REGIONAL ANALYSIS OF CLOUD CHEMISTRY AT HIGH ELEVATIONS IN THE EASTERN UNITED STATES

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Abstract—Results from the collection and chemical analysis of cloudwater samples collected from May to October 1986–1988 from the five high-elevation (\geq 950 m MSL) Mountain Cloud Chemistry Program (MCCP) sites (Whiteface Mountain, NY, Mt Moosilauke, NH, Shenandoah Park, VA, Whitetop Mountain, VA, Mt Mitchell, NC) in the eastern United States are summarized The resulting database documents the regional chemical climatology of high-elevation forest ecosystems in the eastern US Clouds occurred at these sites on 32-77% of the days during the sample collection period. More than 90% of cloud samples were acidic (pH < 50) The lowest cloudwater pH (2 29 integrated 1-h collection period) was recorded at Mt Mitchell, NC At all sites sulfate and nitrate were the dominant anions and hydrogen and ammonium were the dominant cations in cloudwater samples. Mount Mitchell received the most acidic clouds and highest chemical exposures, while the Whiteface summit site received the least acidic and lowest chemical exposures compared to other MCCP high-elevation sites. Cloud pH and major chemical components exhibited a seasonal trend with the maxima during the summer months, and correlated well with temperature and ozone concentrations. The mean equivalent ratios of SO₄²⁻¹ to NO₃ were found to be 19–39 at these sites. It is noted that SO₄²⁻¹ correlated highly with hydrogen ion, suggesting that contribution to cloud acidity by sulfate and/or its precursors may be significant.

Key word index Cloud chemistry, regional analysis, ozone, chemical exposure

1 INTRODUCTION

High-elevation forests in the eastern United States have shown signs of injury and decline during the past two decades In recent years, there has been increasing concern with the possible impact of atmospheric acidity on forested ecosystems (Klein and Perkins, 1988, Cowling, 1989, Bruck *et al* 1989, Jacobson *et al*, 1990b, Hertel *et al*, 1990) It is now believed that acidic cloud deposition may contribute to observed forest decline at high-elevation locations where mountain slopes are frequently immersed in clouds (Jacobson *et al*, 1990a, Saxena and Lin, 1990, Aneja *et al*, 1990a, 1992, Cowling *et al*, 1991)

Acidic clouds and fogs have been characterized over several decades in the US and Europe, both in urban and rural areas Table 1 shows examples of cloud acidity measurements at some of those locations The cloud pH values reported by these investigators ranged from 2.2 to 7.6 Most authors focused on individual case studies, except for Weathers *et al* (1986), who studied a widespread acid cloud event at six non-urban sites in the eastern US However, their study was based on one single event and limited to moderate elevation No research has been done for high-elevation regional cloud chemistry climatological analysis from north to south in the eastern US to compare the acidity exposures between different sites Possible forest decline in high-elevation ecosystems across the eastern US necessitated documentation of the chemical exposure and distribution of clouds at high elevation on a regional scale

Beginning in 1986, a series of measurements, including major cations and anions in cloud water and precipitation, gas-phase measurements of ozone, sulfur dioxide and nitrogen oxides, and meteorological parameters (Aneja et al, 1992) were made at six remote sites in the eastern US These measurements were made as part of the Mountain Cloud Chemistry Project (MCCP) sponsored by the US Environmental Protection Agency Five high-elevation (\gtrsim 950 m MSL) sites were selected from 35 to 45°N to be representatives of the geographic and meteorological variability in this large region One low-elevation site (Howland, ME, 65 m MSL) was instrumented to allow evaluation of the impact of elevational gradient In these ecosystems, red spruce (Picea rubens Sarg) and Fraser fir (Abies fraseri [Pursh] Poir) are the dominant tree species, they have shown signs of decline above the cloud base, which is frequently observed around 800-1200 m (Mohnen et al., 1990a)

The objectives of this research are to (i) characterize the exposure of montane forested ecosystems to chemicals in cloud water at high elevations in the eastern U S, (ii) determine north-south gradients of cloud chemistry based on observations made at five highelevation MCCP sites, (iii) study the regional chemical climatology at high elevations in the eastern U S

Reference	Year of study	Location	Type of collector	Range of pH
Cloud water renorted from low eleva-	tion			
Houghton (1955)	1954	Northeast U S A	stainless steel or nickel screen	4 5-7 2
Mrose (1966)	1957	Germany	previous cloth	38-51
Lazrus et al (1970)	1967	Puerto Rico	aluminum screen	4 9-5 4
Waldman et al (1982)	1981	California, U S A	Caltech rotating arm	22-40
Munger et al (1983)	1981-1982	California, U S A	Caltech Teflon strings	2 2-5 8
Fuzzi et al (1984)	1982	New York, U S A	screen impactor	43-64
Jacob et al (1985)	1982-1983	California, U S A	Caltech rotating arm	22-63
Murr et al (1986)	1985-1986	Midwestern U S A	Caltech rotating arm	29-41
Weathers et al (1986)	1984	Eastern USA	Teflon strings	2 9–3 0
Cloud water collected by aircraft				
Oddie (1962)	1960	United kingdom	glass tube	44-72
Petrenchunk and		,		
Drozdova (1966)	1961–1964	USSR	integrated sample	34-59
Scott (1978)	1976	Australia	centrifuge	46-75
Scott and Laulainen (1979)	1977	Michigan, U S A	nylon wand	37-40
Daum et al (1984)	1981-1983	Eastern U S A	slotted-rod impactor	31-61
Saxena et al (1985)	1982-1983	McMurdo, Antarctica	Teflon probe	49-62
Khemanı et al (1987)	1983-1985	Pune, India	stainless steel sheets	63-76
Hegg and Hobbs (1981)	1979	Northwestern USA	centrifuge	4 2-6 5
Cloud water collected at mountain si	tes			
Okita (1968)	1963	Japan	copper screen	35-65
Castillo (1979)	1976	Whiteface Mtn, NY, U S A	rotating stainless steel tube	34-42
Falconer and Falconer (1980)	1977-1979	Whiteface Mtn, NY, USA	ASRC, Teflon string	27-47
Weathers et al (1986)	1984	Eastern USA	Teflon strings	28-31
Mohnen and Kadlecek (1989)	1982-1987	Whiteface Mtn, NY, USA	ASRC, Teflon string	25-48
Aneja et al (1990a)	1987	Mt Mitchell, NC, USA	Caltech, Teflon string	29-46
Aneja et al (1990b)	1986-1988	Mt Mitchell, NC, U S A	ASRC, Teflon string	22-55
Saxena and Lin (1990)	1986–1987	Mt Mitchell, NC, USA	ASRC, Teflon string	2 2-5 4

Table 1 The ranges of cloudwater acidity observed at other locations

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2 MCCP SITE DESCRIPTION AND MEASUREMENT METHODS

The Mountain Cloud Chemistry Program (MCCP) consists of five high-elevation sampling sites in the eastern US Whiteface Mountain, NY, Mt Moosilauke, NH, Shenandoah Park, VA, Whitetop Mountain, VA, Mt Mitchell, NC, and one low-elevation sampling site, Howland, ME Figure 1 illustrates the location of the MCCP sites

At Whiteface, Whitetop and Mt Mitchell, the main sites are located on the summit of mountains, while the main sites at Shenandoah and Moosilauke are along a ridgeline Subsites, such as those at Whiteface, Shenandoah and Mt Mitchell are located along the slope of the same mountain

The northernmost high-elevation site in the network is Whiteface Mountain (WF) ($44^{\circ}23'N$, $73^{\circ}59'W$), located in the northeastern Adirondack Mountains in New York, at an elevation of 1483 m The summit is above the tree line, providing access to regional air flow (sub-site 1) The Whiteface Mountain-Lake Placid Turn sampling site (sub-site 2) is located at 1245 m, adjacent to a balsam fir canopy

Mt Moosilauke (MS), NH $(43^{\circ}59'N, 71^{\circ}48'W)$, is one of the most southern peaks of the White Mountains It is located about 50 km southwest of Mt Washington (1917 m) and about 10 km northeast of the United States Forest Service (USFS) Hubbard Brook Experimental Forest and Watershed The forest composition ranges from mixed hardwoods at lower elevations to spruce-fir (about 10% spruce) at midelevations, and pure balsam fir at high elevations The meteorological station-MCCP site at Mt Moosilauke is at 962 m and is partially shielded from the prevailing westerly winds

The Shenandoah (SH), VA, site $(38^{\circ}72'N, 78^{\circ}20'W)$ is in the Shaver Hollow Watershed, located in the north-central sector of the Shenandoah National Park The meteorological tower was erected in the watershed at an elevation of 1040 m The tower location is representative of the surrounding deciduous forest canopy In addition to this site, two other sub-sites have been established

The Whitetop Mountain (WT) site (36°38'N, 81°36'W) is located in the Mt Rogers National Recreation Area of the Jefferson National Forest in southwestern Virginia, 6 km southwest of Mt Rogers, the highest peak in Virginia The TVA Whitetop Mountain summit research station (at 1689 m) straddles the main ridgeline of the Appalachian range, strategically located to intercept air from several directions In addition to the summit station, other sub-sites have been established

The southernmost MCCP site is located in Mt Mitchell State Park (MM), NC $(35^{\circ}44'N, 82^{\circ}16'W)$ The site is at Mt Gibbs (1950 m MSL) ~ 2 5 k southwest of Mt Mitchell, which is the highest peak in the eastern US (2038 m MSL) The summit is covered with Fraser fir, and the region from 1500 to 1800 m is an ecosystem composed mainly of mixed fir and spruce

The low elevation site is in the Howland Forest (HF), ME $(45^{\circ}13'N, 68^{\circ}43'W)$ It is located at 65 m elevation near Howland, ME, 35 miles north of Bangor The forest is spruce with some of balsam fir, hemlock and white pine

Each of the locations had a meteorological walk-up tower to provide measurements above the forest canopy The meteorological sensors were mounted on the top of the tower (Mohnen *et al.*, 1990a) With regard to the cloudwater collection, which was performed manually at all sites, an ASRC (Atmospheric Science Research Center, State University of New York at Albany) passive cloud collector (Falconer and Falconer, 1980) was mounted on the top platform of towers above the surrounding canopy at most sites The only exceptions to this are Whiteface Mountain, where the collector was placed on the roof of the summit research lab, and Whitetop Mountain, where it was on a platform built over the research trailer The manual cloudwater collection commenced hourly during the cloud events The cloud event is signaled when a stationary object at a distance of 1 km



Fig 1 Map of eastern United States showing the locations of MCCP sites

from the observation point becomes obscured by cloud and stays consistently out of view for more than 15 min. Once a cloud event has begun, a 500 ml polyethylene bottle was attached to the cloud collector with a clean tube. Collection bottles were changed hourly At the end of each event, the cloud collectors were cleaned by rinsing with deionized water until the conductivity of the rinse water was within $\pm 10 \,\mu {\rm S\,cm^{-1}}$ of that of the deionized water. The collectors were then covered with a plastic bag until the start of the next event. Wash water was discarded

Liquid-water content of each cloud was measured with a gravimetric sampler (Valente *et al.*, 1989) only at the main site The accuracy and precision of the instrument are ± 0.1 and ± 0.05 gm⁻³, respectively, with the time basis of the sample measurement being 1-h integrated sampling The pH-meter was calibrated before every measurement, using standard buffer solutions at pH 400 and 700 The pH and total volume collected were measured immediately after collection Thereafter, these samples were refrigerated at ~4°C and were shipped for pH, conductivity and major-ion chemical analysis to either the site specific wet chemical laboratory or to Illinois State Water Survey (ISWS) laboratory The ionic chemical composition of the samples was determined using ion chromatography (IC)

The maintenance and calibration for these instruments were performed routinely under the MCCP protocol and Quality Assurance/Quality Control plan in order to ensure data quality (Mohnen, 1990b) EPA audits at the sites and in chemical laboratories were made during the first month of each field season The Central Analytical Laboratory (CAL) at the Illinois State Water Survey also provided the QA/QC for analytical measurement for the MCCP Sample collection, analysis, and quality assurance were critical elements of this program At CAL, both non-precipitating (i e clouds) and precipitating (i e rainfall) samples from the sites were analysed for pH, conductivity and concentrations of NH_4^+ , Na^+ , $K^+ Ca^{2+}$, $Mg^{2+} SO_4^{2-}$, NO_3^- and Cl^-

3 CHARACTERIZATION OF CLOUD CHEMISTRY

31 Cloud interception frequency at MCCP sites

The frequency of cloud immersion detected at the five MCCP summit sites for 1986–1988 field seasons is reported in Table 2 At the two northern sites, clouds occurred 37 (WF1) and 19% (MS1) of the time during the 3-year field seasons The three southern sites experienced cloud immersion 11 (SH1), 30 (WT1) and 29% (MM1) of the time during the same period Table 2 suggests that cloud frequency decreased from 1986 to 1988, reflecting a shift from wet weather in 1986 to drought conditions in 1988 over most of the eastern US Mount Moosilauke and Shenandoah Park sites experienced fewer cloudy periods due to their lower elevations In comparison to the long-term climate data, Mohnen *et al* (1990a) also reported that the northern MCCP sites experienced above-normal cloudiness in both 1986 and 1987 and below-normal cloudiness in 1988 However, the southern sites had below-normal cloudiness during all the three field seasons

Diurnal patterns of cloud frequencies reported by Mohnen *et al* (1990a) indicate that a preference for cloud impaction was during night and morning hours (7 pm-10 am) Whiteface Mountain, Whitetop Mountain and Mt Mitchell sites experienced more than twice as much cloudiness during the early morning as in the afternoon This phenomenon at summit sites may be linked to orographic mechanisms as well as to the planetary boundary layer lowering below the level of the mountain top after sunset However, no such diurnal trends were observed at Mt Moosilauke and Shenandoah Park

32 Cloud acidity

The natural pH value of rain is thought to be ~56, which represents the acidity of pure water in equilibrium with the mean atmospheric concentration of CO₂ (~330 ppm) This value is often used as an important reference for acidity of cloud water (Robinson, 1984, Lacaux *et al*, 1987) However, the acidity of natural cloud varies in different parts of the world (Table 1) For example, when there is a lack of the common basic compounds such as NH₃ or CaCO₃, Charlson and Rodhe (1982) showed that the pH of rain water, influenced by sulfur compounds, can be expected to be about 45-50 This result was later confirmed by Noller *et al* (1986) Therefore, the pH of cloud water below ~50 is assumed to be influenced by anthropogenic pollution

	Elevation				
Site	(m)	1986	1987	1988	Mean
Cloud frequen	cy (% of hours in cle	oud)			
WF1	1483	45	40	25	37
MS1	962	25	21	6	19
SH1	1040	18	7	6	11
WT1	1689	38	28	26	30
MM1	1950	35	28	23	29
Percentage of	total days experienci	ing some clo	ud		
WF1	1483	79	80	73	77
MS1	962	52	51	22	42
SH1	1040	46	25	25	32
WT1	1689	76	67	62	68
MM 1	1950	84	75	68	76

Table 2 Cloud frequency at MCCP sites, June to September 1986-1988

Figure 2 shows the frequency distribution of pH for cloudwater samples collected at the MCCP sites during the 3-year (1986–1988) field season For comparison, the per cent occurrences of pH values for rain water at the same locations are also included The pH recorded at MCCP sites varied from 2 29 to 7 3 for cloud samples, and from 2 75 to 5 68 for precipitation, which was due in part to differences in liquid-water content (Aneja *et al*, 1992) The mean and minimum pH are given in Table 3 The mean pH was computed from the standard transformation

pH mean =
$$-\log\left(\frac{1}{n}\sum[H^+]\right)$$
,

where $[H^+]$ is the hydrogen ion concentration in eq ℓ^{-1} and *n* is the total number of samples

The mean pH value for cloud samples $(4\ 01)$ at the Whiteface Mountain summit (site 1) was higher than at the Whiteface slope site $3\ 91$, site 2) This result may reflect the vertical gradient of cloud acidity because the slope site is near the cloud base Several studies has shown that cloud water is more acidic at elevations near the cloud base (Kins *et al*, 1988) This vertical (spatial) variation in cloudwater concentration may be explained if one assumes that LWC increases with height above cloud base (Pruppacher and Klett, 1980) thus providing increased dilution of pre-existing aerosol, vertically LWC data at the slope



Fig 2 Frequency distributions of pH for both cloudwater and rainwater samples collected from May to October 1986–1988 at (a) Whiteface Mountain, summit, (b) Whiteface Mountain, site 2, (c) Mt Moosilauke, (d) Shenandoah Park, (e) Whitetop Mountain, (f)Mt Mitchell

Table 3 Frequency (number of hours) of pH < 40, 35, 30 and 25 at MCCP sites, May to October 1986-1988

Site	No of samples	pH < 40	pH < 3 5	pH<30	pH < 2 5	Mean	Mın
WF1	634	58 8 (373)	22 1 (140)	1 26 (8)	0	4 01	2 75
WF2	66	63 6 (42)	42 4 (28)	9 09 (6)	0	391	2 74
MS1	200	71 5 (143)	39 5 (79)	15 5 (31)	0	3 65	26
SH1	55	85 5 (47)	40 (22)	1 82 (1)	0	3 65	2 92
WT1	601	71 6 (430)	37 1 (223)	6 82 (41)	0	3 77	2 59
MM 1	477	83 9 (400)	50 1 (239)	9 85 (47)	0 21 (1)	3 57	2 29



Fig 3 Cloud pH values vs ozone concentrations measured from May to October 1986–1988 at (a) Whiteface Mountain, summit, (b) Mt Moosilauke, (c) Shenandoah Park, (d) Whitetop Mountain, (e) Mt Mitchell



Fig 4 Cloud pH values vs ambient temperature measured during 1987 at (a) Whiteface Mountain, summit, (b) Mt Moosilauke, (c) Shenandoah Park, (d) Whitetop Mountain, (e) Mt Mitcheil

site (site 2) was not measured and thus, we are proposing a hypothesis to provide insight in the vertical changes in cloudwater pH

The minimum cloud pH was 275 at Whiteface site 1, 274 at Whiteface site 2, 260 at Mt Moosilauke, 265 at Shenandoah Park, 259 at Whitetop Mountain and 229 at Mt Mitchell Falconer and Falconer (1980) reported that 90% of all cloudwater samples ranged in pH from 266 to 466 for the periods of August–September 1977 and 1979 at Whiteface summit Weathers *et al* (1986) observed a single acidic cloud event at several sites in the eastern US in 1984 and found that the pH ranged from 28 to 309 Several other investigators studying urban fogwater acidity in California found that the pH was as low as ~22 (Waldman *et al*, 1982, Munger *et al*, 1983, Jacob *et al*,

1985) The sample with pH value of 2 29 measured at Mt Mitchell in 1986 was more acidic than that reported by Weathers (1986) for other sites in the eastern U S and by Muir *et al* (1986) in an urban midwestern site. It was, in fact, close to the level of urban fog water in California

It is documented that cloud or fog with a pH less than 40 is believed to cause measurable damage to foliage and yield of some plants, such as red oak, white pines and spruce (Jacobson, 1984, Evans 1984, Jacobson *et al*, 1990a) It is also known that even one exposure of pH less than 25 can damage certain crop species (Grantt *et al*, 1984) The number of hourly cloud samples, as well as percentage of sampling time, with pH < 40, 35, 30 and 25 are also given in Table 3 It appears that Mt Mitchell received the most acidic cloud exposure during the sampling period, while the Whiteface summit site received the least acidic exposure Mount Moosilauke and Shenandoah Park sites are lower in elevation, with lower frequency of cloud immersion, but close to the cloud base, thus the percentage of total sampling hours with acidic cloud (pH < 40 and 35) is higher than Whiteface summit and Whitetop Mountain

Based on an empirical analysis, it is found that cloud pH value is a function of ambient temperature and ambient ozone concentration (Figs 3 and 4) The best curve fit between pH and ozone is

$$[\mathbf{pH}] = A/[\mathbf{O}_3]^B,$$

where A and B are constants and greater than zero (for each case, first- and second-order relationships were also considered) The coefficients of determination (r^2) were above ~04, while a linear relationship between cloud pH and ambient temperature (cloud acidity increasing with increasing ambient temperature) was obtained, suggesting a seasonal dependence

A seasonal variation of pH in cloud samples can also be noted (Fig 5) Mean pH values calculated by monthly basis are shown in Fig 5 for the five sites during the 3 years The results imply that strong acidic cloud waters are found in warm and humid summer months Earlier studies by Aneja *et al* (1990a), who analysed the cloud pH collected in 1987 at Mt Mitchell, utilizing the cloud and rain acidity/conductivity (CRAC) real-time automated sampler, show a similar seasonal trend It is observed that the high-pressure system and air stagnation events frequently occurred during the summer months in the eastern US, which allows a greater build-up of those acidic aerosols and atmospheric photochemical oxidants (Aneja *et al*, 1990b, 1991, Claiborn and Aneja, 1991) Enhanced

ozone at the locale by cloud passage appears to contribute to increased cloud acidity as well as to the concentrations of acidic species in the cloud water. It is also found that cloudwater pH seasonal variation was consistent with the trend of atmospheric oxidants, such as O_3 (Fig 6) The oxidation of SO_2 might be a limiting factor for the generation of atmospheric acidity (Calvert et al, 1985) The substantial O3 concentration at high elevation in the eastern US during the warm season signifies an oxidizing condition conducive to the formation of HNO₃ and H₂SO₄ from atmospheric NO_x and SO_2 When the photochemical production of H₂O₂ and O₃ are relatively low in the cold seasons, the amount of oxidants may be limiting for converting SO_2 and NO_x to H_2SO_4 and HNO_3 , which will reduce atmospheric acidity The meteorological conditions, such as temperature and cloud liquid-water content, may also affect the variation of pH in the cloud

33 Cloud chemical composition

Mean inorganic compositions of cloudwater samples collected at five summit sites and one sub-site at Whiteface Mountain from May to October 1986–1988 are presented in Table 4 We are exploring interrelationships with simple normal linear statistics We are appealing to the Central Limit Theorem and thus mean, regression coefficient and correlation, etc, are approximately normal, even if the original distribution may not be normal (Dickey, 1991) The mean inorganic ion balances for all sites were within 6%, indicating that the concentrations of organic acids, such as formic and acetic acid, in cloud water at the sites are small As may be expected, the average concentrations noted at MCCP sites seem to be lower than those reported for urban fog water in



Fig 5 Monthly averaged pH values measured at MCCP sites from May to October 1986–1988

		Table 4	Statistical s	summary (of chemical	species in	cloud wat	ter (in µeq i	(^{- 1}) collect	ed at MCC	P sites for	1986–1988	
Site		SO ^{2 –}	NO ⁷	CI-	+ H	NH4+	Na ⁺	K +	Ca ²⁺	Mg ^{2 +}	Anion	Cation	Anion/cation
WF1	X S % max	245 241 354 2224	91 116 1319 1344	649 103 094 115	203 229 29 32 1778	119 136 17 28 920	3 65 9 64 0 53 148	2 7 24 2 0 39 610	16 373 232 526	41 878 059 74	343	349	0 98
WF2	X S % max	525 573 40 2432	133 142 10 625	937 93 071 367	380 444 28 9 1820	225 212 17 14 878	4 93 7 01 0 37 47	2 59 2 19 0 2 12	267 35 203 135	6 69 8 59 0 51 32 2	668	646	1 03
MSI	X S % max	448 582 32 8 2860	231 325 17 2290	23 7 47 1 1 7 499	440 521 32 3 2511	179 215 13 1 929	179 48 131 556	35 43 026 387	139 216 101 152	7 38 111 0 54 77	703	662	1 06
IHS	X S % max	367 339 323 1238	180 138 158 541	198 248 18 144	325 260 28 5 1202	206 191 18 2 840	11 9 29 5 1 05 174	357 354 031 148	174 202 153 839	5 64 7 9 0 49 46 2	566	569	66 0
WT1	X S % max	400 422 348 2690	169 184 14 7 1489	191 191 17 158	344 376 299 2570	170 169 14 8 1070	8 36 12 1 37 158	304 312 026 31	291 453 253 442	6 32 6 43 0 55 50 1	589	561	1 05
MMI	X S % max	576 608 361 3700	205 239 12 9 2118	32 9 58 8 2 1 691	462 483 29 1 5128	218 248 13 7 2039	194 40 122 587	778 457 049 910	55 1 123 3 47 1189	13 9 24 6 0 88 225	809	776	1 04
C A = X	mean va nion = S(ation = H	$\sum_{4}^{2} = N = St_{4}$ $\sum_{4}^{2} = N = N = \frac{3}{4}$	and ard dev $\frac{1}{5} + CI^{-}$ $\frac{1}{5} + Na^{+} + K$	iations, % $^{+}$ + Ca ²⁺ +	= per cent c	of total me	asured 101	nic species,	max = ma)	umum value	measured	during the	sampling period

High-elevation cloud chemistry





Fig 6 Monthly averaged ozone concentrations and pH values measured at Mt Mitchell from May to October 1986–1988



Fig 7 Mean ion concentrations for the MCCP sites, from May to October 1986-1988

Los Angeles and the Midwest (Munger *et al*, 1983, Muir *et al*, 1986), however, the maximum sulfate concentration (3700 $\mu eq \ell^{-1}$) measured at Mt Mitchell was close to or higher than those at some of the urban locations mentioned above The sulfate and nitrate concentrations were generally higher than fog water reported at Albany, NY (Fuzzi *et al*, 1984), and cloud water at high elevation in the Sierra Nevada (Collett *et al*, 1990) The Ca²⁺ concentration, which is derived from soil dust, was the highest among the trace metals at most sites, with one exception at Mt Moosilauke, where the mean Na⁺ concentration, thought to be of marine origin, was higher than the Ca²⁺ concentration Significant concentrations of metals and non-sea salt Ca²⁺ at most sites show that the air masses are continental in origin (Kim and Aneja, 1992) On some occasions, extreme high concentrations of these minor constituents in the cloud were observed, for example, Cl⁻ concentration reached 499 μ eq ℓ^{-1} at Mt Moosil-auke and 691 μ eq ℓ^{-1} at Mt Mitchell, and Ca²⁺ reached 526 μ eq ℓ^{-1} at Whiteface Mountain site 1 and 1189 μ eq ℓ^{-1} at Mt Mitchell However, the high tracemetal content in cloud may catalyse SO₂ oxidation when atmospheric H₂O₂ and O₃ are relatively low

Figure 7 illustrated the mean total concentrations for all sites The exposure gradient (only in terms



Fig 8 Frequency distributions, May-October 1986-1988, of SO₄⁻ at (a) Whiteface Mountain, summit, (b) Whiteface Mountain, site 2, (c) Mt Moosilauke, (d) Shenandoah Park, (e) Whitetop Mountain, (f) Mt Mitchell

of concentration) along north to south Appalachians can be observed The figure indicates that the northernmost site, Whiteface Mountain site 1, had the lowest chemical concentration exposure in the cloud, while the southernmost site, Mt Mitchell, experienced highest concentration exposure The lower elevation Mt Moosilauke site had more concentrated cloud than Shenandoah Park and Whitetop Mountain

The frequency distributions of the principal ions, SO₄²⁻, NO₃⁻ and NH₄⁺, at the five sites are illustrated in Figs 8–10 The frequency distributions of equivalent concentration of ions are based on hourly samples Our intent is to present extremes in concentrations within events based on 1-hour sampling of clouds Thus volume-weighted averages for events are not utilized At the northern sites, over 60% SO₄²⁻ concentrations were less than 200 μ eq ℓ^{-1} at Whiteface site 1, 40% at Whiteface site 2 and ~50% at Mt Moosilauke At the southern sites, over 40% SO₄²⁻ were less than 200 μ eq ℓ^{-1} at Shenandoah Park and Whitetop Mountain, and 28 5% at Mt Mitchell

34 Ratios of ion concentrations

The ratios of mean major ion concentrations at the high elevation sites are listed in Table 5 The equivalent ratios of mean SO_4^2 to NO_3 were found to be between ~2 and 39 at the MCCP sites Nearly three times higher inputs of SO_4^2 than NO_3 were noted at Whiteface Mountain site 2 and two times higher at Mt Mitchell, suggesting that the contribution of sulfate to



Fig 9 Frequency distributions, May-October 1986-1988, of NO₃ at (a) Whiteface Mountain, summit, (b) Whiteface Mountain, site 2, (c) Mt Moosilauke, (d) Shenandoah Park, (e) Whitetop Mountain, (f) Mt Mitchell

acidity may be considerable at high elevations in the eastern US This is in contrast to the observations in the western US (i.e. southern California), for which nitrate is the dominant anion due to the high NO_x emission in those areas (Waldman *et al*, 1982, Jacob *et al*, 1985, 1986) The mean ratios of SO_4^{2-} to H⁺ were greater than 1 0, and mean ratios of NO_3^- to H⁺ were between 0 35 and 0 55 at all the high-elevation sites

Figure 11 shows the relation between sulfate concentrations and hydrogen ion concentrations in the cloud samples collected at MCCP sites during the 1986–1988 field seasons It is seen that SO_4^{2-} is highly correlated with hydrogen ion at all the high-elevation MCCP sites with a coefficient of determination, $R^2 > 0.8$ The sum of SO_4^{2-} and NO_3^{-} vs H⁺ are illustrated in Fig 12, and in general, higher correlation coefficients are observed at all those sites One sample collected at Mt Mitchell was noted for very high concentration of H⁺ (~5000 µeq ℓ^{-1} with moderate $SO_4^{2-} + NO_3^{-}$ (~3500 µeq ℓ^{-1}), indicating that other species, such as organic acid or HCl, may contribute to cloud acidity under certain biological and meteorological conditions

In general, marine-origin species, Cl^- and Na^+ , have to balance each other if no other sources are present (Saxena and Lin, 1990) The overall equivalent



Fig 10 Frequency distributions, May-October 1986–1988, of NH⁴₄ at (a) Whiteface Mountain, summit, (b) Whiteface Mountain, site 2 (c) Mt Moosilauke, (d) Shenandoah Park, (e) Whitetop Mountain, (f) Mt Mitchell

Cl⁻/Na⁺ ratio in our samples is 1 32-2 29, indicating that a large portion of Cl⁻ in cloud were from sources other than sea salt and the roads in the northern part of the country, especially at Whitetop Mountain This result implies that Cl⁻ may contribute to the cloud acidity in the form of HCl from industrial areas (Petrenchuk and Drozdova, 1966) However, the ratio $Cl^-/(SO_4^2 + NO_3^- + Cl^-)$, on an equivalent basis, averaged 0.02 at Whiteface Mountain, 0.03 at Mt Moosilauke and 0.04 at the three southern sites This indicates that, in general, Cl⁻ can be negligible for contributing acidity to clouds There are two known processes, scavenging of particulate sulfate and in-cloud SO₂ oxidation, which are responsible for cloud SO₄²⁻ concentration The coefficient of determination between SO₄²⁻ and gaseous SO₂ measured at Mt Mitchell during the cloud events was not good ($r^2 = 0.15$), indicating that the particulate sulfate scavenging was responsible for a majority of the sulfate in the cloud This finding is consistent with the results of Reisinger and Imhoff (1989), which showed the cloudwater sulfate concentration to be less than free-air aerosol concentration The gaseous SO₂ concentrations were also very low, in



Fig 11 The relation between sulfate concentrations and hydrogen ion concentrations in the cloud samples collected May-October 1986-1988 at (a) Whiteface Mountain, summit, (b) Whiteface Mountain, site 2, (c) Mt Moosilauke, (d) Shenandoah Park, (e) Whitetop Mountain, (f) Mt Mitchell

general, at Mt Mitchell It is recognized that aerosol particles tend to accumulate in the lower troposphere and can be transported over large distances For this reason they have the potential of making a significant contribution to acid deposition at elevated sites that are remote from source regions Bradow and Aneja (1988) found that cloudwater composition is very similar to aerosol composition at Mt Mitchell These results provide the evidence that in-cloud oxidation contributed little to the chemical composition of cloud water, while aerosol nucleation may have been the primary source of sulfate in cloud water, at least at the

Table 5 Ratios of mean ion concentration in cloud samples at MCCP sites for 1986-1988

	SO4-	SO ₄ ²⁻	SO4 ²⁻	SO4-	NO ₃	NO ₃	NO ₃	C1-	Κ+	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
Site	NO ₃	Cl-	H+	NH ⁺	H+	NH ⁺	Cl-	Na ⁺	Na ⁺	Na ²⁺	Na ⁺	H+
WF1	2 69	37 7	1 21	2 0 5	0 45	0 76	14 04	1 78	0 74	4 39	1 11	0 59
WF2	3 94	56	1 38	2 33	0 35	0 59	14 2	19	0 52	5 4 1	1 36	0 59
MS1	1 94	18 92	1 02	25	0 53	1 29	9 78	1 32	0.2	0 77	041	0 41
SH1	2 04	18 5	1 1 3	1 78	0 55	087	9 0 5	1 67	03	1 47	0 48	0 64
WT1	2 36	209	1 16	2 35	0 49	0 99	8 84	2 29	0 36	3 48	0 76	05
MM 1	2 78	17 37	1 24	2 62	0 44	0 94	6 24	17	04	285	0 72	0 47



Fig 12 The relation between $[SO_4^{2^-}] + [NO_3^-]$ and $[H^+]$ in the cloud samples collected May-October 1986–1988 at (a) Whiteface Mountain, summit, (b) Whiteface Mountain, site 2, (c) Mt Moosilauke, (d) Shenandoah Park, (e) Whitetop Mountain, (f) Mt Mitchell

Mt Mitchell high-elevation site However we cannot exclude the possibility that the aerosol itself may have resulted from an earlier in-cloud oxidation

4 SUMMARY AND CONCLUSIONS

The purpose of this study was to characterize cloud chemistry exposures at high elevations over the eastern US High-elevation locations in the eastern US were frequently immersed in clouds Cloud frequency ranged from 32 to 77% of the days at these sites More than 90% of cloud samples at those sites were acidic (pH < 50) One extreme value of pH 2 29 was recorded at Mt Mitchell The observations we report here document the presence of chemical pollutants that can exert a more subtle stress on these high-

elevation ecosystems (Bormann, 1988), in particular, ozone and acid deposition (predominantly as acid cloud water) (Hertel et al, 1990)

The ionic composition of the cloud water from each field season and for each site was dominated by sulfate and nitrate anions (48–50%), and hydrogen and ammonium cations (43–47%) The southernmost site, Mt Mitchell, received, in general, the most acidic clouds (mean pH 3 57) and major chemical exposures (total averaged ion concentration 1586 $\mu eq \ell^{-1}$) The Whiteface summit, the northernmost site, received the least acidic cloud (mean pH 4 01) and chemical exposures (total averaged ion concentration 691 $\mu eq \ell^{-1}$) compared to the other MCCP sites

Cloud pH and major chemical components exhibited a seasonal trend with the maxima during the summer months, and correlated with temperature and ozone concentrations The seasonal variation may be due to (i) high ozone concentration during the summer which provides the condition of conversion of SO_2 and NO_2 to sulfate and nitrate in the gas phase and cloud droplets, (ii) increased reaction rate dependent on temperature, (iii) other meteorological conditions, such as increased high-pressure systems and reduced hquid-water content

The mean equivalent ratios of $SO_4^2^-$ to NO_3^- were found to be between 19 and 39 at these sites It is observed that $SO_4^2^-$ was highly correlated with hydrogen ion for all events sampled, indicating that the contribution to cloud acidity by sulfate may be significant

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