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Cloud chemistry research at Whiteface Mountain

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ABSTRACT

Cloud collection principles are briefly reviewed; the performance of two collectors in common use is compared. Two cloud event studies (one during winter, the other during summer) are presented to contrast typical time-dependent histories of chemical concentrations for the two seasons. During winter, the oxidation rate of SO_2 is low, resulting in measured sulfate concentrations independent of SO_2 concentrations. During summer, SO_2 is rapidly oxidized by H_2O_2 with a residue of H_2O_2 persisting in cloud water after SO_2 has been converted. Changes in the gas phase concentrations of SO_2 and H_2O_2 are shown during a cloud event. Both gases drop to very low concentrations in cloud with H_2O_2 tending to recover after available SO_2 has been oxidized. The meteorology for each event is presented to illustrate the role of atmospheric structure in the transporting of emitted material and in determining cloud water compositions. Finally, a cloud chemistry climatology for winter and summer is presented, based upon 6 years of observations at Whiteface Mountain.

1. Introduction

A high elevation atmospheric monitoring station has been in operation at the summit (1620 m) and base (600 m) of Whiteface Mountain, NY, (44°23′26″N, 73°5′34″W) since 1961. The primary activity at Whiteface Mountain is related to atmospheric chemistry and physical meteorology. A range of meteorological and chemistry parameters are measured throughout the year. Cloud chemistry measurements have been made at the summit since 1978; initially on an exploratory basis to design and test cloud collectors and sampling methodologies. Since 1982, the measurement activities have been substantially increased in order to establish a chemical climatology for cloud water collected at the summit. Whiteface Mountain now has an extensive data set of cloud water.

The purpose of this paper is to first discuss principle design characteristics for cloud water collectors and show results of a cloud water comparison test for the passive and active cloud collector in use at Whiteface Mountain. The second objective is to describe a typical summertime and wintertime cloud event and to present a summary for all cloud events observed between 1982 and 1987. The final objective of this paper is to discuss the gas and aqueous phase hydrogen peroxide measurement obtained at Whiteface Mountain in support of the cloud chemistry research.

2. Cloud collector design

Recent interest in cloud chemistry has significantly increased the demand for cloud collection systems capable of providing cloud water collected with known efficiencies and with sufficient yield to conduct detailed chemical analysis for all ions currently surveyed in the MAP3S and NTN networks as well as dissolved hydrogen peroxide and selected organic compounds.

Several European and United States designs have been used extensively for the collection of warm and supercooled cloud water from ground-based and airborne stations. While the collection systems available today enable us to collect cloud and fog water, there is still need for improvement, particularly in the areas of automated collection and size discrimination of the droplet spectrum. In addition, there is a need for improved ground-based devices to measure liquid water content in order to follow quantitatively species going into solution and/or oxidized within the droplet, and to calculate cloud water deposition to the surface.

Houghton and Radford (1938) were probably the first to report a cloud collection device specifically designed for chemically analyzing the collected water. A series of seven 18-mesh stainless steel screens (wire diameter 0.023 cm) was mounted in a short wind tunnel through which air was drawn at about 6 m/s. Fukutomi and Tabata (1948) developed an omnidirectional passive collector using an array of wires to intercept cloud or fog droplets. Enameled copper wires (diameter 0.012 cm) were stretched vertically between the rim of a circular disk and that of a cone to form a cylindrical wire screen. Fog and cloud droplets accumulated on the screen, slid down the wires, and were collected by the cone, which led into a central pipe at the bottom of the apparatus. This collector served as the model for an omnidirectional passive cloud water collector developed by ASRC and used at Whiteface since 1979.

Study of the chemical properties of fogs and clouds has increased steadily over the years, ever since Junge initiated a systematic investigation of air chemistry parameters in the 1950s. Several factors have contributed to the increased interest.

(i) Results from field experiments have shown that scavenging of aerosols and gases by precipitation (washout) is not the major process responsible for the observed ion species and concentrations in rainwater. Thus, processes occurring within clouds are of crucial importance.

(ii) Chemical models have been developed for the transformation of sulfur- and nitrogen-bearing components. Sulfuric acid, nitric acid, hydrogen chloride, and hydrogen peroxide (H_2O_2) are now recognized as dominant gaseous end products that must be incorportaed into the chemistry of cloud droplets. In addition, atmospheric models incorporating heterogeneous reactions place an increasing importance on the liquid phase reactions of dissolved gases and aerosols (such as ozone, H_2O_2, sulfur dioxide, nitrogen dioxide, ammonia, and undissolved carbonaceous substances). Field experiments for model validations are urgently needed.

(iii) Attempts at modeling the long-range transport of pollutants and acid rain have exposed a lack of a reliable data base for cloud chemistry.

(iv) Observed forest damage in Europe and North America shows a distinct altitudinal gradient, worsening with increasing altitude (NAPAP, 1987). A relatively sharp altitude range for the onset of increased forest damage appears to coincide with the altitude level for cloud bases. For this reason, monitoring exposures of forest to cloud water is the prime objective of several programs in the United States, Canada and throughout Europe.

To achieve impaction of cloud droplets on a collection surface, cloud collectors depend upon a velocity differential—both in magnitude and direction—between cloud droplets suspended in ambient air and the ambient air itself. The resulting parameter, the Langmuir stopping distance, governs in principle the impaction characteristics of all types of cloud collector designs (Langmuir and Blodgett, 1961). Cloud collectors fall into two basic categories: passive and active. Passive collectors depend upon ambient wind speed to provide the velocity differential between suspended cloud droplets and collector surface, while active collectors provide some physical means for generating this required velocity difference (mostly blowers and/or air deflectors).

Several processes govern the overall efficiency of collectors for accumulation of cloud water. These include the following.

(i) Impaction of cloud droplet on inertial collector surface (based upon Langmuir stopping distance).

(ii) Accumulation/coalescence of individual collected cloud droplets into a continuous water film and/or into a larger water droplet.

(iii) Transport of cloud water from the inertial collector surface to the final storage container by means of gravity, pressure difference or centrifugal forces.

(iv) Evaporation of cloud water after impact on the inertial collector surface but before the water can be removed from contact with the ambient air.

(v) Resuspension, or blow off, of cloud water after accumulation/coalescence due to excessive relative wind speed at or near the collector surface.

Each cloud collector design attempts to maximize the overall efficiency which is determined by the relative fraction of available cloud water that can be collected and diverted to some type of containment for chemical analysis. An optimal design, give the observed droplet size distribution for various types of clouds, would require cloud collectors with inertial impaction efficiencies approaching 100% for all droplets above about 1 μm diameter. While this is in principle achievable, it is undesirable since such a collector would also accumulate interstitial aerosols increasing chemical contamination in environments of high ambient aerosol loadings. Therefore, most collectors have been designed with the 50% cut off size centered around 2 to 5 μm diameter. While this will necessarily yield nonrepresentative cloud water samples, the small droplets that escape capture by the collector would not contribute significantly to the collected bulk cloud water. Such size discrimination is currently tolerated.

Liquid cloud water yield depends significantly on the rate of coalescence of micron sized droplets into larger drops or into a surface water film. Evaporative loss during this critical accumulation period is the most critical design problem and must be kept to a minimum by forcing the cloud droplets to initially impact over a very small surface area only and/or by shielding the impacted cloud droplets from the surrounding air stream. These measures will also minimize the possibility for contaminating the collected cloud water by prolonged exposure to ambient air. Loss of collected cloud water can also occur during the final sampling process when the water film or the large droplets begin to flow towards the storage container. If not properly shielded from high ambient air flows, there exists the potential for resuspension or blow off. Many collectors, particularly passive collectors, suffer from this loss of cloud water at times of high ambient wind speed. Since so many compromises must be made in cloud collector design, it is highly desirable to demonstrate—through extensive field and laboratory tests—the performance of each design, including sampling characteristics and ability to reproduce the correct chemical composition and liquid water content of clouds.

3. Experimental methods

3.1. Gases

Continuous real-time measurements of sulfur dioxide and oxides of nitrogen were made from January 1984 on using commercial detectors. Sulfur dioxide was measured with a Meloy 260 flame photometric detector operated with hydrogen containing 60 ppb of sulfur hexafluoride (SF_5) for enhanced sensitivity. Since 1986, SO_2 is measured with a TECO Model 43S. Oxides of nitrogen were measured with a Monitor Labs 8840 chemiluminescent detector modified for enhanced sensitivity (Tanner et al., 1983). This detector measures total gaseous oxides of nitrogen (NO, NO_2, HNO_3, PAN and organic nitrates). Modifications to the Model 8840 include use of a large pump, increased ozone supply, and larger, more reflective reaction chambers. Since 1986, oxides of nitrogen are measured with a TECO Model 14A. Ozone was monitored by an ethylene chemiluminescence instrument and an ultraviolet absorption TECO Model 49 analyzer. The H_2O_2 measurements made at Whiteface Mountain used the fluorescence technique based on the peroxidase catalyzed reaction. When H_2O_2 is present, along with the hydrogen-donor molecule p-hydroxphenylacetic acid (POPHA), and peroxidase, the result is a dimer which fluoresces. The process is fully described by Kok et al. (1986). Air is sampled at the rate of 2 l min^{-1}. The air sample to be analyzed for H_2O_2 is passed through a coil about 50 cm long where the H_2O_2 dissolves in water. The sample is divided into two channels. One is treated with the enzyme catalase which destroys any H_2O_2 present. This channel serves as the H_2O_2 blank since organic peroxides and other substances may fluoresce in a manner similar to H_2O_2. The fluorescence of the two channels is then compared to determine the amount of H_2O_2 in the sample. The instrument signal has a coefficient of variance of 0.5% at 2.5 ppbv, with a detection limit which varies from 10 to 70 pptv. This same apparatus can be used to analyze aqueous-phase H_2O_2. In this case, the sample is manually injected. The instrument can detect concentrations of aqueous-phase H_2O_2 greater than 0.4 ppbm.

3.2. *Cloud water collection*

The active and passive cloud collectors in operation at Whiteface Mountain use cylindrical rods of various diameters as the inertial collection surface. Cloud droplets suspended in ambient air collide with these cylinders as the air moves around them. The theoretical treatment of this aerodynamic problem is relatively simple and yields collection efficiencies as a function of rod diameter and relative air flow velocity as shown in Fig. 1. The ASRC passive collector uses Teflon threads of 0.04 cm diameter. The collection efficiencies vary with wind speed as is common to all passive devices, however, in the higher wind environment common at the summit of mountains the efficiency cutoff is commonly within the preferred range. Incorporating a string arrangement into a tube or box and attaching an electric blower/fan leads to an active, internal type cloud collector particularly useful in low wind environments. The Daube–Caltech cloud collector (Daube et al., 1987) is the most frequently used of this type of collector. This collector incorporates several mechanical features such as a downward facing inlet to reduce rain contamination, a flow straightener to better define the impaction characteristic, and a removable thread assembly inclined 45° to the flow to reduce the component of the air flow normal to the thread, and increase the force causing the accumulated water to flow down the thread and out of the collector.

The performance of these two collectors (ASRC passive and Daube–Caltech active) was compared at Whiteface Mountain to determine if the concentration of the dominant ions in the water from both collectors were similar. The results from about 120 cloud only samples are shown in Fig. 2. The ratios (ASRC/Daube–Caltech) of the concentrations of H^+, NH_4^+, NO_3^-, and $SO_4^=$ are between 0.9 and 1.1 for about 90% of the samples. This data was taken over a large range of wind speeds (about 3 to 30 m s^{-1}), so for a wide range of operating conditions, both devices produced water with equivalent chemistries. For samples that were collected during rain, about 60% of the concentration ratios were also between 0.9 and 1.1, indicating that only for low wind speeds (<about 5 m s^{-1}) did the precipitation shield completely exclude rain.

During winter, the supercooled cloud water freezes on impact. We take advantage of this property by exposing a linear array of small diameter wires (0.04 cm) normal to the wind direction (Kadlecek et al., 1985). The accumulated rime is then removed manually using a scraper to clean off both sides of the collector array. The removed rime falls directly into a sample bottle fitted onto the bottom of the scraper. The sampling duration was determined during each collection so as to provide sufficient

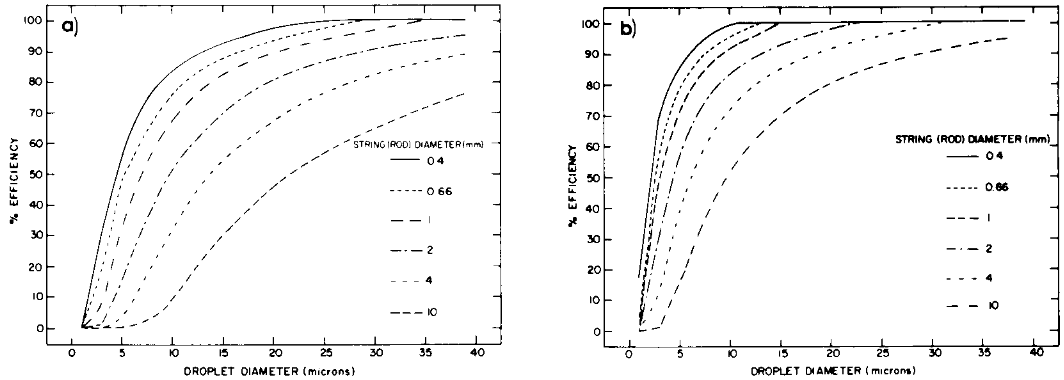

Fig. 1. Collection efficiencies in each block, from left to right 0.4, 0.66, 1, 2, 4, 10 mm diameter rods. Collection efficiency: (a) 5 m s^{-1} winds, (b) 25 m s^{-1} winds.

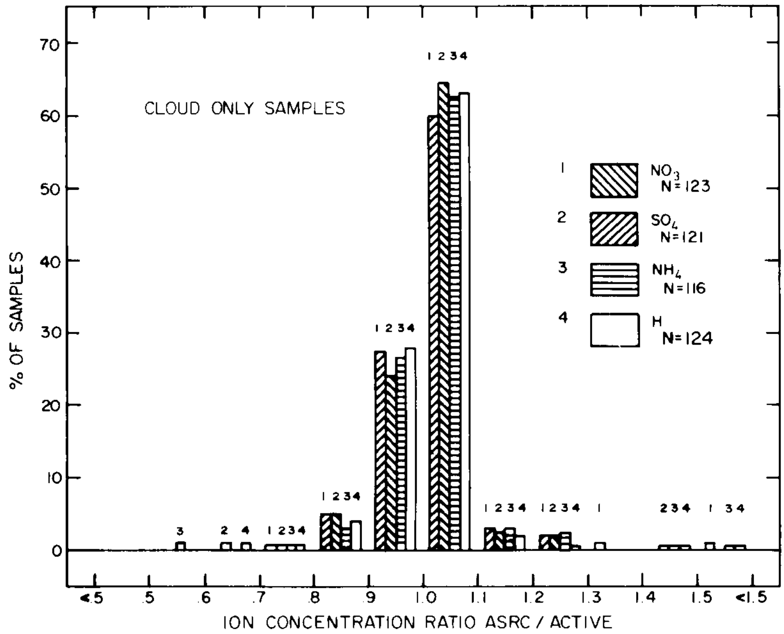

Fig. 2. Ion concentration ratio for ASRC/Active cloud collectors.

sample for the chemical analysis. It varied as needed with atmospheric conditions, but was kept as short as possible (20 to 30 min) to permit good time resolution of any changes in cloud water chemistry. This approach is necessary because as a rime sample grows, it becomes more likely to be broken off the collector wires by wind-induced vibrations; and the size of the collection surface increases, causing reduced collection efficiency (Fig. 1). During our sampling at Whiteface, we observed less than 30% blow-off for most samples, frequently less than 10%. When LWC was low (less than about 0.2 g/m^3) and wind speeds were low, we were unable to obtain sufficient sample during the preferred sampling time, so collections were made about every 20 min and were sequentially bulked until the sample contained adequate rime to provide for all chemical analyses. All samples were kept frozen until immediately before chemical analysis. This was done to prevent the chemical composition of the sample from being affected by liquid phase reactions during storage.

Liquid water content (LWC) measurements were made since the fall of 1986 using the Valente gravimetric technique (Valente, personal communication). Prior to 1986, LWC could only be estimated from the volume of collected liquid water taking into account the average windspeed during the collection period and the collection efficiency of the device.

3.3. Cloud water analysis

The following major ions have been determined for all cloud water samples using ion chromatography (Dionex) and Flame Atomic Absorption Spectrophotometry: SO_4^{2-}, NO_3^-, Cl^-, H^+, NH_4^+, Ca^{2+}, Mg^{2+}, Na^+ and K^+. The focus in this paper will be on the four major ions sulfate, nitrate, hydrogen ion and ammonia which made up over 90% of the ions present in cloud water at Whiteface Mountain.

4. Results

4.1. Chemistry of mountain clouds—case studies

The extensive cloud water monitoring done at the ASRC Whiteface Mountain Field Station during the last 6 years allows some generalizations to be made about the chemical composition of mountain clouds and to the relationship between air mass origin and cloud type, and cloud chemistry. Presented here are case studies showing typical cloud chemistry behaviors for a wintertime supercooled cloud event and a summertime warm cloud event. Shown in Fig. 3 are the results from a winter event, interesting not only because of the uniformity of the ion concentrations despite the large change observed in SO_2, but also because it is a good example of the general tendency for sulfate ion concentrations to be independent of SO_2 concentrations.

The cloud in this event was associated with a weak cold front that was nearly stationary during the 14 h of cloud water collection. Fig. 4 shows this front and the three trajectories that arrived at the start (A), the middle (B), and the end (C) of the event. The flow history (Fig. 5) for the A trajectory shows the mixed-layer capped by a well-defined inversion, which increases in height as the air approaches Whiteface. The observed summit potential temperature (θ) plotted in Fig. 5 lies at the bottom of the inversion, indicating the summit was exposed to mixed-layer air.

The steady meteorological pattern and well-defined mixed layer justify high confidence in the trajectories for this event. The trajectory paths do not change much over the event; all approach with similar speeds from the southwest over regions of high SO_2 and NO_x sources (included in the NO_x measurement are concentrations of other nitrogen oxides present in the air that are converted by the molybdenum catalyst) (Stedman and McEwan, 1983; Grosjean and Harrison, 1985; Fahey et al., 1986). Gas concentrations were relatively high consistent with trajectories from the southwest, but ion concentrations were extremely low. Furthermore, the ion concentrations do not respond to changes in trace gas levels, and account for only a small fraction of the total S or N present in the atmosphere at any time. Throughout the entire event the hydrogen peroxide (H_2O_2) concentration in the gas and aqueous phase was below detection limit. The ozone (O_3) concentration fluctuated between 20–40 ppb, as is typical for wintertime. The meteorological situation that created the cloud in this case is consistent with steady ion concentrations. The stratiform cloud resulted from the convergence and lifting of lower level air as it approaches the front, reflected in the rise of potential temperature lines defining the top of the mixed layer. Satellite images revealed a low, flat cloud top in the region, consistent with the lack of observed precipitation. All indications are that mixed layer air was gently lifted to saturation, and this occurred about 15 hours upstream of Whiteface (based on cloud ceiling observations).

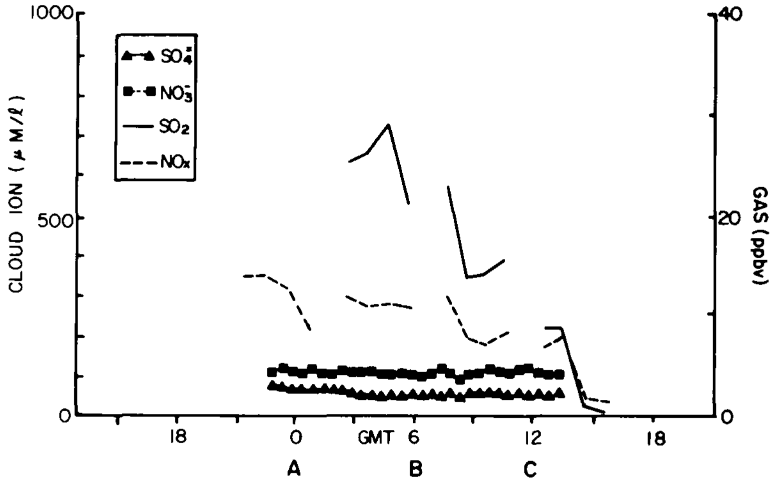

Fig. 3. Trace gas and cloudwater concentrations for the supercooled cloud event of 4 January 1984 (the concentration of hydrogen peroxide in both gas and aqueous phase was below detection limit).

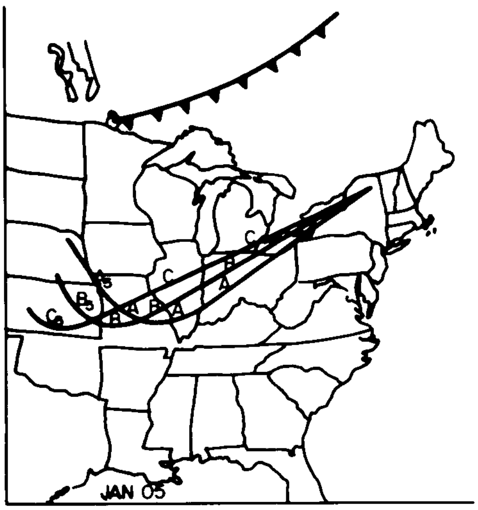

Fig. 4. Trajectories for 4–5 January 1984 event, and frontal position at 01 EST, 5 January 1984. Letters designate trajectory positions 12 hours apart. Calculations of back trajectories ending at Whiteface Mountain have been calculated using the ARL-ATAD single layer model (Heffter, 1980). Trajectories are labelled by A, B, C, or D for end-times at Whiteface Mountain of 00, 06, 12 or 18 GMT respectively. Letter positions designate 12-h intervals upstream from Whiteface Mountain.

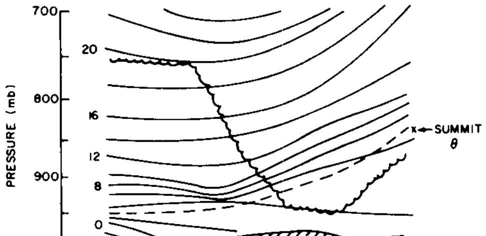

Fig. 5. Flow history for trajectory A.

In conclusion, this case is an example of the lack of response of sulfate concentrations in cloud water to the presence of SO_2 that is typical of winter. The SO_2 levels were high at the beginning of the event. Nitrate concentrations in this case are constant, however the change in $[NO_x]$ through the event is much less than for $[SO_2]$. The absence of rapid liquid phase oxidation for SO_2 is a consequence of very low concentrations (not detectable) of H_2O_2 and of low pH values (<5.0). The changes in cloud water chemistry most easily observed result from meteorological influences on changing source strengths, not from varying atmospheric chemical processes.

In strong contrast to this winter event are the results from a summer event. Beginning on 4 August 1986, high pressure dominated the northeastern U.S. The meteorology is summarized in Figs. 6 and 7. Winds from the southwest brought warm, moist air from the Ohio Valley to the Adirondacks. Relative humidities were high and the temperature increased over the period while winds slowly diminished, meteorological conditions which were conducive to photochemical oxidant formation. Ozone increased steadily from 25 ppb to 80 ppb and sulfate aerosol increased from 5 to 23 $\mu g\ m^{-3}$, while high pressure prevailed over the region. On 7 August, a front approached Whiteface Mountain and clouds moved in at 16:00 local time, marking the start of the cloud event. It lasted over 60 h until 04:00 on the morning of 10 August. There was a very brief rain shower at the onset of the cloud event and intermittent rain showers occurred after about the 21st hour (Fig. 8). The chemical composition of cloud water is shown in Fig. 8. Several of the features presented here are typical for most cloud events: concentration profiles for the major ions hydrogen, sulfate, nitrate and ammonium are very similar, with hydrogen as the dominant ion in almost all samples. The sulfate ion concentration is generally higher than the nitrate and ammonium ion concentrations throughout the warm season. There exists an overall trend to the concentrations, directly linked to the relative emission levels incorporated in the air mass arriving at Whiteface as can be seen in Fig. 9. The concentration of the four main ions present in cloud water (SO_4^{2-}, NO_3^-, H^+ and NH_4^+) show a clear dependency on air mass origin, i.e., back trajectories. Measured concentration levels may be further modified by changes in liquid water content (LWC) and, if occurring, precipitation included in the collected sample. Unfortunately, no measurements of LWC are available prior to the fall of 1986. Assuming that this critical parameter does not change significantly from year to year, the frequency distri-

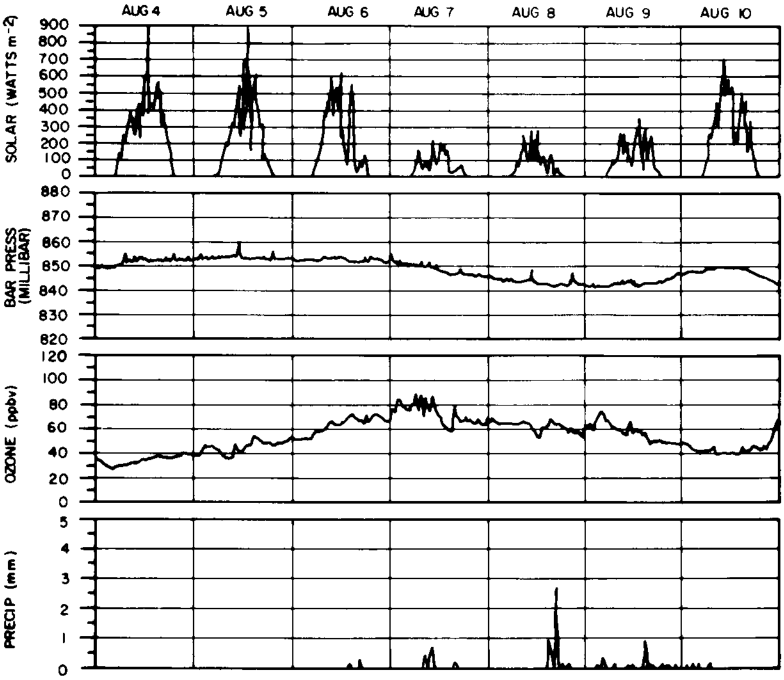

Fig. 6. Ozone and meteorological data summary, Whiteface Mountain, 4–10 August 1986.

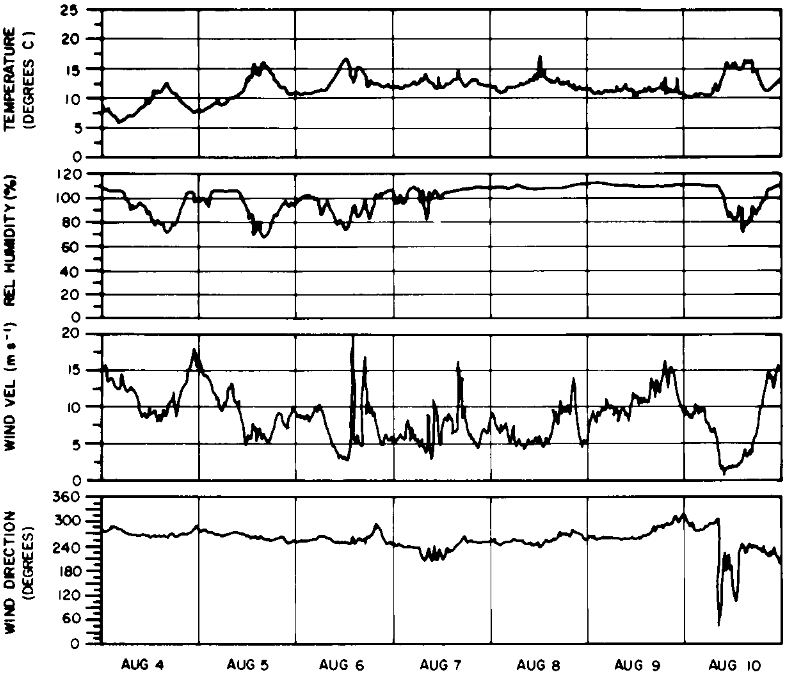

Fig. 7. Meteorological data summary, Whiteface Mountain, 4–10 August 1986.

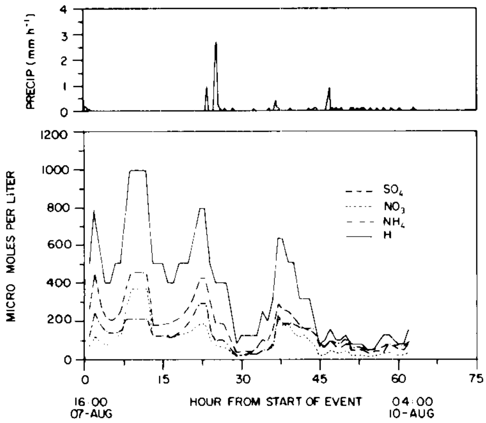

Fig. 8. Time history for cloud water ion composition and precipitation rate. Event of 7–10 August 1986 (Whiteface Mountain).

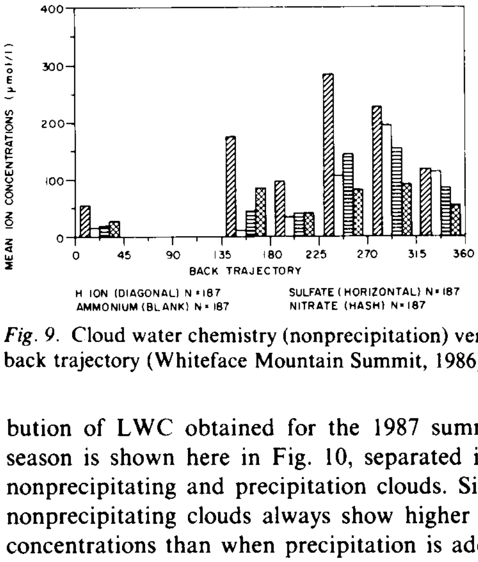

Fig. 9. Cloud water chemistry (nonprecipitation) versus back trajectory (Whiteface Mountain Summit, 1986).

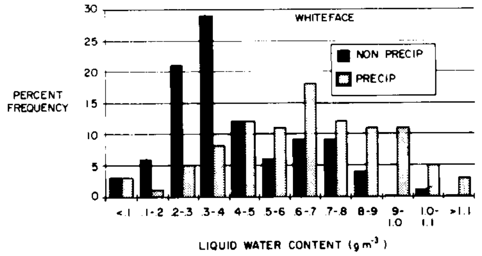

Fig. 10. Frequency distribution of cloud liquid water content (LWC) 1987 field season.

Table 1. *Whiteface Mountain cloud chemistry: summer and (winter). (All concentrations are in micromoles per liter.) Concentrations are for nonprecipitating clouds only*

	Mean	Std dev	Max	Number of hourly samples
Hydrogen [H^+]				
1982	255	286	1660	167
1983	309 (179)	430 (131)	3162 (589)	301 (99)
1984	331 (320)	229 (258)	977 (1906)	124 (125)
1985	(310)	(165)	(724)	(38)
1986	254 (331)	254 (284)	1585 (1122)	306 (69)
1987	174	190	851	91
Ammonium [NH_4^+]				
1982	143	113	788	167
1983	173 (68)	174 (53)	855 (205)	301 (99)
1984	148 (127)	100 (111)	612 (501)	124 (125)
1985	(163)	(91)	(391)	(38)
1986	110 (77)	136 (86)	776 (353)	306 (69)
1987	110	95	493	91
Sulfate [SO_4^{2-}]				
1982	138	127	612	167
1983	192 (79)	235 (68)	1525 (277)	301 (99)
1984	198 (126)	137 (110)	601 (496)	124 (125)
1985	(156)	(81)	(428)	(38)
1986	130 (119)	132 (91)	747 (412)	306 (69)
1987	113	111	492	91
Nitrate [NO_3^-]				
1982	55	92	590	167
1983	49 (98)	184 (63)	2036 (258)	301 (99)
1984	81 (202)	74 (153)	285 (838)	124 (125)
1985	(243)	(136)	(603)	(38)
1986	82 (156)	95 (167)	804 (592)	306 (69)
1987	72	74	417	91

bution of LWC obtained for the 1987 summer season is shown here in Fig. 10, separated into nonprecipitating and precipitation clouds. Since nonprecipitating clouds always show higher ion concentrations than when precipitation is added as a contaminant to the cloud water, the precipitation chemistry may have resulted from two processes: (1) the formation of rain in a cleaner environment aloft along with the addition of more water to further dilute the ion chemistry, and (2) the formation of ice hydrometeors which are generally cleaner than water hydrometeors (Scott, 1981). It is imperative to differentiate between the two cases of precipitating and nonprecipitating clouds. The cloud chemistry statistics shown in Table 1 incorporates data from nonprecipitating clouds only for the time period 1982–1987. The early data (before 1985) were obtained from frequent short term samples, the later data used one hour sampling periods. The data are compared for cloud only periods, when the ion contents of the water change relatively slowly.

Cloud water ion concentration will be strongly dependent on the entire air mass history (meteorology and chemistry) over the last few days prior to arriving at Whiteface, and, on the liquid water content of the clouds at the mountain summit. Since meteorological patterns do not repeat from year to year for a given season, and since the important chemical processes controlling oxidation change from summer to winter, and since some important emission rates change through the year (e.g., NH_3), one should expect considerable fluctuations in ion concentrations from year to year. The range of concentrations are large because the distribution is influenced by two distinct conditions: air masses from the southwest tend to be relatively more polluted, those from the northwest are less concentrated. The averages in the table will be determined predominantly by the fraction of time clouds persisted at the mountain before or after the passage of fronts (most importantly the cold front). Nevertheless, a clear seasonal difference in the concentrations of sulfate and ammonium ions emerges with higher concentrations in summer than in winter. The concentration of nitrate ions appear to be higher in winter. Although no LWC measurements exist for supercooled clouds, rough estimates obtained from rime ice accumulation rates indicate lower values for winter than for summer clouds. If this holds true then the seasonal change of sulfate and ammonium ion concentrations would be enhanced and the nitrate concentration would be more level throughout the year.

4.2. Measurements of gas phase H_2O_2

Aqueous phase hydrogen peroxide (H_2O_2) is believed to be the fastest of the important oxidants of SO_2. Heikes et al. (1987), Kelly et al. (1985) and Daum et al. (1984) have shown that whenever H_2O_2 is present in cloud water, levels of SO_2 are low. Mausch et al. (1986) have further noted the importance of H_2O_2 to acid deposition. Our observations appear to support these conclusions. While H_2O_2 is rarely present at Whiteface Mountain in the winter, it is always found there (even after all available SO_2 has been oxidized) during the rest of the year as shown in Fig. 11.

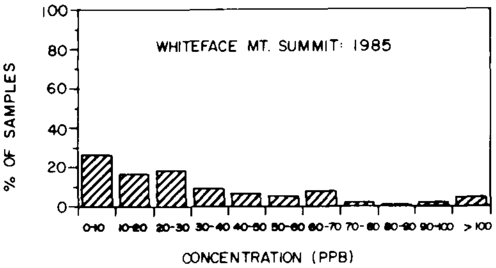

Fig. 11. Frequency distribution of aqueous phase (H_2O_2) hydrogen peroxide.

H_2O_2 was measured on about 40 days during the summer of 1986 and 56 days during 1987 at the Whiteface Mountain summit. The sampling site (1500 m above sea level) rises sharply about 700 m above the surrounding terrain. The concentrations of H_2O_2, SO_2 and ozone, measured at the summit, show no diurnal pattern because the sampling site generally remains isolated from air in contact with the surface. Therefore, local diurnal influences induced by surface-based inversions at night are not usually observed in this data.

The primary influence on gaseous H_2O_2 concentrations observed at the summit is the presence or absence of clouds at the site. Measured gaseous H_2O_2 concentrations drop below the detection limit of the instrument, often abruptly, whenever clouds appear at the summit and remain so as long as SO_2 is present in the cloudy air at concentrations above about 1 ppbv. SO_2, however, usually drops below 1 ppbv soon after clouds appear. Figs. 12 and 13 show two examples of this situation. In both cases, H_2O_2 fell below the detection limit within about an hour of the arrival of clouds as recorded by summit observers. It stayed low until SO_2 reached very low concentrations then gradually started to increase even though cloud was still present. Fig. 14 is an example, from a prolonged period of extensive low and middle cloudiness over northern New York State, which kept the summit in cloud from 14:00 1 August to 3:30 the next morning, producing showers and thunderstorms on the afternoon of 1 August. H_2O_2 was present at substantial levels, but SO_2 was undetectable until near the end of the period. All three cases, Figs. 12 through 14, appear to be consistent with the rapid dissolution of H_2O_2 into cloud water and its subsequent rapid destruction by aqueous-phase oxidation of SO_2. When there is insufficient SO_2 present, H_2O_2 remains at measurable levels in the gas phase, as illustrated at the ends of the events (Figs. 12 and 13) and during almost the entire event in Fig. 14. We cannot explain the substantial fluctuations of gaseous H_2O_2 prior to the cloud event based on the available meteorological data. We do not consider these field studies to demonstrate conclusively that SO_2 is destroyed by H_2O_2 only.

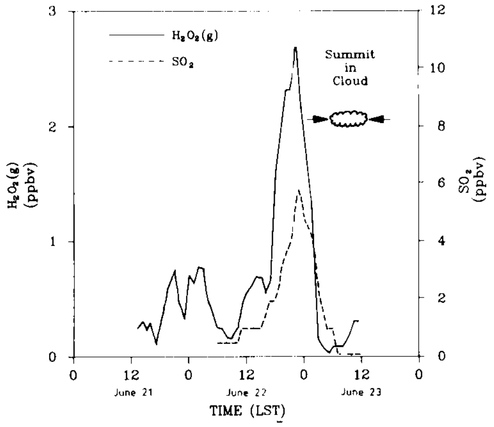

Fig. 12. Whiteface Mountain summit measurements of gaseous H_2O_2 and SO_2, 21–23 June 1986.

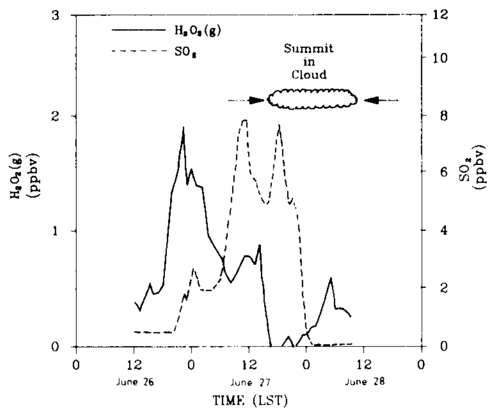

Fig. 13. Whiteface Mountain summit measurements of gaseous H_2O_2 and SO_2, 26–28 June 1986.

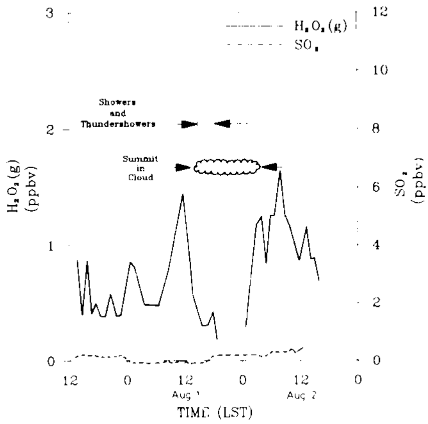

Fig. 14. Whiteface Mountain summit measurement of gaseous H_2O_2 and SO_2, 31 July–2 August 1986.

We also cannot determine rates of production or destruction of the trace gas species from the concentration changes in Figs. 12, 13 and 14 because it is impossible to distinguish chemical effects from advection of air with different composition past the summit. The increases in H_2O_2 after SO_2 drops in Figs. 12 and 13 could reflect the rate at which gas or aqueous-phase processes regenerate H_2O_2, but they could also reflect differences in upstream distributions of H_2O_2, SO_2 or clouds which cannot be determined by summit data alone. Each of the four events where H_2O_2 increases from undetectable levels after SO_2 is depleted in the presence of cloud show increases in H_2O_2 similar to that seen in Figs. 12 and 13. Detailed analysis of meteorological data in the Adirondack region during these episodes suggest that these increases in H_2O_2 result primarily from the advection of air with different chemical character, rather than H_2O_2 generation in homogeneous cloud conditions.

Fig. 15 presents the H_2O_2 summary distributions for all measurements (including when the mountain was in cloud) from the summers of 1986 and 1987. The data were initially averaged to hourly values which were used to create the informtion displayed in the figure. The cloud free periods show relatively fewer samples in the low concentration ranges.

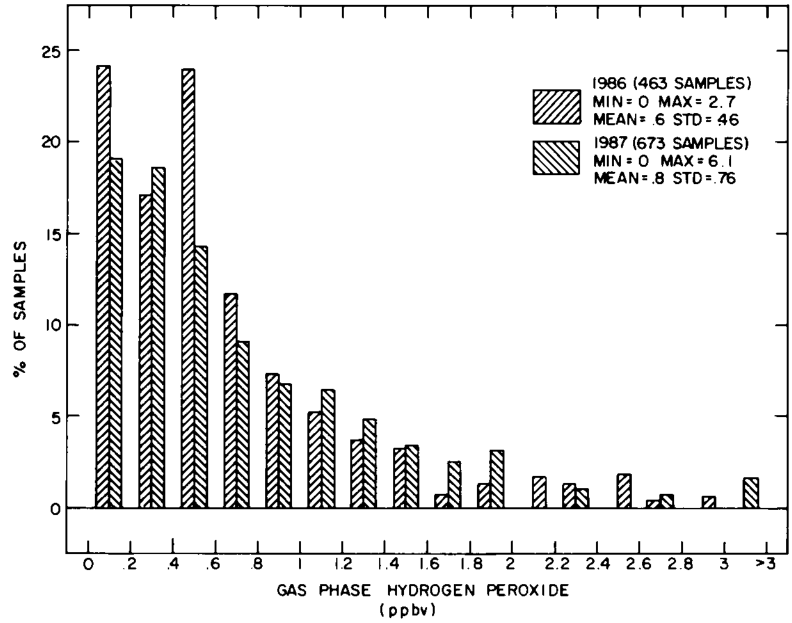

Fig. 15. Gas phase hydrogen peroxide measurements at Whiteface Mountain, Summer 1986/87. Hourly averages from continuous measurements.

5. Summary

Reliable methods now exist for collecting cloud water samples in sufficient quantities for detailed chemical analysis. The chemical composition of clouds collected in the northeastern United States shows significant fluctuations during an event, on a seasonal basis and from year to year. Some of the reasons for these fluctuations have been identified. Significant differences in sulfate ion composition between supercooled winter clouds and warm summer clouds may be caused by the reduced in-cloud oxidation of sulfur dioxide as indicated by the absence of hydrogen peroxide during winter. Air mass history appears to be another important meteorological parameter influencing cloud chemistry. Southwesterly air flow gives rise to highest ion concentrations in cloud water. Precipitating clouds show generally lower ion concentrations than nonprecipitating clouds. Therefore, any cloud statistic should differentiate between these two cases. Hydrogen peroxide appears to be an important oxidizing agent for summer clouds. At Whiteface Mountain there is most of the time sufficient hydrogen peroxide dissolved in cloud water to oxidize sulfur dioxide. The data presented here demonstrate the complexity of cloud chemistry and the difficulties one faces in interpreting and understanding the measurements made at a single mountain top.

6. Acknowledgements

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