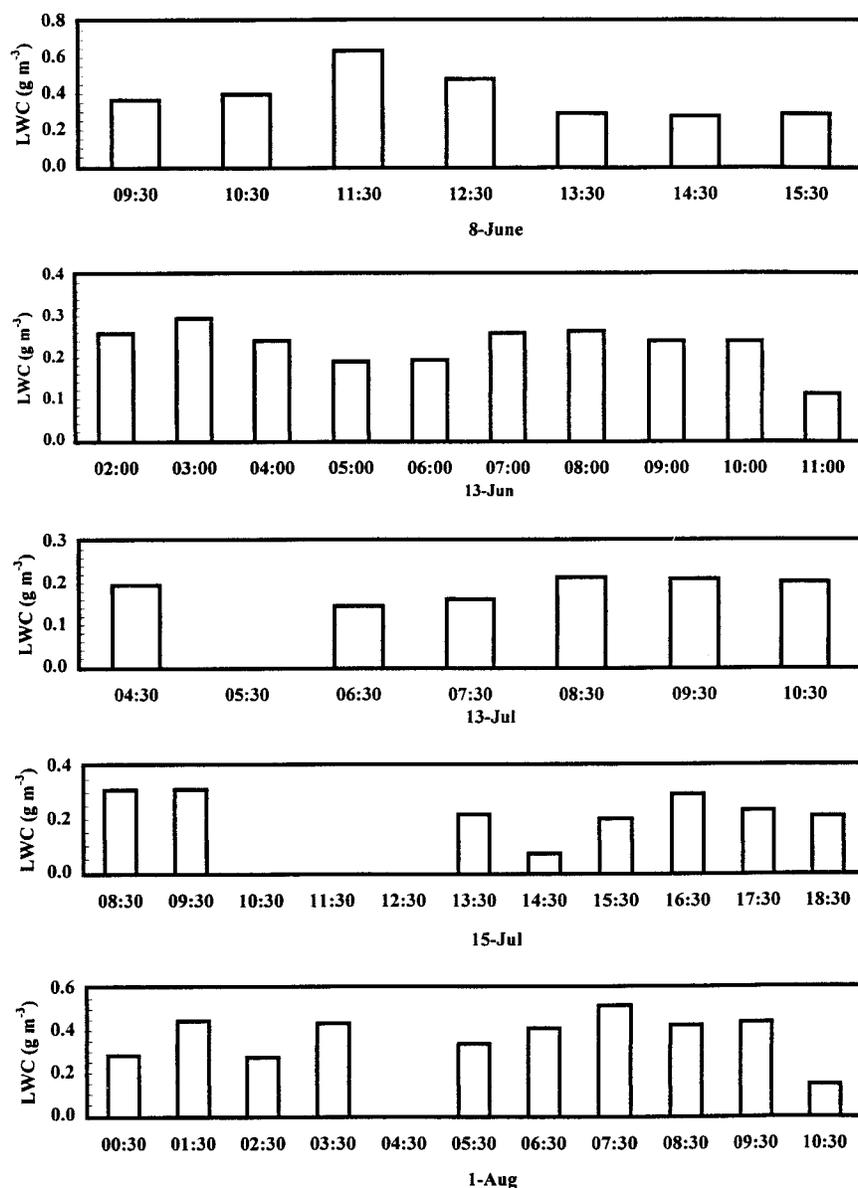
FIG. 7. Time series (UTC) of cloud liquid water content (LWC) calculated for bulk samples collected by the ASRC collector.

lets at the Mount Mitchell site indicated that smaller droplets often, but not always, are more acidic than larger droplets. On 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+}, and Mg^{2+}, supporting the findings of Munger et al. (1989). Samples also were collected for which the reverse was true, however. Smaller droplets usually were 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, whereas those

from the marine sector had the highest sodium content in the larger drops.

For cloud events influenced by frontal activity, higher solute concentrations were found for the smaller drop size range. Slightly higher solute concentrations for the larger droplet size range were found for events caused by orographic lifting as indicated by synoptic charts. The difference in sulfate concentration between large and small drops was found not to be statistically significant for some of the orographic cases sampled, however, possibly due to the scavenging of unactivated aerosol particles by cloud droplets. Schell et al. (1997) also found higher solute concentrations in larger droplets for

droplets that were relatively young and formed by orographic lifting and suggest that droplet growth time is an important factor for the size dependence of solute concentration. Thus, it would be necessary to determine cloud droplet age as well as detailed cloud drop trajectories and cloud dynamics to differentiate fully between cloud properties that result from either frontal or orographic influences.

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