

DYNAMIC CHEMICAL CHARACTERIZATION OF MONTANE CLOUDS

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Abstract—Cloud water collections have been made on Mt. Mitchell using a nearly real-time cloud and rain acidity/conductivity (CRAC) analyzer. Results are reported for integrating times of approximately 5 min during several cloud events in the summer and fall of 1987. Both pH and ionic strength during cloud events were found to be much more variable than previously indicated by integrated cloud collection. Maximum values of H^+ and SO_4^{2-} ion concentrations in 5-min samples were as much as 2.5 times greater than those measured in 1-h integrated collections. These results are not influenced by instrumental variability to any measurable extent. Results from repeated quality control samples were highly reproducible, and agreement between integrated collection data and the average values of 5-min sequential samples was also very good.

Key word index: Cloud chemistry, chemical characterization, automated cloud and rain analyzer, cloud growth.

INTRODUCTION

It is now recognized that clouds and fog are typically more acidic than precipitation at the same location (Falconer and Falconer, 1980; Munger *et al.*, 1983; Muir *et al.*, 1986). The potential for damage from these very acidic systems to human health, vegetation, and material has prompted much interest in the chemical and physical structure of clouds and fog. However, there is essentially no dynamic real-time chemical characterization of these systems, even though acidity of clouds is highly variable over short periods of time. Such a body of information would be of great value to scientists in the study of acidic deposition and changes in global climate by providing a measure of exposure and extremes of chemical exposure. In particular, real-time chemical characterization would be useful both in defining the significance of cloud processes in deposition and in studying the resulting biological interactions. Moreover, acidic exposure to clouds at high-elevation locations (also called 'high mountain fog') may be about fivefold greater than that due to rain over the same time period. Hence, clouds provide a significant pollution deposition pathway to high-elevation ecosystems; in some cases the cloud deposition pathway may deposit several times more pollutants than either rain or dry deposition.

The chemical characterization of cloud water based on integrated samples has been undertaken both at low elevation (i.e. fog) (Houghton, 1955; Mrose, 1966; Okita, 1968; Lazrus *et al.*, 1970; Bressan and Larson, 1979; Waldman *et al.*, 1982; Hoffmann, 1984; Fuzzi and Mariotti, 1983; Fuzzi *et al.*, 1984; Jacob *et al.*, 1985a,b, 1986; Glotfelty *et al.*, 1987) (Table 1) and at high elevation by airborne sampling (Oddie, 1962; Petrenchuk and Drozdova, 1966; Daum *et al.*, 1984; ten Brink *et al.*, 1987) (Table 2). Measurements made for urban fog show pH values ranging from 3 to <2. In an extreme event observed in southern California (Corona del Mar), a low pH of 1.7 with a NO_3^- -to- SO_4^{2-} ratio of approximately 3 was observed (Hoffmann, 1984). The chemical composition of fog has been analyzed (Wilkniss and Bressan, 1972; Bressan, 1976, 1977) for Na^+ , K^+ , Cl^- , F^- , and SO_4^{2-} to better characterize an air parcel and to ascertain if its aerosol composition is dominated by continental aerosols, sea surface aerosols, or integrated seawater droplets. Daum *et al.* (1984) have used aircraft measurements to characterize the forms of sulfur and nitrogen compounds in clouds and their pathways of incorporation into clouds. A single, widespread acid cloud/fog event was recorded by Weathers *et al.* (1986) at six nonurban sites in the eastern U.S. at low, medium, and high elevations.

Table 1. Cloud water pH values reported at low elevations

Reference	Year of study	Location	Range of pH
Houghton (1954)	1954	Northeast U.S.	4.5–7.2
Mrose (1966)	1957	Germany	3.8–5.1
Lazrus <i>et al.</i> (1970)	1967	Puerto Rico	4.9–5.4
Bressan and Larson (1979)	1975	Nova Scotia, Canada	3.0–6.9
Waldman <i>et al.</i> (1982)	1981	California, U.S.	2.2–4.0
Fuzzi <i>et al.</i> (1983)	1980–1982	Italy	2.5–7.0
Munger <i>et al.</i> (1983)	1981–1982	California, U.S.	2.2–5.78
Fuzzi <i>et al.</i> (1984)	1982	New York, U.S.	4.3–6.4
Jacob <i>et al.</i> (1985)	1982–1983	California, U.S.	2.16–6.17
Jacob <i>et al.</i> (1986)	1983–1984	California, U.S.	2.68–7.23
Muir <i>et al.</i> (1986)	1985–1986	Midwestern U.S.	2.85–4.06
Weathers <i>et al.</i> (1986)	1984	Eastern U.S.	2.9–3.0

Table 2. High elevation collection of cloud water by aircraft

Reference	Year of study	Location	Range of pH
Oddie (1962)	1960	U.K.	4.4–7.2
Petrenchuk and Drozdova (1966)	1961–1964	European territory of U.S.S.R.	3.35–5.90
Scott (1978)	1976	Australia	4.6–7.5
Scott and Laulainen (1979)	1977	Michigan, U.S.	3.7–4.0
Daum <i>et al.</i> (1984)	1981–1983	Eastern U.S.	2.5–7.0
Romer <i>et al.</i> (1985)	1981–1983	Western Europe	3.1–6.1

Table 3. pH Values reported for cloud water collected at montane sites

Reference	Year of study	Location	Range of pH
Okita (1968)	1963	Japan	3.5–6.5
Castillo (1979)	1976	Whiteface Mtn., NY, U.S.	3.4–4.2
Falconer and Falconer (1980)	1977–1979	Whiteface Mtn., NY, U.S.	2.66–4.66
Weathers <i>et al.</i> (1986)	1984	Eastern U.S.A	2.80–3.09
Hering <i>et al.</i> (1987)	1983	California, U.S.	3.08

Research has been limited on moderate elevation cloud composition, both in the U.S. (Falconer and Falconer, 1980; Weathers *et al.*, 1986) (Table 3) and in Europe (Fuzzi *et al.*, 1983). All these studies except for the one conducted by Falconer and Falconer (1980) have depended on the acquisition of integrated water samples. Even though Falconer and Falconer (1980) suggest using continuous cloud-water collection, their results are based on 1-h integrated sample collection. Moreover, they report only pH changes in the cloud, rather than a comprehensive chemical characterization.

In the past 10 or so years, researchers have attempted to identify the causes of damage to forests in the Adirondack Mountains of New York (Falconer and Falconer, 1980; Raynal, 1980; Mohnen and Kadlec, 1990), in Vermont (Liedeker *et al.*, 1988), in the Blue Ridge Mountains in Virginia (Duchelle *et al.*, 1982; Chappelka *et al.*, 1984), and various other locations in the U.S. (Evans and Lewin, 1985; Payer *et al.*, 1986; Lovett, 1984; Lovett and Reiners, 1986; Klein and Perkins, 1987; McLaughlin, 1985). The decline of

high-elevation forests has also been of recent concern in Europe, particularly in the Bavarian Alps and the upper portions of medium-range mountains (Schutt, 1984; Schutt *et al.*, 1983).

As part of a program to evaluate the possible impact of relatively acidic clouds on high-elevation forests, we have performed a comprehensive study of high elevation cloud characterization with a very fine time resolution (approximately 5 min) for analysis. This has allowed us to describe, on a nearly real-time basis, the dynamic chemical development of clouds. Real-time monitoring of cloud water pH, in contrast to integrated sampling methods, allows a more detailed study of the development of a cloud event and of its relationship with meteorological processes. In this study we collected enough cloud event data to observe the development of chemical processes of clouds at onset, during the event, and at cloud dissipation.

Several attempts to monitor rainwater pH continuously have been reported (Ames *et al.*, 1987). Most early rainwater sampling stations collected precipitation on an event, weekly, or monthly basis. Short

period, within-event hourly sequential samples were reported by Raynor and Hayes (1983), who noted that the changes in the concentrations of certain chemical species could be studied to infer atmospheric processes. A prototype, continuous, wet-only precipitation monitor was designed, built, and tested in central Colorado during the summer of 1983 (Reddy *et al.*, 1985). This group noted that the precipitation pH decreased rapidly as a storm began, was lowest at about the time of maximum rainfall intensity, and then increased. Other groups developed similar continuous-flow rainwater collection systems for which the sample was injected manually into the monitor (Madson and Doller, 1987).

Our monitoring system is largely based on a prototype, automated, microprocessor-based, realtime pH and conductivity rain monitor (Paur, 1987), which was designed to collect discrete fractions of rain events, analyze for pH and conductivity, and automatically store samples at 4°C for later laboratory analysis.

EXPERIMENTAL METHODS

Equipment

For the present study, a continuous, automated system for collecting, analyzing, and storing samples of rainwater was adapted to cloud analysis as a cloud and rain acidity/conductivity (CRAC) analyzer. The system consists of a rain sampler (Paur, 1987) comprising a Teflon-coated (E.I. Du Pont de Nemours) rain collector and an electrically operated cover. The instrumentation and electronics section includes a conductivity meter and two conductivity cells, a temperature-compensated pH meter, an electrode and a printer. Controlling the entire monitor system is a microprocessor, which is described in more detail elsewhere (Kronmiller and Ellenson, 1986). Precipitation samples are accumulated sequentially in dual accumulator vessels containing the conductivity cells. Upon accumulation of approximately 50 ml of sample, the system directs 12 ml to the pH measurement chamber and the remaining 38 ml into a storage vial in an automatic carousel. Both the storage carousel and the pH cell are located in a refrigerated section. The rain sampler interfaced to a California Institute of Technology (CIT) active cloud-water collector (Jacob *et al.*, 1985). This collector has a 50% cutoff size centered around 2- μm diameter. More details about the performance of this cloud-water collector (capture efficiency, wind speed dependency, etc.) have been reported previously (Mohnen and Kadlec, 1990; Danbe *et al.*, 1987). Collected cloud water was delivered directly via Teflon tubing from the CIT collector to a Y-junction feeding to the sample accumulation system (Fig. 1). To collect cloud water rather than rainwater, the rain detector was disabled.

Experimental set-up

During the summer and fall of 1987, this system was used to collect and analyze cloud-water samples on a continuous basis at a high-elevation site on Mt. Mitchell (latitude 35° 44', longitude 82° 16', elevation 2006 m) in the Black Mountain Range in western North Carolina (Fig. 2). The ecosystem is dominated by red spruce and Fraser fir forests. At this location, the canopy height is approximately 10 m. A meteorological tower (17 m) was installed at the site with a meteorological instrumentation package and cloud water sampling equipment located on top of the tower such that samples could be collected above the forest canopy. A

National Acid Deposition Program (NADP) collector was collocated at this high-elevation site to collect 1-week integrated precipitation samples.

The semi-real-time system continuously monitored cloud-water samples for pH and conductivity. Refrigerated, stored samples were later analyzed for SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Na^+ , K^+ , Ca^{2+} and Mg^{2+} . The stored samples also were reanalyzed for pH and conductivity. Meteorological and climatological data were collected, including wind speed, wind direction, r.h., ambient temperature, barometric pressure, and solar radiation, in addition to data for atmospheric O_3 , SO_2 , NO_x , and cloud liquid water content.

Integrated cloud-water samples also were collected hourly via an ASRC passive cloud water collection system (Falconer and Falconer, 1980). These samples were analyzed on a separate pH monitor in the field and similarly analyzed for major ions, pH, and conductivity in the laboratory 2–4 weeks later.

Before the start of a cloud event, the cloud-water collectors and tubing to the continuous pH monitor were rinsed thoroughly with deionized water until the conductivity of the rinse water was within 5 $\mu\text{mho cm}^{-1}$ of that of the deionized water.

METEOROLOGICAL CONDITIONS AT MT. MITCHELL

During the summer period, the most prolonged periods of cloudiness can be attributed to easterly winds supplying the moisture content necessary for orographic clouds. These periods are enhanced by the nocturnal winds lifting this moist air to the point of saturation. During this time, high pressure is dominant over the Northeast. The anticyclonic flow is the driving force of the easterly winds. These periods of cloudiness often are preceded by a frontal passage and associated clouds. The typical wind direction at Mt. Mitchell is southwest to northwest. In the approach of a zonally propagating front, the southwest winds are preferred, and anticyclones are thus pushed out to the southeast. The frontal events are generally characterized by a shift in wind direction and/or moisture content of the air mass.

The four major frontal systems that passed during the sampling period were preceded and followed by clouds. Wind direction was fairly steady during orographic events, and thus the major fluctuating variables were wind speed and temperature. Seven orographic events were sampled, and these events were accompanied by winds from the northwest, southwest, southeast, and east.

Daily temperature maxima were typically in the mid 60s to low 70s, and nightly lows ranged from the upper 40s to mid 50s (temperature in degrees Fahrenheit). Barometric pressure during this period was 805–810 mb. Daytime wind speeds averaged between 3 and 4 m s^{-1} , and nightly speeds averaged about 8 m s^{-1} .

During the October measurement period, the meteorological parameters were more variable. Typical daytime highs ranged from the mid 40s to low 50s, and nightly lows dropped into the 20s to low 30s. Barometric pressure ranged between 795 and 810 mb. Daytime winds averaged 4–5 m s^{-1} , rising to 9–13 m s^{-1} at night. During the first half of the month,

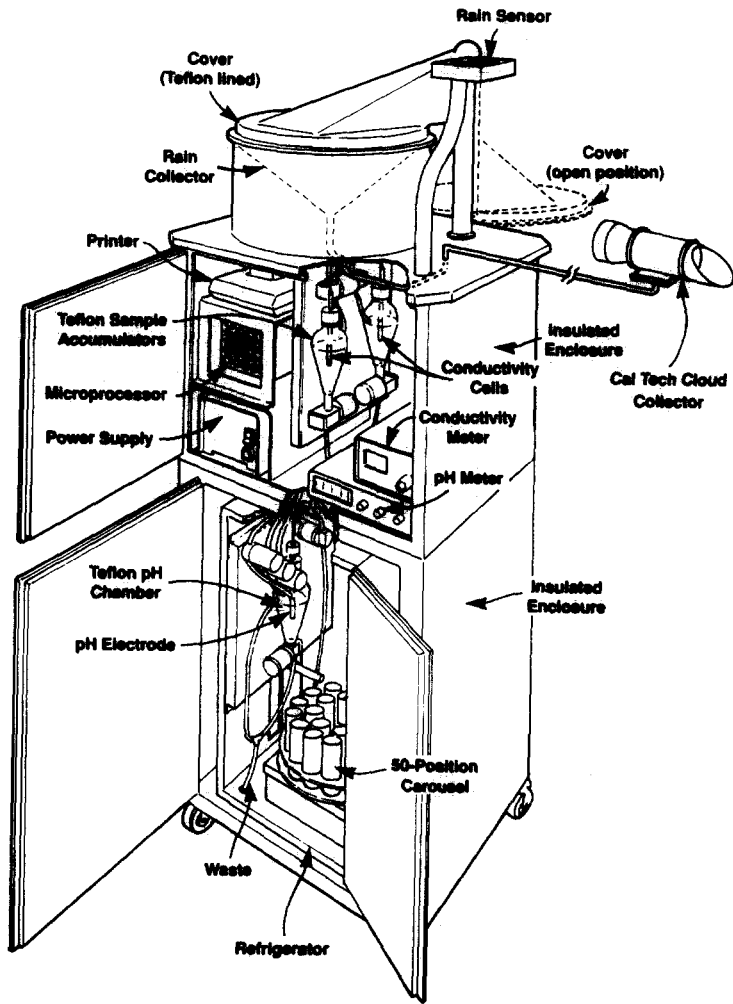


Fig. 1. Automated cloud/rain sampler.

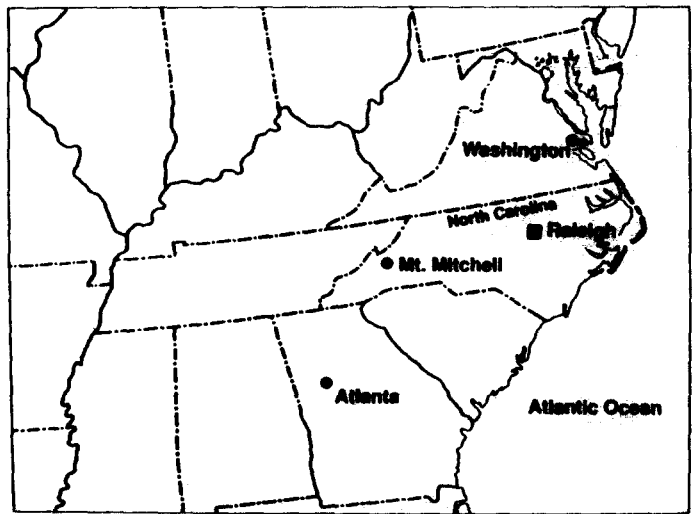


Fig. 2. Location of Mt. Mitchell, Black Mountains Range, NC, U.S.A.

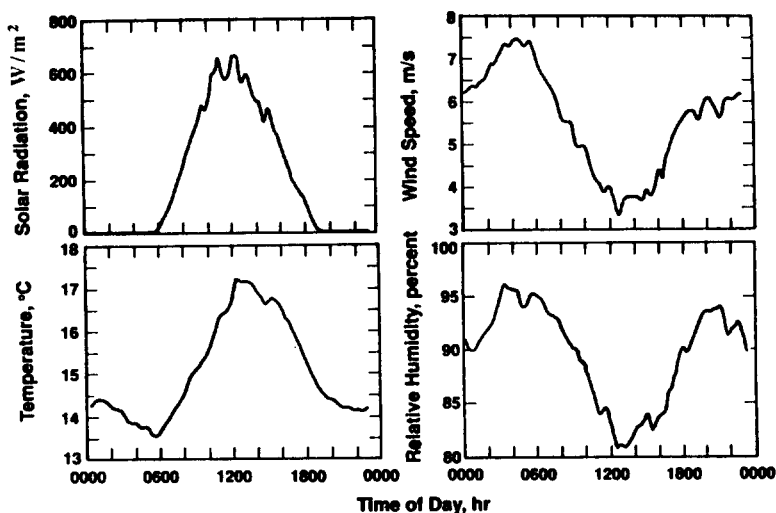


Fig. 3. Averaged meteorological conditions during Summer (1987) at Mt. Mitchell, NC.

winds predominantly from the east, southeast, and south were observed. Later in the month, the winds became southwesterly to northwesterly.

Figure 3 shows the average daily profiles for solar radiation, wind speed, temperature, and r.h. for the summer period. Data from each 15-min interval of each day were averaged over the entire time period to obtain the resultant curves. Here, it is clear that during the daytime period, as the temperature rises and maximum convective mixing occurs, horizontal wind speed and r.h. are at a minimum. The formation of the nocturnal wind maximum is coincident with the maximum in r.h. and a minimum in temperature.

RESULTS AND DISCUSSION

To better characterize the chemical and physical climate at the site (a high montane region), we made continuous and simultaneous measurements of (1) cloud pH and conductivity, (2) major ionic species content, (3) cloud liquid water content, (4) gaseous O_3 , SO_2 , and NO_x concentrations, and (5) meteorological parameters. Measurements were made during the summer (July 29–August 19) and fall (October) of 1987.

For the summer data, the physical and chemical structure analysis of the cloud indicated liquid water content averaging 0.252 g m^{-3} and ranging between 0.014 and 0.781 g m^{-3} . The average O_3 concentration was 52 ppb, mean SO_2 was ~ 1 ppb, and average NO_x was ~ 2 ppb (average NO was 0.5 ppb and average NO_2 was 1.5 ppb). The approximate range for O_3 concentration during the summer was 20–100 ppb.

For the fall data, the above values were 0.551 g m^{-3} average liquid water content, ranging from 0.183 to 1.068 g m^{-3} . Other average values were as follows: $O_3 = 48$ ppb, $SO_2 < 1$ ppb, and $NO_x = 2.1$ ppb (NO

$= 0.2$ ppb, $NO_2 = 1.9$ ppb). Additional data are presented in detail in Table 4. The O_3 concentrations ranged from 10 to 75 ppb.

During the summer period, 20 cloud events were measured. During this time, 421 pH and conductivity measurements were automatically made by the monitor. Corresponding samples were also collected and automatically stored sequentially in the refrigerated (4°C) section of the monitor. Later, 133 of these samples were analyzed in the laboratory for a variety of anions and cations. The pH and conductivity of the samples were remeasured with no appreciable change in these values.

A quality control cycle was programmed into the microprocessor, and the frequency of quality control checks was user-specified. Quality control checks were performed at a minimum frequency of every 24 h. The QC solution pH measurements are plotted in Fig. 4. If the pH is converted to H^+ concentration for averaging, the mean pH is 4.04, with a standard deviation of 0.04 pH units. This is well within the accepted range of ± 0.10 pH units standard deviation.

During the fall period, 62 samples were collected. Of these, 61 were measured by the monitor for pH and conductivity, and 47 were saved and later analyzed in the laboratory for ions, pH, and conductivity.

The dynamic pH development for three cloud events is shown in Figs 5, 6 and 7. These include data for summer (Figs 5 and 6) and for fall (Fig. 7). An unmistakable, dynamic trend is observed. At the beginning of the cloud event, in the absence of rain, the pH is low (approximately 2.9 for summer events and 3.9 for the fall event), rises gradually to a threshold value (about 3.5–3.8 for summer events and 4.5 for the fall event), and drops rapidly to nearly the original value. Figures 6 and 7 also present a comparison between liquid water content as measured with a gravimetric sampler (Valente *et al.*, 1989) and cloud water pH.

Table 4. Mean values (\bar{X}), standard deviations (S), and ranges for chemical species in cloud water samples collected continuously, via bulk sampling, and in rainfall samples

Season	Collector	No. of samples	pH	Conductivity ($\mu\Omega^{-1} \text{cm}^{-1}$)	Cl^- ($\mu\text{equiv l}^{-1}$)	NO_3^- ($\mu\text{equiv l}^{-1}$)	SO_4^{2-} ($\mu\text{equiv l}^{-1}$)	NH_4^+ ($\mu\text{equiv l}^{-1}$)	Na^+ ($\mu\text{equiv l}^{-1}$)	K^+ ($\mu\text{equiv l}^{-1}$)	Ca^{2+} ($\mu\text{equiv l}^{-1}$)	Mg^{2+} ($\mu\text{equiv l}^{-1}$)	H^+ ($\mu\text{equiv l}^{-1}$)	$\text{NH}_4^+ + \text{Ca}^{2+} + \text{H}^+$	$\text{SO}_4^{2-} + \text{NO}_3^-$
Summer	Continuous	\bar{X} :	3.29	267	31.2	180.2	532.2	177.6	14.3	2.4	20.8	9.0	512.9	96%	96%
		S:	(2.86-4.50)	197	27.9	124.0	388.0	128.9	27.4	2.5	18.4	12.8	(31.6-1380.4)	96%	96%
	Bulk sampling*	\bar{X} :	3.37	232	30.8	196.5	452.4	183.4	18.7	2.2	21.8	9.0	426.6	96%	96%
		S:	(3.00-3.79)	113	14.9	104.0	188.4	86.8	17.1	1.7	18.4	5.8	(162.8-1000.0)	94%	96%
	Rainfall† NADP	\bar{X} :	4.01	56.1	5.92	40.96	127.21	32.70	5.00	0.66	12.13	3.54	97.7	94%	96%
		S:	(3.87-4.27)	18.4	3.95	12.90	48.72	11.64	4.35	0.38	9.68	1.81	(53.7-134.9)	94%	96%
Fall	Continuous	\bar{X} :	4.09	33	3.3	28.4	66.0	27.0	4.5	0.9	8.8	2.6	81.3	94%	97%
		S:	(3.60-4.53)	19	6.1	21.4	49.2	26.4	12.7	1.4	13.0	7.6	(26.3-251.2)	94%	96%
	Bulk sampling	\bar{X} :	4.10	35	4.3	33.3	68.2	22.9	2.2	2.4	16.8	3.9	79.4	94%	96%
		S:	(3.88-4.55)	14	6.4	17.5	29.0	18.7	1.6	0.8	15.6	3.0	(28.2-131.8)	94%	96%

* 1 h averaged.

† Weekly averaged.

Cloud water pH measurements made both with the real-time monitor and the ASRC hourly integrated cloud samples are shown. Here, a general positive association between liquid water content and cloud pH can be observed. Such an association would be expected if cloud water ions were diluted to a greater or lesser degree with water.

For example (Fig. 6), at the beginning of the orographic cloud event, the aqueous concentrations of its major chemical components, typically H^+ , SO_4^{2-} , NO_3^- , Cl^- , Ca^{2+} , and NH_4^+ ions, are high. As the cloud develops, the liquid water content rises because of coalescence and condensational growth; hence, the droplets are diluted and the acidity drops, or conversely, the pH rises. Subsequently, as solar radiation begins to heat the air at around 6:00 a.m., evaporation takes place, the r.h. decreases, and the acidity increases, allowing the pH level to lower. Our results showing a decrease in pH of the cloud water during the final hours of a nonprecipitating cloud are consistent with those previously reported by other investigators (Falconer and Falconer, 1980; Castillo, 1979; Scott, 1978; Scott and Laulainen, 1979; Romer *et al.*, 1985). However, no data are presented by these authors elucidating the entire development of the cloud.

We also observe that, in the presence of rainfall, either during (Fig. 5) or just before (Fig. 6) the cloud event, the pH may be as much as 1 pH unit higher. This is in agreement with results reported by Falconer and Falconer (1980).

Integrated cloud-water samples (via the ASRC sampler) also were collected hourly. These sample results for pH are superimposed on Figs 5, 6 and 7. The results from both the continuous pH and the ASRC generally trend together; however, the real-time data give more complete cloud chemistry information than the integrated sample data, as evidenced in these figures. The second hourly sample from the ASRC (Fig. 5) showed a high pH compared to the trend on the continuous monitor. The dip in pH that occurred just before the increase does not appear at all in the hourly samples, suggesting that the integrated sample time period is too large to give good resolution. The continuous analysis of cloud pH data shows that the pH may be approximately 0.25 units different than that reported thus far by the 1-h integrated averaging procedure. This difference suggests that 1-h integration periods are too long to provide detailed dynamic characterization of clouds.

The mean, maximum, and minimum values for the cloud chemical parameters measured continuously during summer and fall are tabulated in Table 4, as are 1-h averaged integrated sample results obtained from the ASRC cloud-water collection system. Cloud-water samples collected during the summer months tended to be more acidic than those collected in fall (Fig. 8). By comparing the cloud pH values with those of rainfall (Table 4), we see that the rainfall value is almost 1 pH unit higher than the cloud pH value.

The cloud water was analyzed for anions (SO_4^{2-} ,

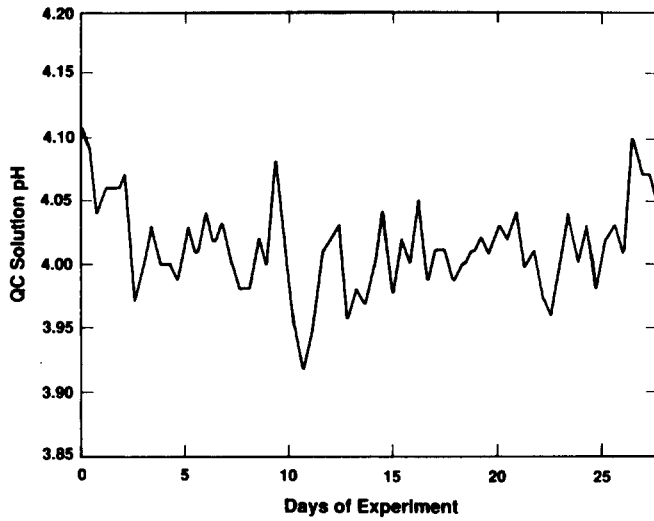


Fig. 4. Mt. Mitchell cloud pH monitor response to pH 4.0 QC solution, summer, 1987.

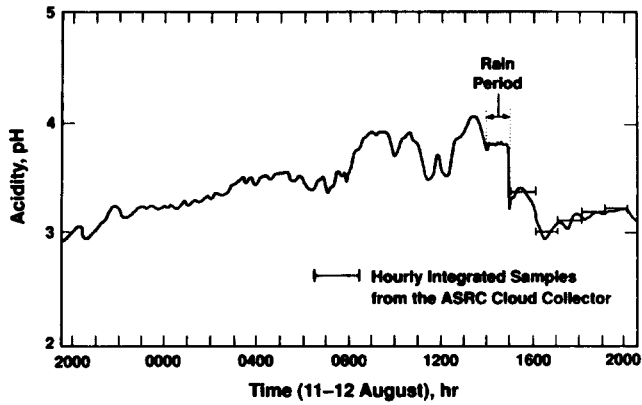


Fig. 5. Dynamic record of chemical development of a cloud at Mt. Mitchell, 11-12 August 1987.

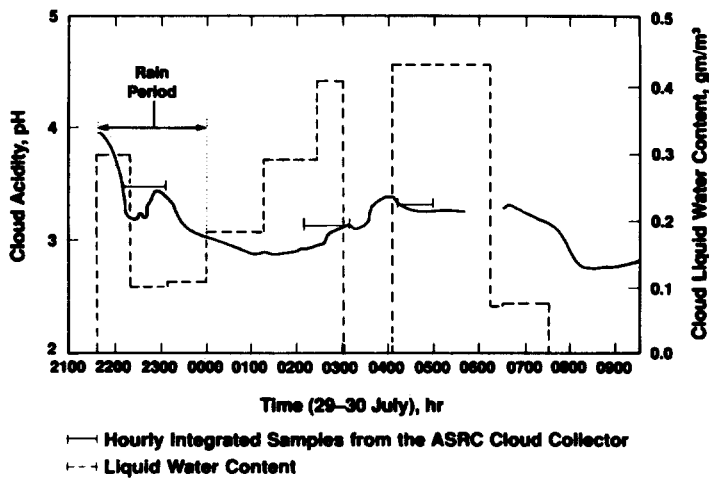


Fig. 6. Dynamic record of chemical and physical development of a cloud at Mt. Mitchell, 29-30 July 1987.

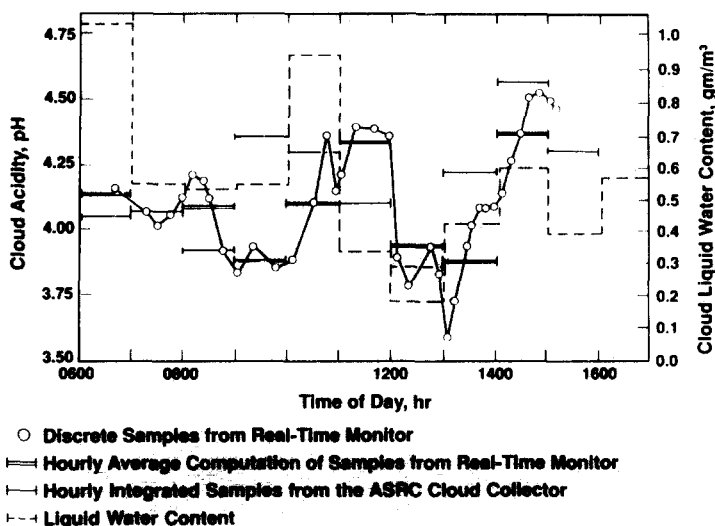


Fig. 7. Dynamic record of cloud development at Mt. Mitchell, NC, 12 October 1987.

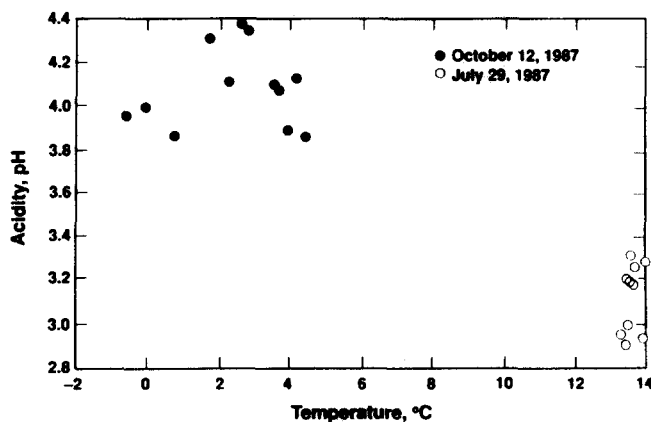


Fig. 8. Seasonal variation in cloudwater pH.

NO_3^- and Cl^-) and cations (H^+ , NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} ; see Fig. 9 and Table 4). An ionic balance for all continuously collected cloud-water samples is shown (Fig. 9). The one-to-one correlation indicates that all the major ionic species have been detected and quantified. The summer samples contained, on the average, greater amounts than the fall samples of all the ions for which analyses were conducted. H^+ , NH_4^+ , and Ca^{2+} are the dominant cations (accounting for almost 95% of the measured cations for either summer or fall, in cloud or in rain), and SO_4^{2-} and NO_3^- are the dominant anions (accounting for almost 95% of the measured anions for either summer or fall, in cloud or in rain). Weathers *et al.* (1986) analyzed lower elevation clouds in the eastern U.S. and reported similar trends for anions, but reported H^+ and NH_4^+ as the dominant cations, accounting for 95% of the

measured cations. Hence, the role of Ca^{2+} may be less significant at lower elevations.

Comparison of SO_4^{2-} and NO_3^- data obtained from the continuous cloud analysis with rainfall data collected at the same site during the same time period (Table 4) shows that the cloud concentrations may be roughly 150 times greater for SO_4^{2-} and roughly 25 times greater for NO_3^- than rainfall concentrations. At lower elevations these concentrations are only 7–43 times greater than the volume-weighted annual mean SO_4^{2-} and NO_3^- concentrations that have been measured in rainfall from locations in the eastern U.S. (Weathers *et al.*, 1986). The Daum *et al.* (1984) cloud data for SO_4^{2-} and NO_3^- collected during the summer in the eastern U.S. by airborne sampling are only 0.2–28 times greater than the volume-weighted annual means of SO_4^{2-} and NO_3^- concentrations in rainfall.

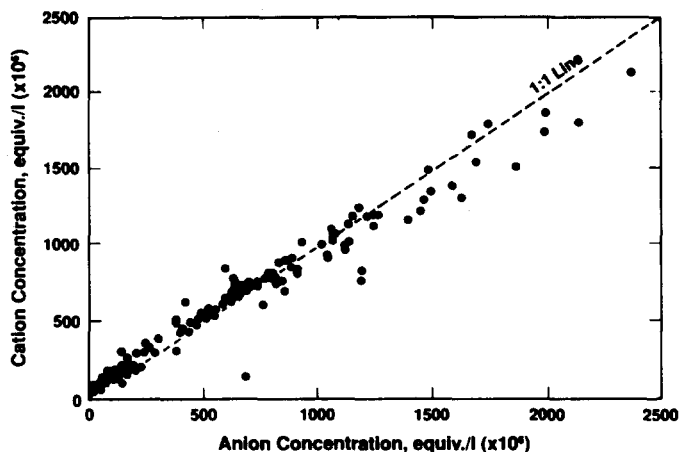


Fig. 9. Ion balance for all continuously collected cloud water samples.

Long-term means for rainfall range from 44 to 61 $\mu\text{equiv } \ell^{-1}$ SO_4^{2-} and 21–29 $\mu\text{equiv } \ell^{-1}$ NO_3^- (Weathers *et al.*, 1986). Similarly, the data presented in Table 4 indicate that the cloud concentrations may be roughly 25 times greater for H^+ and roughly 7 times greater for NH_4^+ than rainfall concentrations. Ionic species mean concentrations measured by continuous cloud water monitoring were similar in value to those average concentrations from the integrated (ASRC) samples. The continuous samples, however, displayed a much wider range of values. Often the upper range from the continuous sampler was 2–2.5 times the high value for the same ion (e.g. NH_4^+ , Na^+ , K^+ , Mg^{2+} and Cl^-).

CONCLUSIONS

The development and successful operation of a near real-time cloud water sampler/analytical system have been demonstrated. Despite the generally adverse environment in which the instrument was deployed, it performed reliably. Both collection volumes and pH measurements were repeatable. For example, root-mean-square variation of pH quality control samples was $< \pm 0.05$ pH units.

Hourly averages of pH values from the real-time sampler compared very well with integrated 1-h samples from a passive, string (ASRC) cloud-water collector. For the data shown in Fig. 7, the average pH values agreed to within 0.1 pH units. However, the maximum values in H^+ ion and in total ion strength were considerably greater for the short-term (approximately 5-min) samples. For several cloud water events, the maximum values for ions in cloud water were between 2 and 2.5 times greater for the short-term samples compared to conventional hourly integrated collections.

The range of pH and chemical composition of cloud-water samples obtained with this real-time instrument on Mt. Mitchell, North Carolina, are gen-

erally comparable with those obtained in urban cloud studies, while SO_2 and NO_x concentrations at the mountain site are much lower than typical urban values.

The real-time sampler is very useful for studying the development of orographic clouds. Some properties of these clouds, reported in previous investigations, are shown here to be outlined more definitively with short-term samples. Examples of these phenomena are increased ion concentrations in leading and trailing edges of cloud events and decreased ion concentrations in deposition during rain events.

Increased use of these techniques to study cloud deposition on Mt. Mitchell is planned for future field-testing seasons.

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