

Chemical composition of clouds at Mt. Mitchell, North Carolina, USA

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ABSTRACT

Using a recently developed cloud and rain acidity/conductivity (CRAC) real time analyzer, clouds atop Mt. Mitchell State Park, North Carolina—the highest peak (~2038 m MSL) in the eastern US—were investigated from May to October during 1987 to 1989. Measurements for chemical and physical climatology were performed to estimate exposure of pollutant at the forest canopy resulting from direct capture of cloud droplets. The mountain peak is exposed on the average to cloud episodes about 70% days per year. Results are reported for integrating times of cloud collection, approximately 5 min, during several precipitating and non-precipitating cloud events. Cloud water was found to have higher acidity and higher concentrations of sulfate, nitrate and ammonium than previously observed in rain droplets. The pH of the cloud water was in the range of 2.4 to 4.9 during 1987 through 1989 field seasons, while the pH of the rain water was in the range of 3.5 to 5.5. The cloud water collected in summer season was more acidic than those collected in any other seasons (spring and fall). The maximum of average cloud pH value (i.e., low acidity) was found when the predominant wind direction was from southeast. On the other hand, the low average cloud pH values (i.e., high acidity) were found when the predominant wind direction was west through northeast. Total concentrations of major chemical species in cloud water at Mt. Mitchell State Park are significantly higher (~1250 to ~3020 $\mu\text{eq/l}$) than those reported for other rural locations. According to the time-sequential chemical concentration, a concave trend with total concentration decreasing at the beginning and rising toward the end of event was observed. It was also observed that changes in the individual ionic concentration are proportional to the changes in total concentration. It suggests that condensation and evaporation of cloud droplets are the important processes, during various stages of a cloud event, in determining the total pollutant concentration of cloud water.

1. Introduction

Much interest has developed recently in trying to ascertain the role of clouds in contributing to high elevation forest decline in the United States, Canada and western Europe (Blank, 1985; Waldman et al., 1985; Weathers et al., 1986; Aneja et al., 1988, 1990; Saxena et al., 1989; Saxena and Lin, 1990); since it is now recognized that clouds and fogs are more acidic in nature than precipitation at the same location (Falconer and Falconer, 1980; Muir et al., 1986). Cloud exposure may be about five times greater than the corresponding number of rain hours. In the high elevation mountain areas, it was indicated that cloud deposition pathway may account for a large fraction of both

moisture and chemical loading (Lovett et al., 1982; Saxena et al., 1989) because the cloud droplets are frequently developed onto terrestrial surface; and the higher wind speed aloft also enhance the cloud droplet capture efficiency. It has now been shown (Murthy and Aneja, 1990), based on an analytical analysis, that clouds provide the primary pathway (~60%) for pollutant deposition on high elevation forest ecosystem when compared to wet (~20%) and dry (~20%) deposition processes.

Recently, questions have been raised about the chemical and physical structure of clouds regarding their potential role in adding chemicals such as nutrients, mineral acids and trace metals to such ecosystems. However there is paucity of data on chemical composition of clouds, and limited

dynamic real-time chemical characterization of these systems (Aneja et al., 1990), and essentially no simultaneous measurements of cloud chemical and microphysical parameters. To understand the dynamic chemical characterization of these acidic clouds, and in identifying the role of chemical stresses on high elevation forest ecosystems; the analysis of samples collected on real-time basis would be needed because of the variability of the acidity and chemical composition in space and

time. These analyses will be useful both in defining the significance of cloud processes in deposition and in the study of resulting biological interactions.

Table 1 shows the results of the chemical analysis of cloud or rainwater sampled at different high elevation sites, in southeastern United States (Dasch, 1988; NADP, 1988; Reisinger and Imhoff, 1989; Saxena and Lin, 1990). The bulk water chemical characterization of a cloud has been

Table 1. Ranges in ionic concentrations ($\mu\text{eq/l}$) of cloud or rainwater observed at different southeastern

Location	Date	pH	H ⁺	NH ₄ ⁺	Ca ⁺⁺	Mg ⁺⁺	Na ⁺
Mt. Mitchell, NC (Cloud)	1987.7-8	2.87-3.68	209-1349 (695)	72-678 (259)	6.0-71.0 (29)	0.5-4.3 (12)	1.0-82.0 (16)
real-time samples	1987.1	3.85-4.21	62-141 (94)	22-127 (61)	8.0-60.0 (21)	0.8-30 (8)	0.2-51 (14)
Mt. Mitchell, NC (cloud)	1987	(3.51) ± 0.38	(423)	(197)	(24)	(8)	(19)
1-h integrated samples							
Clingman, NC (cloud)	1986.8-9		(180) ± 23	(120) ± 20	(19) ± 6	(6.7) ± 1.6	(9) ± 2.7
Clingman, NC NADP, weekly avg. (rain, 1987)	summer	4.02-5.03	9.0-96 (52)	7.0-26.0 (11)	1.0-30.0 (2)	0.5-15.0 (1)	1.0-33.0 (2)
	fall	4.24-6.12	1.0-58.0 (29)	1.0-64.0 (10)	1.0-67.0 (2)	0.5-18.0 (1)	1.0-38.0 (2)
Whitetop Mt, VA (cloud)	1986-87		55-1657 (451)	2-716 (180)	12-108 (32)	4.0-26.0 (12)	1.0-71.0 (12)

United States locations (the values in parentheses are weighted average)

K ⁺	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Σcation	Σanion	Σca/Σan	Σions	Ref.
1.0-8.0 (4)	202-1814 (761)	36-556 (255)	4-121 (44)	1015	1060	0.96	2075	present work
1.0-6.0 (2)	52-252 (113)	14-114 (49)	2.0-21 (12)	200	174	1.15	374	present work
(3)	(446)	(179)	(29)	674	654	1.03	1328	Saxena & Lin (1990)
(3.5) ± 0.6	(290) ± 42	(110) ± 16	(16) ± 3					Dasch (1988)
0.1-0.6 (0)	38.0-135.0 (52)	13.0-50.0 (19)	2.0-20.0 (2)	68	74	0.92	142	NADP (1988)
0.1-3.0 (0)	5.0-190.0 (33)	5.0-96.0 (11)	1.5-12.0 (2)	44	46	0.96	90	
2.0-9.0 (5)	54-1642 (494)	25.0-559 (179)	5.0-50 (20)	692	693	1.00	1385	Reisinger & Imhoff

undertaken at low elevation (Houghton, 1955; Hoffmann, 1984; Glotfelty et al., 1987) and at high elevation utilizing airborne sampling (Oddie, 1962; Daum et al., 1984; ten Brink et al., 1987). Measurements made for urban fog show pH values ranging from 3 to less than 2. In an extreme event observed in southern California (Corona del Mar) a low of pH 1.7, with a nitrate to sulfate ratio of approximately 3 was observed. Chemical composition analysis of fog for the elements of ions Na^+ , K^+ , Cl^- , F^- , and SO_4^{2-} , has been utilized (Wilkniss and Bressan, 1972; Bressan, 1976; Bressan and Larson, 1979) to better characterize an air parcel and to ascertain if its aerosol composition is dominated by continental, sea surface aerosols, or bulk seawater droplets. Based on aircraft measurements, Daum et al. (1984) have attempted to characterize the forms of sulfur and nitrogen compounds in clouds and their incorporation in cloud pathways. A single, widespread acidic cloud/fog event was recorded by Weathers et al. (1986) at six non-urban sites in the Eastern United States, including low, medium and high elevation sites.

There has been limited research on moderate elevation cloud composition characterization in the US (Falconer and Falconer, 1980; Weathers et al., 1986). All these studies except Falconer and Falconer (1980) have depended upon the acquisition of bulk water samples. Even though they suggest using continuous cloud water collection, their results are reported based on one-hour integrated sample collection. Moreover they reported only pH changes in the cloud rather than a comprehensive chemical characterization.

We have performed high elevation cloud characterization study with a very finite time resolution (approximately 5 min) for analysis. In this study, an automated cloud sampler was installed at Mt. Gibbs (~ 2006 m MSL) located in Mt. Mitchell State Park, North Carolina, in the eastern United States. It was used to measure the pH, conductivity, chemical and physical structure of clouds on a near real-time basis. This has allowed us to visualize, nearly on a real-time basis, the dynamic chemical development of clouds and their association with dynamic and microphysical processes.

The ability to monitor cloudwater pH in real time gives a distinct advantage over bulk sampling methods, because it allows more detailed studies to be conducted on the development of a cloud event

and its relationship with cloud microphysics and meteorological processes, thus elucidating the chemical and physical climate at these locales and the underlying processes controlling the cloud water chemistry. It is therefore essential to explore the real-time dynamic chemical developmental behavior of clouds at the onset, during the entire event, and as the cloud dissipates; simultaneously attempting to measure cloud liquid water content and cloud droplet size distribution. This will provide us with insight on the extremes of chemical exposure and its significance in contributing to decline of mountain forests.

This study was collocated at the Mountain Cloud Chemistry Program (MCCP) site, and the National Acid Deposition Program (NADP) site at Mount Mitchell State Park, North Carolina. This arrangement has provided additional data on clouds and rain composition for comparative analysis.

2. Experimental measurements

The cloud water, for a variety of cloud types, was collected with a continuous rain sampler equipped with California Institute of Technology (Cal Tech) active cloud collector (Jacob et al., 1985). The combined system is called cloud and rain acidity/conductivity (CRAC) real time automated sampler (Aneja et al., 1990). A conductivity meter and two conductivity cells, a pH meter, an electrode, and a printer are included in the instrumentation and electronic section. The entire monitoring system is controlled by a microprocessor. Cal Tech cloud collector has a 50% cutoff particle size centered around $2 \mu\text{m}$ diameter. More detail about the performance of this cloud collector have been reported previously (Daube et al., 1987). Cloud samples are accumulated sequentially in dual accumulation chambers containing the conductivity cells. Upon accumulation of ~ 50 ml of cloud water sample, the system directs ~ 12 ml to the pH measurement chamber and the remaining sample into a storage vial (at $\sim 4^\circ\text{C}$) for later chemical analysis. The major anions (SO_4^{2-} , NO_3^- and Cl^-) were measured in the laboratory using a Dionex 2010i ion chromatograph, and the major metal cations (Na^+ , Ca^{2+} , K^+ and Mg^{2+}) were determined by atomic absorption spectrophotometry. NH_4^+

Table 2. Ranges in concentrations ($\mu\text{eq/l}$) observed, mean values, fractions of equivalents of total ionic constituents (%), ionic balances and total ionic concentrations of cloud water sampled for the events at Mt. Mitchell, N.C., during 1987, 1988 and 1989; the ranges shown are from sequential samples during the individual events

Date	Time(EST)	pH	H ⁺	NH ₄ ⁺	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	SO ₄ ⁻	NO ₃ ⁻	Cl ⁻	Σ cation	Σ anion	Σ ca/ Σ an	Σ ions
87/7/30 (short)	0100-0825 mean % of total	2.87-3.37 (3.07)	427-1349 (848) 33	163-677 (353) 14	13-68 (35) 1	2.0-23.0 (9) <1	1.2-14.9 (5) <1	1.5-8 (4) <1	367-1814 (930) 37	131-486 (305) 12	16-121 (53) 2	1253	1288	0.97	2541
87/8/13 (long)	0650-1610 mean	3.09-4.03 (3.43)													
88/6/30 (short)	1020-1500 mean % of total	2.80-3.25 (2.94)	562-1585 (1137) 38	167-539 (273) 9	29-189 (56) 2	3.3-29.6 (8) <1	3.6-15.5 (6) <1	4.0-19.0 (7) <1	896-1544 (1194) 40	131-456 (285) 9	20-118 (78) 3	1488	1531	0.97	3019
88/7/12 (long)	mean	2.83-4.34 (3.26)													
89/7/31 (short)	0900-1130 mean % of total	3.24-3.52 (3.37)	302-575 (429) 35	106-272 (171) 14	8.5-17 (12) 1	1.7-3.8 (3) <1	1.2-7.2 (4) <1	0.2-2 (1) <1	382-555 (465) 38	94-199 (137) 11	12.0-20.0 (15) 1	619	616	1.00	1253
89/7/19 -7/20 (long)	1900-0300 mean % of total	3.43-3.88 (3.67)	132-372 (213) 32	51-146 (86) 13	5-22.6 (11) 2	0.7-5.4 (2) <1	0.5-6.9 (2) <1	0.6-3 (1) <1	160-465 (270) 40	51-154 (75) 11	5.5-22 (10) 1	316	355	0.90	671
fraction of equivalents (%) of total constituent			35	13	<1	<1	<1	<1	39	11	1				

concentration was determined by standard colorimetric method. At the start of a cloud event, the cloudwater collector and tubing to the continuous monitor are thoroughly cleaned by deionized water until the conductivity of the rinse water is within $5 \mu\text{mhos cm}^{-1}$ of that of the deionized water. The cloud water samples were collected at the site during the periods (mid-May through October), in 1987, 1988, and 1989.

3. Results and discussion

Major chemical components of cloud water samples collected during four separate cloud events (three short events and one long event) are investigated. Cloud events were categorized (Saxena et al., 1989) into long cloud event (duration > 8 h), and short cloud event (duration < 8 h). Generally, the former are caused by the frontal passages or associated with large scale disturbances, and the latter are caused by the orographic lifting mechanisms (Saxena and Lin, 1990). Cloud event associated with precipitation are defined as mixed events.

The concentration range of major chemical components observed during four separate cloud events are listed in Table 2. For comparison the pH ranges for two additional long events for 1987

and 1988 (for which no chemical analysis was performed) are also listed in Table 2. Data in the table shows the mean and range of ionic concentration, and mean pH of cloud water. For the 1987 (July 30) short event, the chemical analysis of the cloudwater samples indicates H^+ ranging between 427 and $1349 \mu\text{eq/l}$, and averaging $848 \mu\text{eq/l}$; NH_4^+ ranging between 163 and $677 \mu\text{eq/l}$, and averaging $353 \mu\text{eq/l}$; SO_4^{2-} ranging between 367 and $1814 \mu\text{eq/l}$, and averaging $930 \mu\text{eq/l}$; and NO_3^- ranging between 131 and $486 \mu\text{eq/l}$, and averaging $305 \mu\text{eq/l}$. For the 1988 (June 30) short event, the ranges and averages for the corresponding chemical ionic concentrations are 562 to $1585 \mu\text{eq/l}$, and $1137 \mu\text{eq/l}$; 167 to $539 \mu\text{eq/l}$, and $273 \mu\text{eq/l}$; 896 to $1544 \mu\text{eq/l}$, and $1194 \mu\text{eq/l}$; and 131 to $456 \mu\text{eq/l}$, and $285 \mu\text{eq/l}$; respectively. For the 1989 (July 31) short event, the above values are 302 to $575 \mu\text{eq/l}$, and $429 \mu\text{eq/l}$ for H^+ ; 106 to $272 \mu\text{eq/l}$, and $171 \mu\text{eq/l}$ for NH_4^+ ; 382 to $555 \mu\text{eq/l}$, and $465 \mu\text{eq/l}$ for SO_4^{2-} ; and 94 to $199 \mu\text{eq/l}$, and $137 \mu\text{eq/l}$ for NO_3^- ; respectively. Comparing these chemical analysis results for the short events to those with the long cloud event (July 19, 1989) we ascertain H^+ ranging from 132 to $372 \mu\text{eq/l}$, and averaging $213 \mu\text{eq/l}$; NH_4^+ ranging from 51 to $146 \mu\text{eq/l}$, and averaging $86 \mu\text{eq/l}$; SO_4^{2-} ranging from 160 to $465 \mu\text{eq/l}$, and averaging $270 \mu\text{eq/l}$; and NO_3^- ranging from 51 to

Table 3. Summary of CRAC sampled events, time-averaged pH, pH ranges, and average LWC values for different event types (1987–1989); the values in parentheses are standard deviations.

Year	Type	Events	Samples	Accu. hrs	Ave. hrs	Ave. pH	pH ranges		LWC (g/m^3)
							CRAC	ASRC	
1987 (July– Oct.)	short	14	226	67.99	5.23	3.23(0.17)	(continuous)	(1-h integrated)	0.15(0.11)
	long	3	222	36.79	12.26	3.40(0.02)			0.54(0.20)
	mixed	5	47	8.09	1.62	4.05(0.02)			0.71(0.24)
	total	22	495			3.34(0.07)	2.87–4.82	3.00–4.55	
							CRAC	ASRC	
1988 (June– Sept.)	short	9	149	41.22	4.58	3.03(0.29)	(continuous)	(1-h integrated)	0.24(0.17)
	long	2	257	36.70	18.35	3.55(0.21)			0.39(0.24)
	mixed	12	572	102.35	8.53	3.57(0.38)			0.39(0.21)
	total	23	978			3.44(0.29)	2.44–5.64	2.53–5.27	
							CRAC	ASRC	
1989 (May– Aug.)	short	8	77	31.14	3.89	3.09(0.18)	(continuous)	(1-h integrated)	0.20(0.13)
	long	5	211	54.67	10.93	3.59(0.20)			0.22(0.14)
	mixed	7	125	30.52	4.36	4.03(0.34)			0.32(0.15)
	total	20	413			3.57(0.24)	2.79–4.91	2.94–4.50	

154 $\mu\text{eq/l}$, and averaging 75 $\mu\text{eq/l}$; respectively. It indicates that the concentrations for short cloud events are much higher (two to four times) than those for long events. Based on cloud event categories, the total ionic concentrations in short cloud events (1253 to 2541 $\mu\text{eq/l}$) are much higher than those in a long cloud event (671 $\mu\text{eq/l}$) (Table 2). Table 3 shows a summary of the sampled cloud events, accumulated and averaged time, averaged pH values, and average liquid water content (LWC) for the different types of the events observed during the field seasons in 1987 through 1989. The results show that the pH value for short

cloud events (3.23 ± 0.17 for 1987; 3.03 ± 0.29 for 1988; and 3.09 ± 0.18 for 1989) were much lower than those for long cloud events (3.40 ± 0.02 for 1987; 3.55 ± 0.21 for 1988; and 3.59 ± 0.20 for 1989). The pH values for mixed events (4.05 ± 0.02 for 1987; 3.57 ± 0.38 for 1988; and 4.03 ± 0.34 for 1989) were much higher than those for both short and long cloud events.

Results of chemical composition of cloud water at Mt. Mitchell revealed that dominant chemical species of the cloud samples were H^+ , NH_4^+ , SO_4^{2-} and NO_3^- ions. Their combined fractions of equivalents of total ionic constituents was about

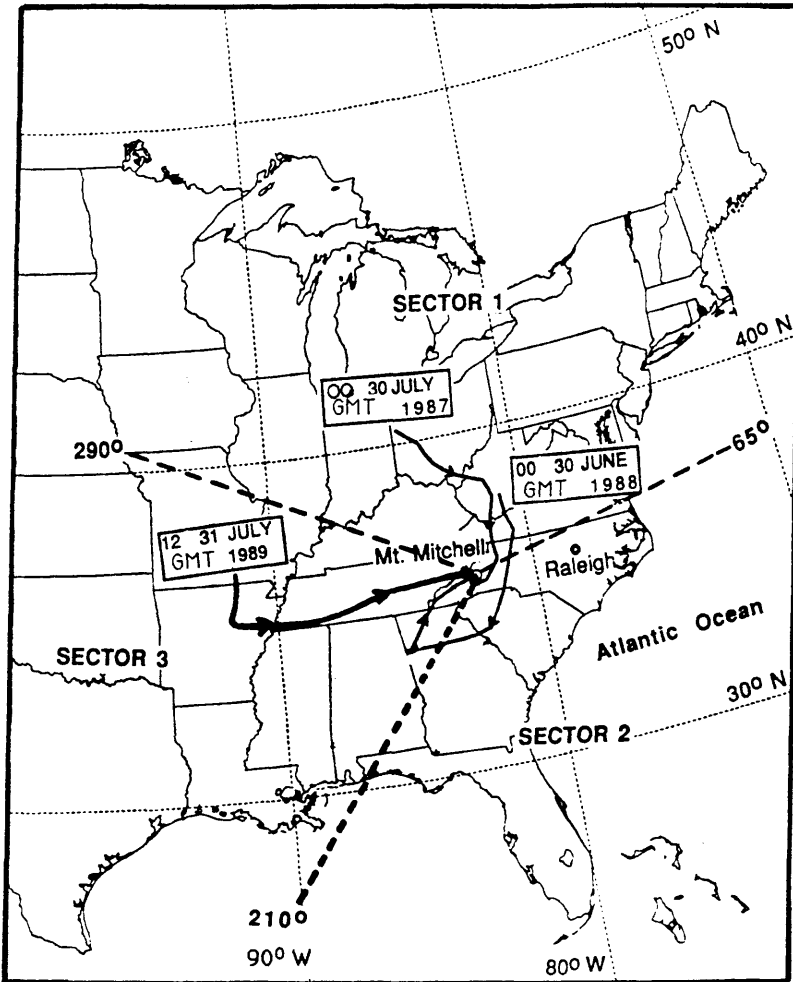


Fig. 1. Air mass back-trajectories arriving at Mt. Mitchell, North Carolina, site on 30 July 1987, 30 June 1988, and 31 July 1989.

$98 \pm 1\%$. Mean fraction of individual component to the total ionic constituent indicates that the contribution of H^+ ($\sim 35 \pm 3\%$) is similar to that of SO_4^{2-} ($\sim 39 \pm 2\%$), and NH_4^+ ($\sim 13 \pm 2\%$) is similar to NO_3^- ($\sim 11 \pm 1\%$), and contribution of the remaining cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) is similar to Cl^- anion. The results also revealed that the contribution of each chemical species to the total concentration were almost consistent in the case of these four cloud events.

Chemical structure of the three orographic cloud events is explained based on the back-trajectory analysis. Fig. 1 shows the 72-h back-trajectory analysis result for the short cloud events of 30 July 1987, 30 June 1988, and 31 July 1989. The cloud water samples collected in these three events were found to have a high ionic concentration and high acidity (Table 2). Results of dynamic chemical analysis for the three cloud events shows that the acidity and total ionic concentration of cloudwater sampled in 1989 event are low; mean pH is 3.37 and total concentration is $\sim 1250 \mu eq/l$, while corresponding values are pH 3.07 and total ionic concentration $\sim 2540 \mu eq/l$ in 1987, and pH 2.94 and total ionic concentration $\sim 3020 \mu eq/l$ in 1988.

The back-trajectory analysis indicates that the air masses arriving at the Mt. Mitchell site, on these dates, when clouds were sampled was coming

from the northwest (30 July 1987), southwest (30 June 1988), and west (31 July 1989) of the site. Back-trajectories for the 1987 and 1988 event show that the origins of these air masses, arriving at the site, was similar i.e. the air masses came from one of the most polluted continental region in the mid-western US (i.e. the Ohio River Valley region). On the other hand, back-trajectory analysis for the 1989 cloud event shows that the origin of the air mass, arriving at the site, is from the central US (which has low pollutant emissions).

To investigate the variation of cloudwater acidity as a function of winds arriving from different source regions, mean pH values of cloudwater sampled during 1987, 1988 and 1989 field seasons are illustrated with different wind sectors (Fig. 2). Using the National Emission Inventory provided by the US Environmental Protection Agency, source regions were categorized into three predominant wind sectors (Saxena and Yeh, 1988); 1) wind sector 1 ranging from 290° to 65° (most polluted sector); 2) wind sector 2 ranging from 65° to 210° (moderate polluted sector), and 3) wind sector 3 ranging from 210° to 290° (least polluted sector). Emissions of sulfur and nitrogen in sector 1 are higher than those in the other two sectors; (least polluted sector) while the lowest emissions were found in

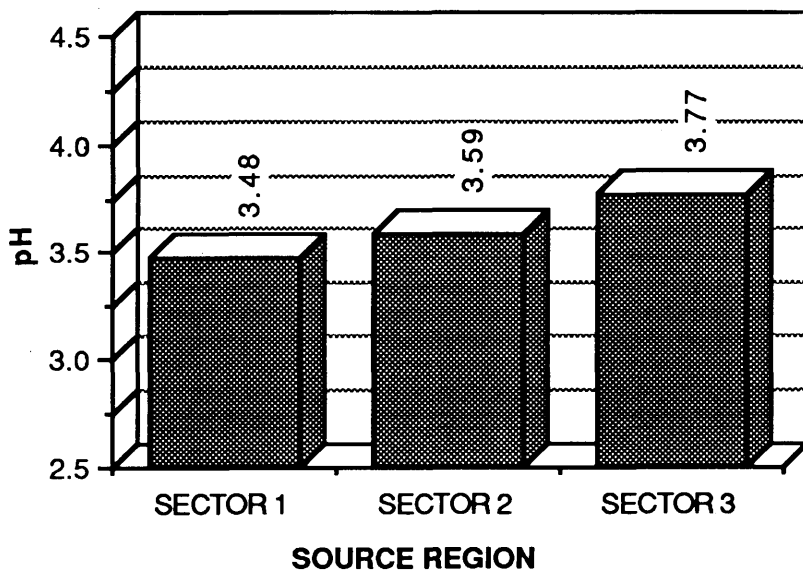


Fig. 2. Sector analysis of cloud water mean pH with different source regions at Mt. Mitchell site (1987–1989).

sector 3. The differences of particulate emissions are small among these sectors.

Fig. 2 shows the results for acidity of clouds categorized according to source regions during 1987 through 1989. The results show that mean acidity of cloud water collected when the wind direction is from sector 1 is the highest (pH 3.48); while the acidity of cloudwater collected when the wind direction is from sector 2 is pH 3.59, and acidity of cloudwater collected when the wind direction is from sector 3 is the lowest (pH 3.77).

To separate the effects of variations in cloud liquid water content from variations in pre-cloud pollutant concentrations, to determine the relationship between pollutant source intensity and cloudwater concentrations, cloudwater concentrations were converted to equivalent gas phase concentrations by using the cloud liquid water content. Fig. 3 shows the concentrations in the cloudwater of the primary ions in the aqueous phase, equivalent gas phase, and the liquid water content. In this analysis only data when liquid water content information are available in short cloud events were used. The concentrations of the primary ionic constituents (H^+ , NH_4^+ , SO_4^{2-} and NO_3^-) in the aqueous phase are the highest when the wind direction is from sector 1, followed by sector 2, and the lowest when the wind direction is from sector 3. This corresponds to the order of the pollutant source intensity of the sectors. The average liquid water content for the three sectors 1, 2, and 3 are $0.24 \pm 0.07 \text{ g m}^{-3}$, $0.28 \pm 0.29 \text{ g m}^{-3}$, and $0.31 \pm 0.19 \text{ g m}^{-3}$ respectively. The calculated gas phase concentration of the primary species when the wind direction is from sector 1, sector 2, and sector 3 are following: $0.15 \mu\text{g m}^{-3}$, $0.09 \mu\text{g m}^{-3}$ and $0.07 \mu\text{g m}^{-3}$ for H^+ ; $1.10 \mu\text{g m}^{-3}$, $0.69 \mu\text{g m}^{-3}$ and $0.57 \mu\text{g m}^{-3}$ for NH_4^+ ; $7.11 \mu\text{g m}^{-3}$, $4.88 \mu\text{g m}^{-3}$ and $4.35 \mu\text{g m}^{-3}$ for SO_4^{2-} , and $4.10 \mu\text{g m}^{-3}$, $2.32 \mu\text{g m}^{-3}$ and $1.66 \mu\text{g m}^{-3}$ for NO_3^- respectively. These observed and calculated ionic concentration levels are thus highest when the wind directions are from sector 1, followed by sector 2, and lowest when the wind directions are from sector 3 (at the $>95\%$ significance level based on *t*-statistic). This suggests the relationship between source intensity and cloudwater concentrations. Furthermore long range transport of air pollutants to the site may have a significant effect on the cloud water chemistry.

Average cloud liquid water content (LWC) range for short events sampled during 1987, 1988 and 1989 was from 0.15 to 0.24 g m^{-3} , the range for long events was from 0.22 to 0.54 g m^{-3} , and the range for mixed events (simultaneously occurrence of precipitating (rain) and non precipitating clouds) was from 0.32 to 0.71 g m^{-3} (Table 3). The liquid water content was measured with a gravimetric sampler (Valente et al., 1989). The accuracy and precision of the instrument are $\pm 0.1 \text{ g m}^{-3}$ and 0.05 g m^{-3} respectively; with a time basis of the sample measurement being 1 hour integrated sampling. This increase in LWC from short event to mixed event may be explained as follow: in general, the short cloud events are associated with stratus (St) and stratocumulus (Sc) cloud types, in which the cloud droplets are very concentrated solution of soluble cloud condensation nuclei (Saxena and Fisher, 1984). According to the observation, it can be suggested that these short cloud events were attributed to the orographic lifting mechanism along the slope of the Mt. Mitchell site and thereby, bringing some near-surface or soil-derived aerosols and scavenging of pollutants (aerosol and gases) which have already accumulated in the valley (Bradow and Aneja, 1988; Saxena and Lin, 1990). 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 (Saxena and Lin, 1990). The highest value of pH for the mixed events may suggest that the rain drops are considerably more dilute than the non-precipitating cloud droplets. An analysis of the total ionic concentration of cloudwater ($\sim 2075 \mu\text{eq/l}$) sampled in the present work at Mt. Mitchell, N.C. is about 15 times greater than total concentration in rainwater ($\sim 140 \mu\text{eq/l}$) sampled by NADP at Clingmann Peak, N.C. during the summer season (Table 1).

The dynamic chemical changes in a cloud event is shown in Fig. 4. It illustrates the changes in total ionic concentration with respect to time for the three short cloud events during 1987, 1988 and 1989. These cloud events were observed during the growing season (June and July) at the site. A concave trend in the profile of cloudwater pollutant concentration versus time was observed for orographic clouds (Fig. 4). Waldman et al. (1982) also observed a concave trend in the profile of

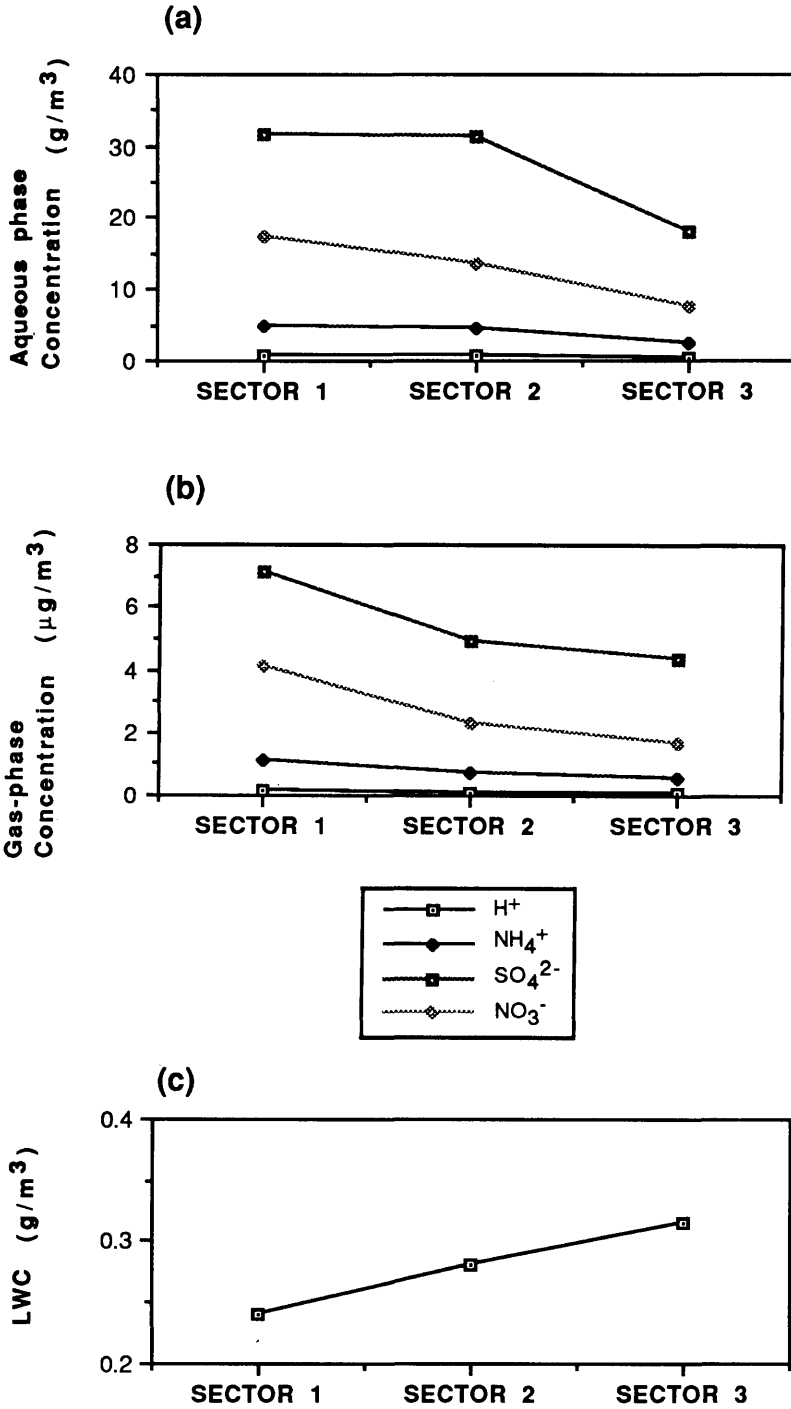


Fig. 3. Primary ionic concentrations for short cloud events (a) aqueous-phase, (g/m³); (b) calculated corresponding gas-phase, (µg/m³); (c) liquid water contents (LWC, g/m³).

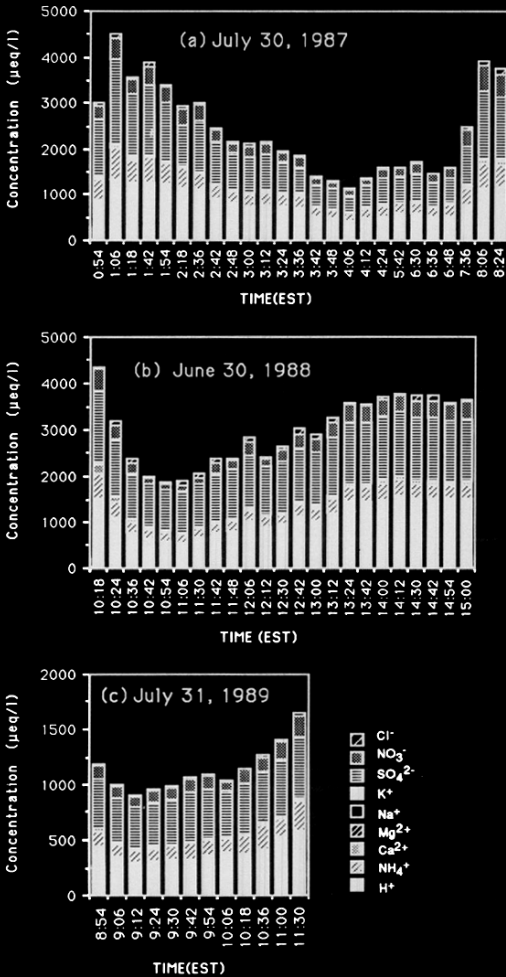


Fig. 4. Dynamic variation in cloud ionic concentration for three short events (a) 30 July 1987; (b) 30 June 1988; and (c) 31 July 1989 at Mt. Mitchell, North Carolina.

cloud pollutants concentration versus time (total concentration decreasing at the beginning and rising toward the end of event) for the chemical composition of an urban environment (i.e., Los Angeles, California) fog water. It is also revealed that the changes in absolute concentration of individual ions are proportional to the changes in total concentration (Fig. 4). These observations suggest that water vapor condensation and evaporation of cloud droplets are the dominant processes in determining the total concentration of cloud water (Waldman et al., 1982). Sharp decreases in concentration during the first few

hours of the cloud events were attributed primarily to initial droplet deliquescence on preexisting aerosol. Similarly, most of the increase in concentration that was observed at the end of the event was due to evaporation and the regeneration of fine aerosol which are induced by increasing temperature at the end of an event as clouds dissipate (Fig. 5). These mechanisms are thought to play a dominant role in determining, at least, orographic cloud chemistry at the Mt. Mitchell site. The dominant ions in the cloud water were H⁺, NH₄⁺, SO₄²⁻ and NO₃⁻; and these ions make up almost 98% of the total ionic concentration. This result suggests that preexisting aerosol is a major determinant of the chemical composition of cloud water, since these four species are the major components of the daytime aerosol (Bradow and Aneja, 1988).

Chemical analysis of cloudwater at Mt. Mitchell shows that the equivalent ratio of SO₄²⁻ to NO₃⁻ in cloud water is about 3.5 during these orographic events, which is comparable to the reported ratio of 3.2 in the eastern United States (Weathers et al., 1986). The corresponding ratio in rain water was about 3.2 during summer (Aneja et al., 1990). In Los Angeles fog (Waldman et al., 1982), the same ratio was about 0.4 and corresponding ratio in Los Angeles precipitation (Liljestrand and Morgan, 1981) was close to 1.0. As it would be expected, there is thus a significant difference in the ratios of SO₄²⁻ to NO₃⁻ between the Mt. Mitchell site (an eastern U.S. remote high elevation forest area) and the Los Angeles area (the western U.S. urban coastal area).

Time variations of ozone during the same time periods as these three events were also presented in Fig. 5. According to our observations, the concentration of ozone tends to decrease at the end of event as clouds dissipate. Similar trends in pH time variation were also observed during the cloud event. In the event of 30 July 1987, sharp increase of ozone concentration during the night-time and gradually decrease during the morning-time were observed. Sharp increase of ozone over the site during the night-time may be attributed principally to either the transport of ozone from the higher level due to atmospheric subsidence (Aneja et al., 1991); and/or owing to the location of the site above the nocturnal inversion layer, thus isolating the site from the effects of surface deposition.

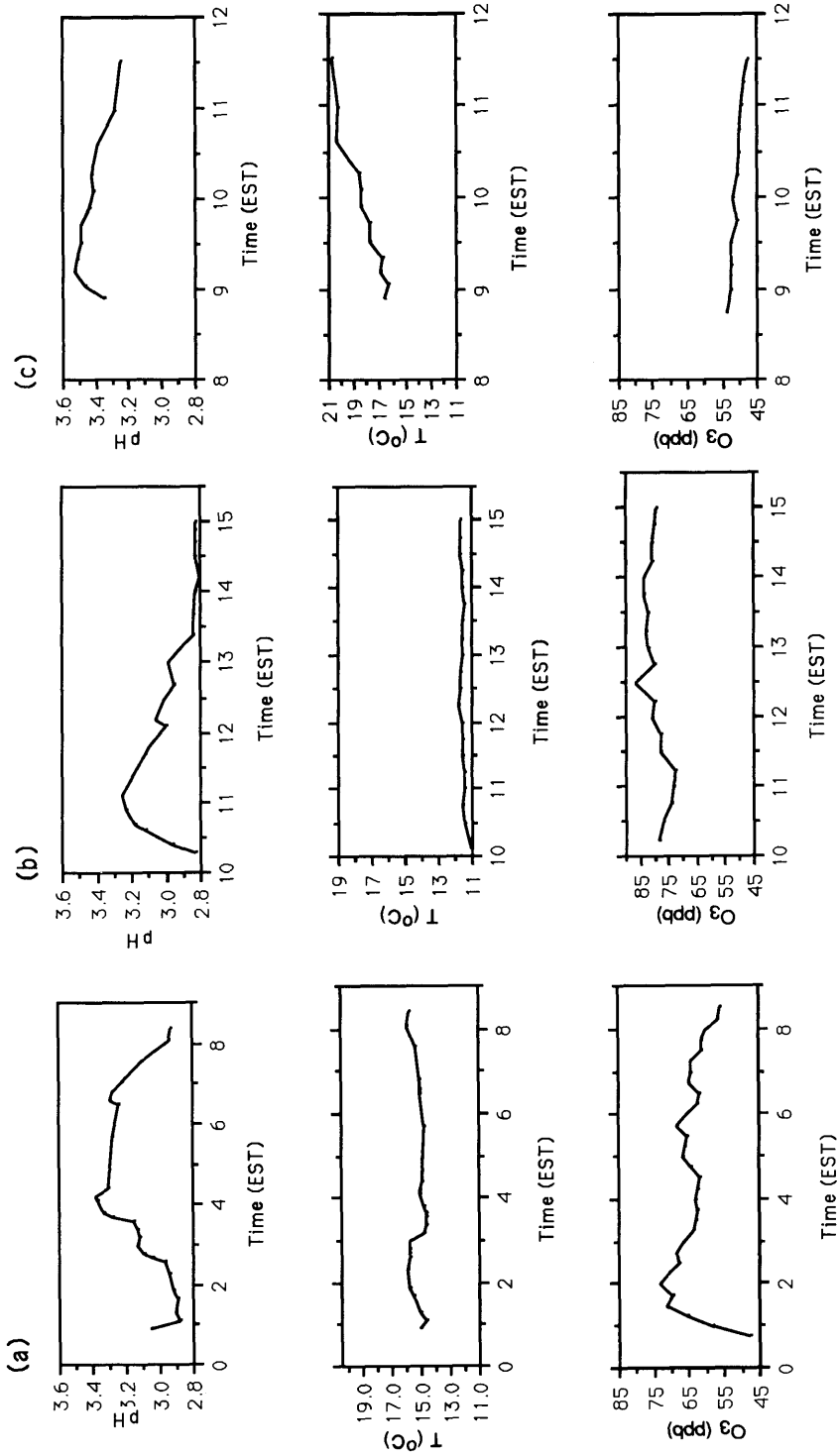


Fig. 5. Dynamic variation in cloud water pH, temperature and O_3 for (a) 30 July 1987; (b) 30 June 1988; and (c) 31 July 1989 at Mt. Mitchell, North Carolina. (EST-Eastern Standard Time).

4. Conclusion

The results of this study show that the total concentrations of major chemical species in cloud water at Mt. Mitchell State Park are significantly higher (~ 1250 – $\sim 3020 \mu\text{eq/l}$) than those reported for other remote locations. Dominant chemical components in cloud water samples were H^+ , NH_4^+ , SO_4^{2-} and NO_3^- , and the % of sum of these dominant species to the total equivalent concentration was about 98%. The contribution of individual chemical species to the total mass were consistent in the cloud events. The total ionic concentrations in short cloud events (which is attributed to the orographic effects) were much higher than those in long cloud events (which is attributed to the frontal cloud). Cloud water collected in the short cloud events (pH 3.23 for 1987; pH 3.03 for 1988, and pH 3.09 for 1989) was also more acidic than those in the long cloud events (pH 3.40 for 1987; pH 3.55 for 1988, and pH 3.59 for 1989).

According to the time-sequential chemical concentration, a concave trend with total concentration decreasing at the beginning and rising toward the end of the event was observed. It was observed that changes in the individual ionic concentration are proportional to the changes in total concentration. It suggests that condensation and evaporation of cloud droplets are the important processes in determining the total concentration of cloud water. The equivalent concentration ratio of SO_4^{2-} to NO_3^- in cloud water at the site is about 3.5, which as would be expected is significantly different than the corresponding value 0.4 in

Los Angeles area. 72-h back-trajectory analysis indicates that the origin of the air masses arriving at Mt. Mitchell site on the event days discussed were from the most polluted continental region. These results indicate that the observed changes in cloud water composition are thought to be a combination of chemical and microphysical changes, i.e., sharp decrease in concentration during the first few hours of the orographic cloud events were attributed primarily to initial droplet deliquescence on preexisting aerosol. Similarly, most of the increase in concentration that was observed at the end of the event was due to evaporation and the regeneration of fine aerosol which are induced by increasing temperature at the end of an event as orographic clouds dissipate.

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REFERENCES

- Aneja, V. P., Claiborn, C. S., Chiswell, S., Bradow, R. L., Paur, R. J. and Baumgardner, R. 1988. Dynamic chemical characterization of montane clouds. Air Pollution Control Association Annual Meeting, Paper No. 88-129.2, Dallas, Texas.
- Aneja, V. P., Claiborn, C. S. and Bradow, R. L., Paur, R. J. and Baumgardner, R. 1990. Dynamic chemical characterization of montane clouds. *Atmospheric Environment* 24A, 563–572.
- Aneja, V. P., Businger, S., Li, Z., Claiborn, C. S. and Murthy, A. 1991. Ozone climatology at high elevations in the southern Appalachians. *J. Geophys. Res.* 96, 1007–1021.
- Blank, L. W. 1985. A new type of forest decline in Germany. *Nature* 314, 311–314.
- Bradow, R. L. and Aneja, V. P. 1988. Aerosol composition effects on mountain clouds. In: *Proceedings of the 12th International Conference on Atmospheric Aerosols and Nucleation* (ed. P. E. Wagner and G. Vali), Univ. of Vienna, Austria, Springer-Verlag publisher, 309, 40–43.
- Bressan, D. J. 1976. Naval Research Laboratory Review

- for 1975, Naval Research Laboratory, Washington, DC, 120–122.
- Bressan, D. J. and Larson, R. E. 1979. The history of air forming various marine fogs off Nova Scotia in August 1975. *J. Geophys. Res.* 84, 1746–1754.
- Dasch, J. M. 1988. Hydrological and chemical inputs to fir trees from rain and clouds during a 1-month study at Clingmans Peak, N.C. *Atmospheric Environment* 22, 2255–2262.
- Daube, B. C., Flagan, R. C. and Hoffmann, M. R. 1987. Active cloudwater collector. U.S. Patent Number 4, 697, 462.
- Daum, P. H., Kelly, T. J., Schwartz, S. E. and Newman, L. 1984. Measurement of the chemical composition of stratiform clouds. *Atmospheric Environment* 18, 2671–2684.
- Falconer, R. E. and Falconer, P. D. 1980. Determination of cloud water acidity at a mountain observatory in the Adirondack Mountain of New York State. *J. Geophys. Res.* 85, 7465–7470.
- Glotfelty, D. E., Seiber, J. N. and Liljedahl, L. A. 1987. Pesticides in fog. *Nature* 325, 602–605.
- Hoffmann, M. R. 1984. Acid Fog. *Engineering Sci.* 48, 5–11.
- Houghton, H. G. 1955. On the chemical composition of fog and cloud water. *J. Meteorol.* 12, 355–357.
- Jacob, D. J., Waldman, J. M., Haighi, M., Hoffmann, M. R. and Flagan, R. C. 1985. An instrument to collect fog water for chemical analysis. *Rev. Sci. Instrum.* 56, 1291–1293.
- Lovett, G. M., Reiners, W. A. and Olson, R. K. 1982. Cloud droplet deposition in sub-alpine balsam fir forest: hydrological and chemical inputs. *Science* 218, 1303–1304.
- Muir, P. S., Wade, K. A., Carter, B. H., Armentano, T. V. and Pribush, R. A. 1986. Fog chemistry at an urban midwestern site. *J. Air Pollut. Control. Assoc.* 36, 1359–1361.
- Murthy, A. and Aneja, V. P. 1990. Deposition and interaction of nitrogen containing pollutants to a high elevation forest canopy. 83rd Annual Meeting of Air and Waste Management Association, Pittsburgh, Paper No. 90–100.4.
- NADP, 1988. National Atmospheric Deposition Program: NADP/NTN ANNUAL DATA SUMMARY. Precipitation Chemistry in the United States. 1987. Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO, 353 pp.
- Oddie, B. C. V. 1962. The chemical composition of precipitation at cloud levels. *J. R. Meteorol. Soc.* 80, 535–538.
- Reisinger, L. M. and Imhoff, R. 1989. Analysis of summertime cloud water measurements made in Southern Appalachian Spruce Forest. *Water, Air, and Soil Pollution* 45, 1–15.
- Saxena, V. K. and Fisher, G. F. 1984. Water solubility of cloud active aerosols. *Aerosol Sci. Technol.* 3, 335–344.
- Saxena, V. K. and Lin, N. H. 1990. Cloud chemistry measurements and estimates of acidic deposition on an above cloud base coniferous forest. *Atmospheric Environment* 24A, 329–352.
- Saxena, V. K. and Yeh, R. J.-Y. 1988. Temporal variability in cloud water acidity: physico-chemical characteristics of atmospheric aerosols and wind field. *J. Aerosol Sci.* 19, 1207–1210.
- Saxena, V. K., Stogner, R. E., Hendler, A. H., DeFelice, T. P., Yeh, R. J. Y. and Lin, N. H. 1989. Monitoring the chemical climate of the Mt. Mitchell State Park for evaluation of its impacts on forest decline. *Tellus* 41B, 92–109.
- Valente, R. J., Mallant, R. K., McLaren, S. E. and Shemenauer, R. E. 1989. Field intercomparison of ground based cloud physics instruments at Whiteop Mtn., Va. *J. Atmos. Oceanic Technol.* 6, 396–406.
- ten Brink, H. M., Schwartz, S. E. and Daum, P. H. 1987. Efficient scavenging of aerosol sulfate by liquid-water clouds. *Atmospheric Environment* 21, 2035–2052.
- Waldman, J. M., Munger, J. W., Flagan, R. C., Morgan, J. J. and Hoffmann, M. R. 1982. Chemical composition of acid fog. *Science* 218, 677–680.
- Waldman, J. M., Munger, J. W., Jacob, D. J. and Hoffmann, M. R. 1985. Chemical characterization of stratus cloud water and its role as a vector for pollutant deposition in a Los Angeles pine forest. *Tellus* 37B, 91–108.
- Weathers, K. C., Likens, G. E., Bormann, F. H., Eaton, J. S., Bowden, W. B., Andersen, J. L., Cass, D. A., Galloway, J. N., Keene, W. C., Kimball, K. D., Huth, P. and Smiley, D. 1986. A regional acidic cloud/fog water event in the Eastern United States. *Nature* 319, 657–658.
- Wilkniss, P. E. and Bressan, D. J. 1972. Fractionation of elements, F, Cl, Na, and K at sea-air interface. *J. Geophys. Res.* 77, 5307–5315.