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# Chemical Dynamics of Clouds at Mt. Mitchell, North Carolina

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### FEATURE

# Chemical Dynamics of Clouds at Mt. Mitchell, North Carolina

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The role of clouds as the primary pathway for deposition of air pollutants into ecosystems has recently acquired much attention. Moreover, the acidity of clouds is highly variable over short periods of time. Cloud water collections were made at Mt. Mitchell State Park, North Carolina, using a real-time cloud and rain acidity/ conductivity (CRAC) analyzer during May to September 1987, 1988 and 1989 in an effort to explore extremes of chemical exposure. On the average, the mountain peak was exposed to cloud episodes about 70 percent of experimental days. The lowest pH of cloud water in nearly real-time (~10 min.) samples was 2.4, while that in hourly integrated samples was 2.6. The cloud pH during short cloud events (mean pH 3.1), which results from the orographic lifting mechanism, was lower than that during long cloud events (mean pH 3.5), which are associated with mesoscale or synoptic atmospheric disturbances. On the average, the pH values in nonprecipitating cloud events were about 0.4 pH unit lower than those in precipitating cloud events. Sulfate, nitrate, ammonium and hydrogen ions were found to be the major constituents of cloud water, and these accounted for ~90 percent of the ionic concentration. Total ionic concentrations were found to be much higher in non-precipitating clouds (670-3,010 µeq/L) than those in precipitating clouds (220-370 µeq/L). At low acidity, ionic balance is sometimes not obtained. It is suggested that organic acids may provide this balance.

The profile of cloud water ionic concentration versus time was frequently observed to show decrease at the beginning and rising toward the end during short cloud events. Before the dissipation of clouds, a decrease in cloud water pH and an increase in ionic concentration were found. At the same time, temperature and solar radiation increased, and relative humidity and microphysical parameters (liquid water content, average droplet size, and droplet concentration) decreased. These observations suggest that evaporative dissipation of cloud droplets leads to acidification of cloud water. Mean pH of cloud water was 3.4 when the prevailing wind was from the northwest direction, and it was 3.9 when the wind was from the west direction. The effects of variations in cloud liquid water content have been separated from variations in pre-cloud pollutant concentrations to determine the relationship between source intensity and cloud water concentrations.

In 1986, the Mountain Cloud Chemistry Program (MCCP), funded by the U.S. Environmental Protection Agency, began a routine program of one hour integrated cloud water collection, chemical analysis, gas monitoring and meteorological data sampling at Mt. Gibbs [~2,006 m mean sea level (MSL)] located in Mt. Mitchell State Park (35°44' N, 82°17' W). This program was designed to evaluate the hypothesis that acidic and other airborne chemicals contribute to the observed decline in spruce-fir forests in the eastern United States. A real-time cloud and rain acidity/ conductivity (CRAC) analyzer was developed in 1987 as part of





a research program aimed at determining the chemical dynamics of montane clouds, to complement cloud chemistry information from MCCP at the same site.

It is now recognized that deposition of cloud water may significantly contribute to the water, nutrient and health status of high-elevation forests where immersion in clouds occurs frequently.<sup>1</sup> This recognition arises largely from the recent studies which address the frequency of cloud interception, cloud water deposition and chemical composition of the intercepted cloud water at a number of high-elevation locations in the U.S. and other places.<sup>2-12</sup> It has now been shown<sup>13</sup> that clouds provide the primary pathway (~60 percent) for pollutant deposition on high elevation forest ecosystems when compared to rainfall (~20 percent), and dry deposition (~20 percent).

The majority of the rain monitors in operation today are designed to collect rain either on an event basis or weekly basis. There have been fewer attempts to design remote monitors that can collect rain events on a near real-time basis, chemically analyze the samples in real-time and also preserve the samples for more thorough laboratory analysis to be conducted later.<sup>14</sup> In the same way, most of the studies done so far on chemical characterization of clouds were also based on integrated water sampling. Only recently<sup>9,11</sup> have dynamic pH characterization of clouds been performed. However, here we describe and present results of an automated CRAC real-time sampling system, which stores nearly real-time samples for more thorough chemical analysis

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later in the laboratory. This instrument was field tested during 1987, 1988 and 1989 in a stand-alone configuration at a remote location at Mt. Gibbs in Mt. Mitchell State Park, NC.

The analysis of the real-time cloud samples collected by using the CRAC sampler has provided more fundamental understanding of cloud chemistry during an entire event than the currently available integrated water chemical characterization. In particular, real-time chemical characterization would be useful both in the study of acidic deposition, and in the study of the effects of deposition on biological systems.<sup>6</sup>

In this study, cloud water was collected by a CRAC real-time sampler as part of the Dynamic Chemical Characterization of Montane Clouds Project. The objectives of this paper are to: (1) characterize the extremes in chemical exposure to these ecosystems due to cloud water by the use of the CRAC real-time analyzer; (2) characterize the extremes of physical exposure; (3) examine the temporal variabilities of cloud water acidity for short (orographic effect) and long (frontal effect) cloud events; (4) investigate the dependency of cloud water acidity on meteorological parameters; and (5) examine the effects of microphysical processes on cloud water acidity. These data will provide us with insight on the extremes of chemical exposure and their significance in contributing to the water, nutrient and health status of mountain forests.

# Table I. Measured parameters and instruments used at the Mt. Mitchell Research Station during the observational periods (1987 - 1989).

Parameter	Instrument	Frequency
Automatic Mode		
* Wind speed	Propeller anemometer	Continuous
* Wind direction	Vane potentiometer	Continuous
* Air temperature	Thermistor	Continuous
* Barometric pressure	Piezoresistive	Continuous
* Relative humidity	Capacitor	Continuous
<ul> <li>Solar radiation</li> </ul>	Silicon photocell	Continuous
* Precipitation	Tipping bucket	Continuous
* Cloud water sample	CRAC system (Caltech active collector)	Continuous
*0,	UV photometry	Continuous
* SO <sub>2</sub>	Pulsed fluorescence	Continuous
" NO, NO <sub>2</sub> , NO <sub>x</sub>	Emission spectroscopy	Continuous
* Cloud detector	Forward scattering optical device	Continuous
Manual mode		
* Cloud water sample	ASRC passive collector	Hourly
* Cloud droplet spectrum	Forward Scattering Spectrometer Probe	Event
	(FSSP)	
* Liquid water content	Intergration of FSSP data,	Hourty
	and gravimetric sampler	
* Throughfall	Funnel and buckets	Weekly
Cloudwater and Throughta	1	
* pH	Electrode probe	
* Conductivity	Electrode probe	
* Anions	Ion exchange chromatography	
* Metal cations	Atomic absorption spectrophotometer	
Ammonium Ion	Spectrophotometer	1.00

#### **Experimental Site and Instrumentation**

The experimental site is located in Mt. Mitchell State Park. Mt. Mitchell is the highest peak ( $35^{\circ}44'03''$  N,  $82^{\circ}17'15''$  W; ~2,038 m MSL) in the eastern United States, and is located about 600 km west of the Atlantic coast. A topographical map of Mt. Mitchell area is shown in Figure 1. Mt. Mitchell State Park has a forest ecosystem composed primarily of red spruce (*Picea rubens sarg.*), and Fraser fir {*Abies fraseri (Pursh.) Poir.*}.

According to the survey results of the Mt. Mitchell forest from 2,024 m elevations to above 1,575 m:<sup>15</sup> (1) red spruce growing at elevation of 1,935 m or higher are in a severe state of decline; (2) defoliation and significant annual increment suppression was not observed for spruce below 1,935 m MSL; (3) the growth suppression cannot be attributed to lack of moisture; (4) red spruce's short roots at high elevation would be affected at pH <4.0; and (5) no fir or spruce trees are thought to reproduce successfully at altitudes above 1,935 m MSL.

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 2.0 km southwest of Mt. Mitchell. The tower is equipped 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, cloud liquid water content (LWC),<sup>16</sup> cloud detector,<sup>17</sup> and gas pollutant sensors (O<sub>3</sub>, SO<sub>2</sub>, and NO<sub>x</sub>). The instruments used are described in Table 1. The maintenance and calibration for these instruments were performed on a routine basis under the instructions of MCCP protocol and Quality Assurance/Quality Control plans.<sup>18</sup>

The meteorological sensors were placed at least 10 m above the forest canopy which mostly consists of 6-7 m tall Fraser fir trees. There are no known anthropogenic emission sources in the vicinity of the tower.<sup>19</sup> The investigation of the dynamic chemical characterization of clouds was performed by coupling a Caltech (California Institute of Technology) active cloud water collector, installed at the tower-top, to an automated precipitation monitoring (APM) system, which is located on the ground near the tower. The combined system of the APM and the Caltech cloud water collector is defined as the CRAC (cloud and rain acidity/conductivity) automated sampler in this research. A detailed description of the CRAC automated sampling system is presented in the next section.

#### Description of Cloud and Rain Acidity/Conductivity (CRAC) Automated Sampling System

The monitoring system is based on a prototype Automated Precipitation Monitoring (APM) system which was developed by Kronmiller et al.<sup>14</sup> APM was modified by interfacing a Caltech active cloud collector to automatically collect the cloud samples delivered from a cloud water collector.<sup>9</sup> The modified device includes a switching mechanism which can direct the sample flow from either a rain or a cloud collector. The CRAC analyzer is a robotic monitoring system to collect cloud and/or rain samples on a real-time basis. Figure 2 gives an information flow diagram for the operation of the CRAC analyzer during a cloud and/or rain event.



Figure 2. CRAC real time sampler information flow diagram.

The CRAC analyzer has three major units: (1) a cloud or rain collector unit, (2) a microprocessor-based electronics unit for the pH and conductivity measurements, and (3) a sample storage unit. The major components of the CRAC analyzer include the cloud collector, rain sensor, rain cover, microprocessor electronics modules, pH meter, conductivity meter, accumulation chambers and printer. The main sensor and the rain cover mechanism are both mounted on top of the monitor.

In the case of a rain event, once the event is detected by the sensor, the microprocessor sends a signal to a series of pneumatic cylinders that control the opening and closing of the rain cover. The cover remains open until the rain event is over. During a cloud event, cloud water samples are collected with the Caltech active cloud water collector.<sup>20</sup> The Caltech cloud water collector consists of a sampler duct, e.g., in the form of a square box open at both ends with a fan at the back of the duct. Droplets in a cloud sample are drawn into the sampler from the front of the duct by the fan. The velocity of flow is about 9 m s<sup>-1</sup>. The droplets are impacted on a series of vertical Teflon strings (diameter 510µm) which are arranged in the form of a screen on a frame. The 50 percent collection efficiency cutoff predicted from impaction theory corresponds to a droplet diameter of about 3.5µm<sup>8</sup>. Once ~50 ml of cloud water is collected in the accumulator, it is diverted to a sample vial which is equipped in a storage unit of CRAC monitoring system, and collected cloud water is then analyzed chemically. The conductivity is measured with a Cole-Parmer conductivity meter in conjunction with a conductivity probe. An Orion Model 611 pH meter, in which the temperature is automatically compensated, and an Orion 91-62 electrode has been used because it responds quickly at 5°C. A special quality assurance procedure has been included in the microprocessor programs so that the electrode response is automatically checked at programmed intervals.

A modified commercial refrigerator is used to store the cloud water samples. The collected samples are stored in the refrigerator slightly above freezing temperatures to minimize chemical changes in the samples. For the convenience of the storage and later analysis in a laboratory, an Eldex carousel is placed in the bottom of the refrigerator. The carousel holds 50 polycarbonate sample vials. The carousel is controlled by the microprocessor and advances after each sample is collected. The samples are kept refrigerated until collection.

Other components include an ALPS AGS 1100 printer. Data reports produced on the roll-paper printout include a station identification code, time of sample collection, sample vial position in the carousel, final pH, and conductivity readings and quality control solution results.

#### **Quality Control/Quality Assurance**

The CRAC system was serviced on a weekly basis though it was usually also checked daily. In addition, it was serviced after each event. The routine weekly service included once-a-week pH electrode calibration checks with pH buffers of 3.0 and 7.0. The calibration of the conductivity meter was also evaluated on a weekly basis with 36 and 186  $\mu$ mhos/cm potassium chloride solutions. At the start of a cloud event, the cloud water collector and Teflon tubing to the automated precipitation monitor are thoroughly cleaned by deionized water until the conductivity of the rinse water is within 5  $\mu$ mhos/cm of that of the deionized water.

The system has been designed to have an automatic quality control solution processed at programmable intervals. The pH of the quality control solution, ignoring any temperature or activity effects, was 4.00. The pH measurements of the QC solution are plotted in Figure 3 for the 1987, 1988 and 1989 field seasons at Mt. Mitchell. The average and standard deviation values for the pH of QC solution during 1987, 1988 and 1989 field seasons are pH 4.02  $\pm$  0.03, pH 4.01  $\pm$  0.03, and pH 4.03  $\pm$  0.04, respectively. The average value for all three years is pH 4.02  $\pm$  0.03. The response to the QC solution is a good indicator of the state of the electrode for pH field measurement during the field seasons, and it functioned satisfactorily.

#### Cloud Chemistry at Mt. Mitchell as Revealed by the CRAC Analyzer

The field season for cloud events observation for each experimental year are as follows:

- (1) 1987: July 29 October 12 (22 events monitored, and 492 total samples)
- (2) 1988: June 3 September 16 (23 events monitored, and 978 total samples)
- (3) 1989: May 30 August 1 (20 events monitored, and 402 total samples)





The pH and conductivity of the cloud samples were measured immediately after collection, and aliquots were separated for later chemical analyses. The major anions, Cl<sup>-</sup>, SO<sup>2-</sup> and NO<sup>2-</sup>, were measured in the laboratory using a Dionex 2010i ion chromatograph. The concentrations of major metal cations, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>, were determined by atomic absorption spectrophotometry. NH<sub>4</sub><sup>+</sup> concentration was determined by a standard colorimetric method. Detailed chemical analysis in the laboratory was performed for only selected cloud events each year. Four hundred and sixteen cloud water samples were analyzed for the major cations and anions to explore the chemical dynamics of the clouds at the site and their association to meteorology and microphysical parameters.

The average and/or extreme values of meteorological parameters observed during 1987 through 1989 field seasons are summarized in Table 2 to aid in the interpretation of the cloud water chemical data, and to describe the climatic condition at the site. Summary of the sampled events for different types of clouds, accumulated hours, mean pH of cloud water, and average LWC during 1987, 1988 and 1989 field seasons are presented in Table 3. The liquid water content was performed by a gravimetric sampler, as described in detail by Valente et al.<sup>16</sup> Based on Saxena and Lin's<sup>12</sup> terminology, cloud events were categorized into long cloud events (duration >8 hours), and short cloud events (duration  $\leq 8$  hours). Generally, the former are caused by a frontal passage or associated with large-scale disturbances, and the

latter are caused by the orographic lifting mechanisms. Cloud events accompanied with precipitation are defined as precipitating cloud events (or mixed events). Otherwise, they are defined as non-precipitating cloud events. The cloud pH data shows seasonal variation in cloud water acidity. The pH value in the summer season (pH  $3.15 \sim pH 3.82$ ) was significantly lower than those in spring and fall seasons (pH  $3.48 \sim pH 4.02$ ). This reflects the influence of the seasonal shift

Table III. Summary of CRAC sampled events, time-averaged pH, pH ranges, and average LWC values for different event types (1987 - 1989).

Year Tj	Туре	Events	Samples	Accum. hrs.	Ave. hrs.	Ave. pH	pH r	enges	LWC (g/m3)
							(Continuous)	(1 hr integrated)	
<b>1987</b> (July- Oct.)	Short Long Mixed Total	14 3 5 22	226 222 47 495	67.99 36.79 8.09	5.23 12.26 1.62	3.23(0.17) 3.40(0.02) 4.05(0.02) 3.34(0.07)	2.87 - 4.82	3.00 - 4.55	0.15(0.11) 0.54(0.20) 0.71(0.24)
<b>1988</b> (June- Sept.)	Short Long Mixed Total	9 2 12 23	149 257 572 978	41.22 36.70 102.35	4.58 18.35 8.53	3.03(0.29) 3.55(0.21) 3.57(0.38) 3.44(0.29)	2.44 - 5.64	2.53 - 5.27	0.24(0.17) 0.39(0.24) 0.39(0.21)
<b>1989</b> (May- Aug.)	Short Long Mixed Total	8 5 7 20	77 211 125 413	31.14 54.67 30.52	3.89 10.93 4.36	3.09(0.18) 3.59(0.20) 4.03(0.34) 3.57(0.24)	2.79 - 4.91	2.94 - 4.50	0.20(0.13) 0.22(0.14) 0.32(0.15)

 Table II. Summary of meteorological data during the field seasons at Mt. Mitchell Research Site (1987 - 1989).

Year	May	June	July	August	September
Average Ten	perature (C)				
1987	12.8	13.3	15.1	14.6	10.3
1988	10.8	13.6	14.8	15.2	12
1989	10.9	13.3	14.6	13.6	12.7
Maximum	20.5	22.1	23.5	23.5	19.9
Minimum	2.0	0.4	6.1	-0.6	2.2
Mean	11.5	13.4	14.8	14.5	11.7
Average Rela	tive Humidity	(%)			
1987	90.2	84.4	84.4	88	90.8
1988	71.4	73.3	84.2	88.1	88.5
1989	79.2	89.6	94.8	90.1	95.8
Mean	80.3	82.4	87.8	88.7	91.7
Total Precipi	lation (mm)				
1987	79.2	145.3	51.3	47.2	306.6
1988	26.9	36.8	96.8	105.2	145.3
1989	32.2	130.6	173.2	110.8	4.4
Mean	46.1	104.2	107.1	87.7	152.1
Average wind	Speed (m/s)				3.95
1987	4.2	6.5	5.3	6.5	6.6
1988	5.6	5.8	5.5	5.6	6.5
1989	8.2	6.7	5,9	5.6	5.6
Max. hourly	21	19.2	21.6	20	18.9
Mean	6.0	6.3	5.6	5.9	6.2
Average Wind	d Direction (de	arees)			
1987	267	290	293	350	83
1988	285	293	271	245	266
1989	247	227	229	234	193
Mean	266	270	264	276	181

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Table IV. Non-precipitating and precipitating cloud events summary sampled during observational periods of 1987 through 1989.

Types of Events	Number of Events	Total Hours	pH Ranges	Time-averaged means pH(±SD)
Non-precipitating (Short and Long Event	41 Is)	268.51	2.44 - 4.88	3.32(±0.29)
Precipitating (Mixed Events)	24	140.96	2.71 - 5.64	3.69(±0.45)

accompanied by significant change in large scale weather systems e.g., changes in typical pressure systems and predominant wind direction. In addition, the variability of pH and chemical compositions in cloud water depends on the origin of air masses. These dynamic effects on variability of pH and chemical composition in cloud water are discussed later.

Table 3 also shows that mean pH values for short cloud events (pH  $3.23 \pm 0.17$  for 1987; pH  $3.03 \pm 0.29$  for 1988; and pH  $3.09 \pm 0.20$  for 1989) were much lower than those values for long cloud events (pH  $3.40 \pm 0.02$  for 1987; pH  $3.55 \pm 0.21$  for 1988; and pH  $3.59 \pm 0.20$  for 1989). The pH values for mixed cloud (cloud and rain together) events (pH  $4.05 \pm 0.02$  for 1987; pH  $3.57 \pm 0.38$  for 1988; and pH  $4.03 \pm 0.34$  for 1989) were much higher than those values for both short and long cloud events.

During the field seasons, average LWC values ranged from 0.15 to 0.24 g m<sup>-3</sup> for the short cloud events, 0.22 to 0.54 g m<sup>-3</sup> for the long cloud events, and from 0.32 to 0.71 g m-3 for the mixed cloud events. The results of cloud water acidity data and LWC data analyses revealed an increase of cloud acidity from mixed cloud events (pH 3.57 to pH ~4.05) to short cloud events (pH 3.03 to pH ~3.23) as the LWC increases from short cloud events (0.15 ~0.24 g m<sup>-3</sup>) to mixed cloud events (0.32 ~0.71 g m<sup>-3</sup>). This increase in LWC may be explained as follows: in general, the short cloud events are associated with stratus (St) and stratocumulus (Sc) cloud types, in which the cloud droplets are a very concentrated solution of soluble cloud condensation nuclei.<sup>21</sup> According to these observations, it appears that these short cloud events can be attributed to the orographic lifting mechanism along the slope of Mt. Mitchell site, and thereby bring some near-surface or soil-derived aerosols and scavenging of pollutants (aerosol and gases) which have already accumulated in the valley.<sup>22</sup> On the other hand, long cloud events are attributed to the frontal clouds of nimbostratus (Ns) and altostratus (As) type which have larger cloud droplets as well as abundant moisture.<sup>12</sup> The highest pH of cloud water for the mixed events suggests that the rain drops are considerably more dilute than the non-precipitating cloud droplets.

Table 4 illustrates the time-averaged mean pH values and pH range (from minimum pH to maximum pH) for non-precipitating clouds (short and long cloud events), and precipitating clouds (mixed cloud events). The time-averaged mean pH values show that the cloud water samples collected in non-precipitating events (mean pH 3.32) are more acidic than those collected in precipitating events (mean pH 3.69).

A hypothesis-test (t - statistic test) has been used to evaluate the statistical significance of differences in sample mean pHs for non-precipitating cloud events  $(pH_{nonp})$  and precipitating cloud events  $(pH_{prec})$ . A one-sided hypothesis was used in this statistic test because it was suspected that  $pH_{prec}$  is greater than  $pH_{nonp}$  in the sample mean pH. The null hypothesis,  $H_{a}$ , stated as follows:

$$H_{o}: pH_{prec} - pH_{nonp} = 0$$

The alternate hypothesis,  $H_{A}$ , is:

$$H_{A}: pH_{prec} - pH_{nonp} > 0$$

where pH<sub>prec</sub> is a time-averaged mean pH value for precipitating cloud events, and

 $pH_{nonp}$  is a time-averaged mean pH for non-precipitating cloud events. A 5 percent level of significance has been used for the hypothesis test. According to the results of t-statistic by using the statistic information listed in Table 4, we reject the null hypothesis,  $H_0$ , at the 5 percent level of significance (t - statistic value = 4.035, t  $_{63,05} = 1.670$ ). It indicates that there is enough evidence in these samples to suggest that the cloud water acidities of non-precipitating cloud events were significantly higher than those of precipitating cloud events. According to confidence interval analysis, a 95 percent confidence interval for ( $pH_{prec} - pH_{nonp}$ ) was [0.187, 0.553] pH units. Therefore, we are 95 percent confident that our confidence interval covers the true value of ( $pH_{prec} - pH_{nonp}$ ), and this interval does not contain zero.

Figure 4 shows the cloud water pH variation with time and precipitation during a long mixed cloud event which occurred on September 16 through 17, 1988. A trend in cloud water pH variation with time was observed. For the first few hours (about 4 hours) of the event there was no precipitation. In this nonprecipitating period, the cloud water pH value gradually rose at the beginning of the event (pH ~3.11) for about two hours (pH ~3.50) and decreased to its initial pH value (pH ~3.10) just before precipitation began. This kind of time trend of cloud pH in absence of precipitation was generally observed in non-precipitating short cloud events sampled at the Mt. Mitchell site. On the other hand, in the presence of precipitation, the cloud pH gradually rose as the amount of precipitation increased, and it reached the maximum pH value ( $pH \sim 5.4$ ) when the maximum amounts of precipitation were observed. After the precipitation had ceased the cloud pH value decreased gradually as the cloud dissipated. This is in agreement with results reported by Aneja et al.<sup>9</sup> The reduced acidity of precipitating cloud water during the time precipitation is present may be explained by dilution of air pollutants (aerosol and gases) with rain water.

Based on 416 cloud water samples collected during the field seasons of 1987 through 1989, the duration of the cloud event, the mean acidity and ion concentration of cloud water are summa-



Figure 4. Cloud water pH variation with time and amount of precipitation for a mixed cloud event on September 16, 1988.

Date D	uration	(hrs)	pH	H+	NH4+	68++	Mg++	Na+	K+	804	N03-	CI-	∑cations	Saujous	Ratio
1987															
30-Jul	7.7	mean	3.07	848.0	353.0	35.0	9.0	5.0	4.0	930.0	305.0	53.0	1253.0	1288.0	.97
		SD	0.15	236.9	133.1	17.7	5.2	3.0	1.8	318.8	93.7	24.9			
		% of sum		33.4	23.9	1.4	0.3	0.2	0.1	36.6	12.0	2.1	49.3	50.7	
6-Aug	4.1	mean	3.14	726.3	218.7	12.3	3.2	3.7	1.4	832.7	160.0	26.3	965.7	1019.0	.96
		SD	0.26	343.1	104.6	5.2	2.6	3.5	1.7	449.0	85.0	18.3			
		% of sum		36.6	11.0	0.6	0.2	0.2	0.1	42.0	8.1	1.3	48.7	51.3	
17-Aug	4.7	mean	3.24	577.1	243.5	44.0	29.4	54.9	4.6	761.3	254.8	73.2	951.4	1079.3	0.88
		SD	0.21	231.0	67.2	17.4	13.2	25.5	1.5	315.6	95.1	19.8			
		% of sum		28.4	12.0	2.2	1.4	2.7	0.2	37.0	12.5	3.6	46.9	53.1	
19-Aug	3.7	mean	3.17	679.8	198.8	24.4	10.2	11.0	2.6	673.7	340.9	26.2	926.8	1040.8	0.89
		SD	0.07	104.0	76.5	10.5	4.8	5.5	1.2	186.9	68.6	11.6			
		% of sum		34.5	10.1	1.2	0.5	0.6	0.1	34.2	17.3	1.3	47.1	52.9	
12-Oct	4.1	mean	4.02	96.0	58.0	22.0	9.0	19.0	2.0	108.0	47.0	11.0	200.0	166.0	1.20
		SD	0.12	26.8	24.4	18.5	11.9	21.0	1.9	47.3	26.8	8.3			
		% of sum		26.2	15.8	6.0	2.5	3.6	0.5	29.5	12.8	3.0	54.6	45.4	
1988															
30-Jun	5	mean	2.94	1137.5	273.5	56.0	7.7	5.9	7.5	1194.0	285.1	77.8	1488.0	1531.0	0.97
		SD	0.15	354.6	87.0	34.0	5.6	2.8	3.1	177.4	96.2	38.1			
		% of sum		37.7	9.1	1.9	0.3	0.2	0.2	39.5	9.4	2.6	49.3	50.7	
30-Jun	3.1	mean	3.02	970.7	132.8	32.7	3.3	9.4	7.5	893.0	194.7	40.5	1156.0	1128.2	1.02
		SD	0.49	695.1	88.3	18.8	2.8	7.8	4.8	467.6	148.7	27.3			
		% of sum		42.5	5.8	1.4	0.1	0.4	0.3	39.1	8.5	1.8	50.6	49.4	
16-Sept	4.8	mean	3.25	564.0	90.0	15.0	1.4	6.9	3.5	357.0	130.0	19.0	681.0	506.0	1.35
		SD	0.18	236.6	30.7	5.9	0.9	3.9	3.5	87.1	72.3	12.5			
		% of sum		47.5	7.6	1.3	0.1	0.6	0.3	30.1	11.0	1.6	57.4	42.6	
1989															••••••
20-Mav	13.3	mean	3.44	364.0	274.0	33.0	7.0	9.0	5.5	515.0	213.0	15.0	692.0	743.0	0.93
		SD	0.18	158.8	145.5	11.5	3.2	4.4	3.6	203.6	81.4	5.0			
		% of sum		25.4	19.1	2.3	0.5	0.6	0.4	35.9	14.8	1.0	48.2	51.8	
6-Jun	13.4	mean	3.64	228.9	65 1	18.3	32	3.9	3.6	229.2	111.3	17 1	323.0	357.6	0.90
		SD	0.21	92.4	20.7	124	37	41	21	101.4	41 1	31.5			0.00
		% of sum	••••	33.6	9 A	97	0.5	0.6	0.5	33.7	18.4	25	47 5	<b>52 5</b>	
19lul	78	mean	3.67	212 7	86.2	10.9	24	21	13	270.4	74.9	9 A	315.8	355.0	0.89
		SD	0.12	57.8	25.8	42	12	18	0.6	78 1	26.0	3.6	010.0	00010	0.00
		% of sum	<b>W</b> E 7 100	317	12 9	16	04	03	0.2	40.3	11.2	14	47 1	52.0	
23-, Iul	26	mean	4 31	48.2	19.7	03	41	17.8	3.6	40.5	44 1	21 5	102.2	115.9	n so
	6.9	SU	0.00	0.0	61	0.0 2.6	17	9.4	A 1	71	10.2	67	IVGrG	11016	0.00
		% of eum	0.00	20.0	01	43	10	8.7	1.6	00 8	20.2	0.7	47.0	62 A	
97. Jul	2 64	maan	3 17	677 9	122.6	150	20	22	10	EAA O	20.0	40.7	0.020	770.0	1 09
CI 1001	0.07	en	0.11	140.7	20.0	10.0	4.0	4.0	0.0	49 E	200.4 20 A	10.1 C A	000.0	110.0	1.00
		% of eum	0.00	140.7	9.00	4.0	02	1.0	0.8	94.0	10.0	4.0	59 A	40 0	
09.111	0.07		9.00	46.C 507 4	160 0	1.0	0.6	0.6	U.I	04.0 405 0	100 0	1.6	02.U 702 0	40.U	4 04
1000	9.21	niesn op	0.40	300 /	108.0	22.0 E 0	3,4	2.3	1.0	990.0	100.0	10.0	120.8	700.4	1.04
		00	U. 10	138.4	0.00	0.9	1.2	2.4	0.8	08.9	40.2	4.8	FA 4	44.4	
nd 1-1	0.00	% or sum	0.07	37.0	11.8	1.0	0.2	U.Z	U.1	34.7	13.2	1.2	00.9	49.1	
31-JUI	2.92	mean	3.37	429.0	1/0.9	12.3	2.1	3.6	0.7	464.8	136.6	14.8	619.2	616.2	1.00
		5U	U.1	93.3	52.4	2.4	0.7	1.9	0.8	55.1	33.9	2.6			
		% OT SUM		34.7	13.8	1.0	0.2	U.3	U.1	37.6	11.1	1.2	50.1	49.9	

Table V. Statistical summary of cloud chemical analysis for the events sampled during 1987, 1988 and 1989. Concentration units are in µcq/L.

rized (Table 5) with respect to cloud events for 1987, 1988 and 1989. From these analysis, the ionic balance between anions and cations for cloud water from each event are presented in Figure 5. In general, for most cloud water samples, a good balance between anions and cations was obtained (slope = 1.04 and coefficient of determinations,  $R^2 = 0.98$ ). The slight imbalance between measured anions and cations can only mean either or both of the following: (1) some anions or cations were not measured; we did not measure organic acid (e.g., HCOOH) in this study. Formic acid may be produced because of the reaction of HCHO (aq) with OH (aq) in cloud water<sup>23</sup> and (2) there were errors in one or more species' measurements,<sup>3</sup> From Table 5, it appears that H<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2</sup>, and NO<sub>3</sub><sup>-</sup> ions are the principal ions of cloud water at Mt. Mitchell as also reported in recent studies by other investigators.<sup>4,12,24,25</sup> On average, for cloud events, the fraction of equivalents of all ionic constituents expressed as a percent (hereafter referred to as mass contribution) found these four principal ions in cloud water to range from 90 percent to 98 percent during the field seasons. For individual chemical components of cloud water samples, mean mass contribution ranged from ~23 percent to ~42 percent for SO<sub>4</sub><sup>2-</sup>; from ~22 percent to ~47 percent for H<sup>+</sup>; from ~8 percent to ~20 percent for NO<sub>3</sub><sup>-</sup>; and from ~6 percent to ~19 percent for NH<sub>4</sub><sup>+</sup>. According to Saxena and Lin,<sup>12</sup> in general, ammonium is attributed mostly to



Figure 5. Ion balance for the continuously collected cloud water samples.

bacterial production from agricultural activities and hydrolysis of urea, and partly to man-made pollutants, and is thought to neutralize the cloud water acidity. Sulfate and nitrate are mainly derived from anthropogenic sources, and are mainly thought to acidify the cloud water. In addition, Cl<sup>-</sup>, Na<sup>+</sup> and Ca<sup>2+</sup> were other minor constituents. The first two, which in general are derived from the ocean, have to balance each other, if no other sources exist. Nevertheless, our results show that more Cl<sup>-</sup> than Na<sup>+</sup> was mea-

sured during cloud events. This high concentration of Cl<sup>-</sup> may be the result of HCl gas uptake.<sup>26</sup> Ca<sup>2+</sup> was also found to be less than Cl<sup>-</sup> in our cloud water samples. Primarily, Ca<sup>2+</sup> is a component of carbonate and silicate soil minerals blown into the atmosphere after cultivation.<sup>27</sup> Secondly, it may be derived from dirt roads and construction sites.

Figure 6 shows contribution of chemical composition to total fraction of equivalents of all ionic constituents expressed as a percent with respect to cloud event categories for 1987, 1988 and 1989. Contribution diagrams for long events during 1987 and 1988 field seasons are missing because no chemical analysis were performed on the samples during those years. Figure 6 shows that the mass contribution of the four principal ionic species (SO<sup>2-</sup>,  $NO_3$ , H<sup>+</sup>, and  $NH_4^+$ ) in long and short events are above 95 percent for 1989 field seasons. However, those chemical species in mixed events contribute less to total concentration (~74 percent), while the rest of chemical species in mixed events are much more (five to ten times) than in cloud only events. It also shows that the mass contribution of SO<sup>2-</sup> (~35 percent) and H<sup>+</sup> (~35 percent) in non-precipitating cloud events (both long and short events) was much greater than in precipitating cloud events (mixed events) (~23 percent for SO<sub>4</sub><sup>2-</sup> and ~22 percent for H<sup>+</sup>). On the other hand, mass contribution of Cl and other metal cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup>) was about ten times greater in nonprecipitating cloud events (~1 percent for

Cl and  $\sim$ 2 percent for metal cations), than in precipitating cloud events ( $\sim$ 10 percent for Cl and  $\sim$ 23 percent for metal cations).

Scatter plots of the principal anions' concentrations versus cations' concentrations were performed for all cloud water samples collected, during 1987, 1988 and 1989 field seasons, which were analyzed chemically (total number of samples = 416). A scatter plot of sulfate ion concentration versus hydrogen ion concentration is shown in Figure 7. The plot shows that, based on statistical analysis (slope of regression line = 1.03,  $R^2 = 0.70$ ), the sulfate ion concentrations were slightly higher than hydrogen ion concentrations. The nitrate ion concentrations were slightly lower than ammonium ion concentrations. The sum of sulfate and nitrate ion concentrations is almost equivalent to the sum of hydrogen and ammonium ion concentration (Figure 7). However, Saxena and Lin<sup>12</sup> observed that sulfate and nitrate ion concentrations were 5 to 10 percent more than hydrogen and ammonium ion concentrations in cloud water, based on one hour integrated sample chemical analysis during 1986 and 1987 field seasons. Figure 7 shows that for most cloud water samples, the ammonium ion concentration has a linear relation with sulfate and nitrate  $([SO_4^2] + [NO_5])$ ]) ion concentration on the basis of our chemical data results ( $\mathbb{R}^2$ = 0.70). This could be due to neutralization of acidic species by gaseous ammonia, or it could be due to the dissolution of ammonium aerosols in cloud water.

 $[SO_4^{-2}]$  and  $[NO_3^{-1}]$  are negatively correlated with the pH of cloud water with a correlation coefficient of 0.84 ( $R^2 = 0.70$ ) for sulfate, and 0.71 ( $R^2 = 0.50$ ) for nitrate. These negative correlations between the anions and pH of cloud water were also found



Figure 6. The major ionic contribution to the total mass for different cloud event categories of 1987, 1988 and 1989.

in earlier research of one hour integrated cloud water samples at Mt. Mitchell.<sup>12</sup> Their correlation coefficients were about -0.70 for both ions. This is about the same as our results. On the other hand, the correlation coefficient between sulfate ion concentration and pH of cloud water over the Los Angeles Basin was 0.42.<sup>28</sup> This is attributed to the effect of alkaline sea salt in on-shore air during the sampling period. Mt. Mitchell is about 600 km west of the North Carolina coast line, and even the on-shore air flow does not bring as many marine aerosols into clouds as in the Los Angeles Basin, which is on the coast.

The initial chemical composition of orographic clouds has been shown to be determined largely by the composition of aerosol that serves as condensation nuclei,<sup>22</sup> and to some extent by the ambient concentration of soluble gases.4 The composition of aerosols largely depends on the transport routes and chemical reactions in cloud water during the sampling period. Figure 8 shows the mean pH of cloud water with respect to sixteen predominant wind direction sectors for the cloud events collected during 1987, 1988 and 1989 field seasons. The most acidic cloud water samples (mean pH 3.37) were found in the northwest (NW) direction sector which has large industrial areas

(i.e., midwestern U.S.), and also in the south-southeast sector which has relatively high acidity. On the other hand, the lower cloud water acidity was usually observed in unindustrialized continental areas (southwest and west direction: pH  $3.85 \sim 3.90$ ) and oceanic regions (east-northeast direction: pH 3.84).

To investigate the variation of cloud water acidity as a function of different source regions, sixteen different sectors are defined.<sup>11</sup> Using the 1985 NAPAP Emissions Inventory of SO<sub>x</sub>, NO<sub>x</sub> and total suspended particulate (TSP) for eastern and middle United States provided by the U.S. Environmental Protection Agency<sup>29</sup> source regions were categorized into sixteen predominant wind sectors (Table 6). The emissions of sulfur, nitrogen and total suspended particulate in each sector corresponds with the variation of cloud water acidity (at a correlation coefficient of ~0.5).

This suggests the relationship between source intensity and cloud water acidity.

To separate the effects of variations in cloud liquid water content from variations in pre-cloud pollutant concentrations in order to further examine the relationship between pollutant source intensity and cloud water concentrations, cloud water hydrogen ion concentrations were converted to equivalent gas phase concentrations by using the cloud liquid water content. Figure 9 and Table 6 show the concentrations in the cloud water of the hydrogen ion in the aqueous phase, the liquid water content, and the equivalent gas phase hydrogen ion concentration. The concentrations of the hydrogen ions in the aqueous phase correspond well (at a correlation coefficient of ~0.5) in the same order as a pollutant source intensity of the wind



#### **Summary and Conclusions**

This study addresses the chemical dynamics of mountain clouds by using the real-time CRAC analyzer. The principal



Figure 8. Mean pH of cloud water as a function of wind direction during the field seasons of 1987, 1988 and 1989.



Figure 7. (a) Sulfate versus hydrogen, (b) nitrate versus hydrogen, (c) ammonium versus sulfate plus nitrate, and (d) hydrogen plus ammonium versus sulfate plus nitrate ion concentration for cloud water samples collected during 1987, 1988 and 1989.

#### FEATURE

Table VI.  $SO_2$ ,  $NO_x$ , and total suspended particulate emissions in a 500 mile radius from Mt. Mitchell, NC (units:  $10^5$  tons/yr); and wind direction frequency, liquid water content, pH of cloud water in short events, and equivalent gas phase [H<sup>+</sup>] for the corresponding wind sectors.

Wind Sector	N	NNE	NE	ENE	E	ESE	8E	88E	8	8W8	SW	WSW	W	WNW	NW	NNW
S02	9.6	4.2	3.7	3.6	3.5	5.4	3.5	3.0	3.4	4.0	4.3	4,4	5.2	4.3	8.7	9.1
NOx	3.2	3.0	2.7	3.1	1.8	1.9	0.9	0.9	1.0	1.0	1.5	1.8	1.2	1.8	2.3	2.9
TSP	2.5	2.5	1.7	2.5	0.7	0.9	0.5	0.5	0.6	0.6	0.8	0.8	0.7	1.2	1.4	1.7
Wind Freq.(%)	<0.1	<0.1	<0.1	0.2	19.6	16.1	2.4	0.8	2.1	3.7	5.6	5.0	7.1	29.7	7.5	<0.1
LWC (g/m <sup>3</sup> )		-	-	-	0.28	0.35	0.23	0.09	0.33	0.33	0.62	0.25	0.20	0.35	0.27	-
pH	-	-	-	3.84	3.48	3.66	3.51	3.57	3.79	3.75	3.90	3.72	3.85	3.58	3.37	•
Gasphase (H+)	•	-	-		0.093	0.077	0.071	0.024	0.054	0.059	0.078	0.048	0.028	0.092	0.115	, -
(µg/m <sup>3</sup> )																

results of this study are summarized as follows: The lowest pH value in real-time samples was 2.44 during the field seasons, while that in hourly integrated samples was 2.58 in the same event. Seasonal variation of cloud water acidity was also observed. In general, the cloud pH in summer seasons ( $pH = 3.15 \sim 3.82$ ) was lower than those in spring and fall ( $pH = 3.48 \sim 4.02$ ); suggesting that the amount of moisture in the atmosphere may be important in determining the acidity of cloud water. Cloud water acidity in wet season is low due to dilution effects of air pollutant into abundance of moisture in the atmosphere. Mean pH of cloud water in 1987, 1988 and 1989 were 3.34, 3.44 and 3.57, respectively.

The pH found in short cloud events (mean pH 3.12 for all three years combined) was substantially lower than that in long cloud events (mean pH 3.52). Based on the statistical analysis, it was



Figure 9. H<sup>+</sup> Concentration for short cloud events for the field seasons of 1987, 1988 and 1989 (a) liquid phase; (b) liquid water content (LWC); and (c) calculated corresponding gas phase.



Figure 10. Comparison of pollutant emission source strength and calculated corresponding gas phase [H\*] versus wind sector.

shown that the acidity in non-precipitating cloud water (mean pH 3.32) was higher than that in precipitating cloud water (mean pH 3.69). The initiation of precipitation was demonstrated to dilute the cloud water acidity.

Sulfate, nitrate, ammonium and hydrogen ions were found to be the major constituents of the cloud water. Their total equivalent concentration was above 90 percent of the total analyzed fraction of equivalents of all ionic constituents expressed as a percent in short and long cloud events. However, these species in mixed events contributed about 74 percent to the total fraction of equivalents of all ionic constituents. Sulfate and nitrate ions are mainly thought to acidify the cloud water, whereas ammonium is thought to neutralize the cloud water acidity.

Sulfate ion concentrations were generally higher than hydrogen ion concentrations for most cloud water samples. Nitrate ion concentrations were slightly lower than ammonium ion concentrations. The sum of sulfate and nitrate ion concentrations is almost equivalent with the sum of hydrogen and ammonium ion concentration. Consequently, the sum of other minor cations  $(Mg^{2+}, Ca^{2+}, Na^+, and K^+)$  have to be responsible for neutralizing the other anion (Cl<sup>-</sup>) of cloud water samples. It was found that sulfate concentration rather than nitrate correlated better with hydrogen ion concentration. This suggests that the cloud water acidity may be coming predominantly from sulfate aerosol and less from nitric acid.

The variation in cloud water acidity as a function of sixteen different source regions was explored. Mean acidities measured when wind direction is from the northwest sector (most polluted region) are the highest (pH 3.37). Thus the results showed that, in general, the highest pollutant concentration in cloud water was found in the air masses coming from the northwest (midwestern U.S., i.e., Ohio River Valley region). On the other hand, the lowest concentration was found in the air mass coming from southwest or west (i.e., central U.S.) and east-northeast direction (oceanic region). Separating the effects of variations in cloud liquid water content from variations in pre-cloud pollutant concentrations, the relationship between source intensity and cloud water concentration was ascertained, which suggests that long-range transport has a significant effect on determining the chemical characterization in cloud water at Mt. Mitchell, North Carolina.

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