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# Monitoring the chemical climate of the Mt. Mitchell State Park for evaluation of its impact on forest decline

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ABSTRACT

During the last decade, a new type of forest decline has become increasingly apparent, especially at high elevations, in north America and western Europe. One of the causes for this decline could be anthropogenic air pollutants, the deposition of which is facilitated by natural causes at high elevations such as strong windfield, direct cloud capture by the forest canopy, high frequency of frosting and riming etc. At Mt. Mitchell, North Carolina (35°44′05″N, 82°17′15″W) which is the highest peak (2,038 m MSL) in the eastern United States, the decline of red spruce and Fraser fir forest is noticeable above the cloud-base which is frequently observed around 1585 m MSL. In order to quantitatively assess the chemical climate of Mt. Mitchell State Park, we erected a 16.5 m tall aluminium walk-up tower and instrumented it with an electronic weather station, cloud water collectors and ozone analyzers. Our observations during summer 1986 confirm that Mt. Mitchell has a high frequency of being immersed in clouds. During early morning hours, cloudiness is maximum in frequency and results in short duration cloud events ranging from 2–8 h. Although the average pH of precipitation was about 4.4, the pH of cloud water ranged between 2.2–5.4. Short-duration cloud events (8 h or less) were more acidic, in general, than the long duration ones during which the cloud water was most acidic at the onset and dissipative stages. Both types of event were characterized by highly variable liquid water content (LWC) which was lower for the short events. The pH of the cloud water was demonstrated to be a function of wind direction at the site. For the average wind direction of 210°, the pH was 3.4. During early summer episodes, neutralization of the acidic anions ($SO_4^=$ and $NO_3^-$) was not as effective as in the later summer episodes. During all cloud episodes, ozone concentration registered a dramatic decrease. The average minimum ozone concentration of about 63 ppb during the whole summer of 1986 was above the background level (50 ppb) in the United States. Diurnal ozone variation revealed a nocturnal maximum of about 75 ppb after sunset. This is contrary to conventional midday maximum in ozone concentration reported in the literature. Episodic excursions in ozone concentration equal to or exceeding 100 ppb level were found on 5 occasions. The maximum cloud water deposition rate, which is estimated using a micrometeorological model, is found to be 1.30 mm $h^{-1}$. Ionic deposition on the forest canopy is found to be similar to that reported for the Mt. Moosilauke (New Hampshire) forest. Ionic deposition due to direct cloud capture is found to be 2 to 5 times the deposition due to precipitation, and the evaporation associated with wind speeds as high as 15–18 m $s^{-1}$ realized during some episodes is pointed out to be of great significance regarding the canopy exposure.

## 1. Introduction

First noticed in West Germany and named as "Waldsterben", and later referred to as "Waldschaden", it has now been accepted that a new trend in the decline (e.g., Blank, 1985) and dieback of forest is becoming increasingly apparent in western Europe and on the North American continent. Although the extent of this new forest damage is debatable (Moses et al., 1987), there is every reason to suspect that such symptoms are wide-spread at high elevations

(NAPAP, 1987). The decline is easily discernible at high elevations in the eastern United States and Canada, particularly in forests that directly intercept clouds (e.g. Saxena, 1987; Saxena and Stogner, 1987) thereby accumulating pollutants/nutrients via capture of highly concentrated solution droplets of forming and dissipating clouds and fogs. In Mount Mitchell State Park of North Carolina, the red spruce and Fraser fir forest has registered decline beginning 1980, the severity of decline being undisputedly noticeable above frequently observed cloud-base at 1585 m MSL. High elevation forests are also exposed to natural climatological stresses, such as a strong windfield which induces evaporation (Unsworth, 1984) of deposited cloud droplets on the forest canopy, consequently exposing the canopy to even higher transient concentrations of air pollutants. McLaughlin (1985) has recently discussed the impact of air pollutants on forests.

Before asserting the cause-and-effect relationships between the rate of the new forest decline and deposition of chemical species, it is imperative that a quantitative assessment of the fluxes of chemical species to the forest canopy be undertaken. Obviously, those meteorological events which are significant in this respect and those chemical species which have greater depositional fluxes, when averaged over a number of years during variable weather patterns, may provide a clue to the air pollutant or pollutants which are crucial in triggering the decline process. Logically, the timing of the occurrence of high depositional episodes may prove to be of importance because the dosages of little significance to already matured and established trees may be consequential to the survival of new forest growth.

In above cloud-base forests, pollutant/nutrient aerosols and gaseous species that are incorporated in clouds and fogs, are deposited on the forest canopy through impaction and sedimentation which are basically dry deposition mechanisms (Saxena, 1987) and are driven by increased inertia of cloud droplets and turbulent transport associated with highly organized windfields. Resulting hydrologic flux to the canopy—sometimes referred to as occult precipitation—could considerably exceed that deposited by incident precipitation (Lovett et al., 1982; Lovett and Reiners, 1983, 1986; Saxena and Stogner, 1987). Several studies during the last three decades (Yosida, 1953; Oberlander, 1956; Nagel, 1956; Ekern, 1964; Vogelmann et al., 1968; Vogelmann, 1973; Azevedo and Morgan, 1974; Schlesinger and Reiners, 1974; Waldman et al., 1985), carried out at various high elevation sites, amply stress the importance of water deposition by horizontal interception. The pH of cloud or fog water has been found (Houghton, 1955; Mrose, 1966; Okita, 1968; Falconer and Falconer, 1980; Lovett et al., 1982; Waldman et al., 1982; Scott, 1978; Hegg and Hobbs, 1981, 1982; Parungo et al., 1982; Richards et al., 1983; Daum et al., 1984) to be substantially lower than the pH of carbon dioxide equilibrated water. Even the rain water at cloud base has been found (Lazrus et al., 1983) to be considerably acidic. Cloud water pH is not only dependent upon the contents of the cloud forming air but also upon the scavenging and sulfate production mechanisms (Hegg and Hobbs, 1981, 1982; Saxena and Hendler, 1983) within the clouds. Consequences of exposure of sensitive plant tissue to aqueous acids have been studied in the field and laboratory (see, for example, Tukey, 1970; Evans, 1982). Such studies reveal injury and growth retardation for several plant and tree species during exposure (Wood and Bormann, 1974; Haines et al., 1980; Scherbatskoy and Klein, 1983) to water with pH in the range of 2 to 3. The mechanisms which bring about damaging effects are controversial in plants as well as humans (Avol et al., 1988).

Forest decline could also be initiated by exposure to higher concentrations of ozone alone. Ozone concentrations between 100 and 200 ppb have been known to cause damage (e.g. NAPAP, 1987; Schüt, 1985; Haggestad and Bennett, 1984). Seedlings exposed to ozone concentrations greater than 70 ppb, on the average, for relatively long periods have been shown (Peterson et al., 1987; Shafer et al., 1987; Reich and Amundson, 1985) to cause reduced growth. Peterson et al. (1987) have demonstrated that younger trees, when exposed to high ozone concentrations, had no significant decrease in growth, but possibly reduced vigor, while older trees suffered from significant growth retardation. Concentrations of ozone, hydrogen peroxide, and formaldehyde are important parameters in a recently proposed cloud model (Walcek and Taylor, 1986) which

develops a method for determining the vertical distributions of cloud water acidity.

Beginning in May, 1985, we have equipped a mountaintop station in a North Carolina state park surrounding Mount Mitchell (35°44′05″N, 82°17′15″W) which is the highest peak (2,038 m MSL) in the eastern United States. During summer of 1986, the station started monitoring the relevant chemical and meteorological parameters. Ozone concentrations were continuously measured and hourly cloud water samples were collected during 46 cloud episodes for pH measurements and chemical composition analyses using ion exchange chromatography. We used a micrometeorological model proposed by Lovett (1984) to estimate deposition fluxes of cations and anions on the forest canopy. Climatologically, summer 1986 was on record as being the worst drought period within the last 100 years in the southeastern United States but cloud episodes occurred frequently at Mt. Mitchell. In this paper, we report the frequency of cloud occurrence, ozone concentrations and associated diurnal pattern, measurements of cloud water pH and its ionic content along with our estimation of deposition fluxes for six cations: $H^+$, $NN_4^+$, $Na^+$, $K^+$, $CA^{++}$, $Mg^{++}$, and three anions: $NO_3^-$, $SO_4^=$, $Cl^-$.

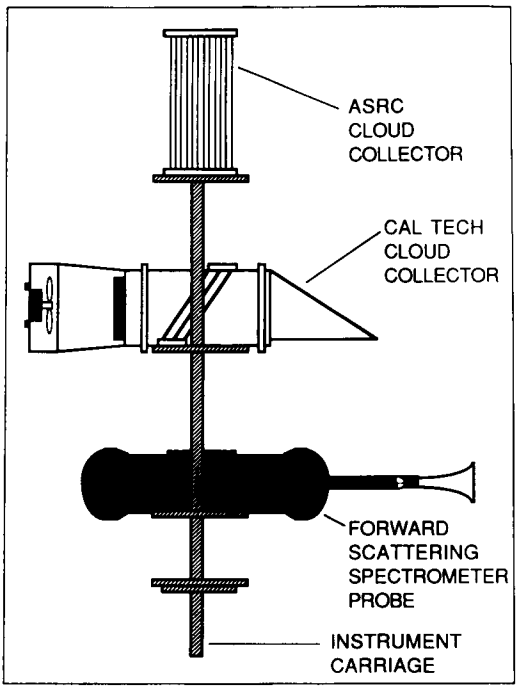


*Fig. 1.* Instruments mounted on the Tower Carriage which can traverse along the 16.5 m tall tower located at 2,006 m MSL in the Mount Mitchell State Park, North Carolina.

## 2. Experimental site and instrumentation

Under a national program entitled, "Mountain Cloud Chemistry/Forest Exposure Study" (MCCP) launched by the US Environmental Protection Agency (EPA), 6 sites are monitoring chemical and meteorological variables in eastern United States. Mount Mitchell is the southern most site of this network. The other sites are: Howland (Maine), Mount Moosilauke (New Hampshire), Whiteface Mountain (New York), Whitetop Mountain (Virginia), and Shenandoah (Virginia). The Mt. Mitchell State Park has red spruce and Fraser fir trees. Our 16.5 m tall meteorological tower is installed at the Gibbs peak (elevation: 2006 m MSL) in the park. The aluminium walk-up tower was equipped with an electronic weather station capable of measuring temperature, relative humidity, wind speed and direction, solar radiation, ambient pressure, and a precipitation sampler at the tower-top. The meteorological sensors were placed at least 10 m above the forest canopy which mostly consists of 6–7 m tall Fraser fir stands. No source of anthropogenic emissions were located in the vicinity of the tower.

Additionally, the tower was equipped with a raisable, rotatable, instrument carriage, on its North side. This carriage, shown in Fig. 1, was used to mount two cloud water collectors: one passive (Kadlecek et al., 1983, referred to as ASRC collector hereafter) and one active (Jacob et al., 1985, abbreviated as Caltech collector), as well as a Forward Scattering Spectrometer Probe (FSSP). The cloud water collectors were used to collect hourly samples of cloud water for the determination of the chemical composition of clouds using conventional ion chromatography. Samples were tested for acidity on site, immediately upon retrieval, by use of an ion specific electrode and then stored under refrigeration for subsequent chemical analysis. The FSSP allowed determination of the droplet size distribution of

the clouds by sizing photoelectronically. Data from the probe has been used (Saxena and Stogner, 1987) to estimate the deposition fluxes. An excellent description of the probe and its operation is given by Dye and Baumgardner (1984). An ozone analyzer manufactured by Thermo-Electron corporation (TECO) was also added to the site and data obtained from this instrument are reported below. The FSSP and the TECO analyzer were factory-calibrated before the beginning of the field season, and their calibrations were frequently checked during the field study.

## 3. Results and discussion

The cloud climatology of the Mt. Mitchell State Park shows that the peak is exposed to cloud episodes 258 days per year, on the average. Under such environmental conditions, the mountaintop trees have a potential to accumulate considerable acidic substances due to direct cloud capture (Lovett, 1984; Lovett et al., 1982).

### *3.1. Occurrence and persistence of clouds, and collection of cloud water samples*

Three types of cloudy airmasses pass by the tower, namely; frontal clouds (cumulus, stratocumulus), orographic clouds (mainly stratus), and fogs mainly induced by radiative cooling of the surrounding topography. When the fog is lifted along the mountain slope during early morning hours, it produces fractostratus clouds at the site. During June–August, 1986, orographic clouds and radiation fogs were more common than the frontal clouds.

The following features were observed during June–August 1986.

- The cloud events, which were of short duration (2–8 h) had a high frequency of occurrence during the early morning hours.
- The cloud events of longer duration that were associated with a frontal passage and upper level disturbance, had relatively low frequency of occurrence. This could be the result of the prevailing drought and remains to be verified during future summers with climatologically normal precipitation.

In Fig. 2, diurnal periodicity of cloud cover at the tower is shown. It is noteworthy that clouds

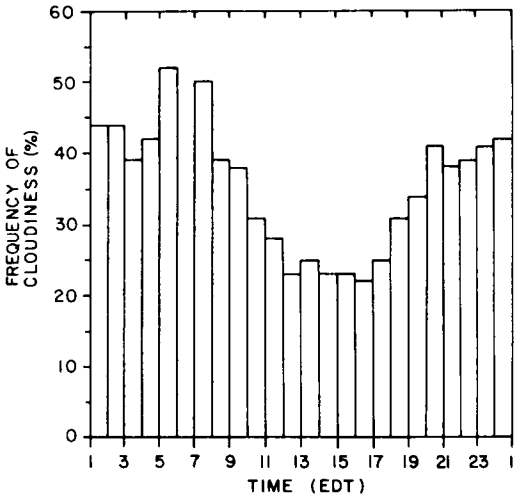


*Fig. 2.* Frequency of cloudiness (in percent) as a function of eastern standard time (EST) on a diurnal basis is shown for June–August 1986.

were most prevalent nocturnally and least prevalent during the afternoon hours. Cloud and fog episodes during early morning hours were particularly helped by radiative cooling as the temperature was observed to decrease until saturation was reached. Between 18:00 EDT and midnight, clouds occurred on 31 to 42% of the days; from midnight to 10:00 EDT, clouds occurred on 38 to 52% of the days; and between 10:00 and 18:00 EDT, clouds occurred on only 22 to 31% of the days. The highest frequency of cloud events was between 05:00 and 07:00 EDT in the morning. During these hours, clouds were present on about 50% of the days. Particularly noteworthy are the features that 58% of the cloud episodes had durations shorter than eight hours and that the prevailing wind direction at the site was westerly.

In interpreting the significance of these observations, it should be noted that: (1) the southeastern United States sustained the longest period of continuous drought in about 100 years during the summer of 1986; and (2) at a location called Commissary Ridge and located 266 m below the Mt. Gibbs tower, clouds occurred at any time of the day or night on less than 5% of these same days in June, July, and August, 1986. For the purpose of estimating deposition fluxes, we have classified cloud episodes into two categories: namely, short duration (lasting less than 1/3 day)

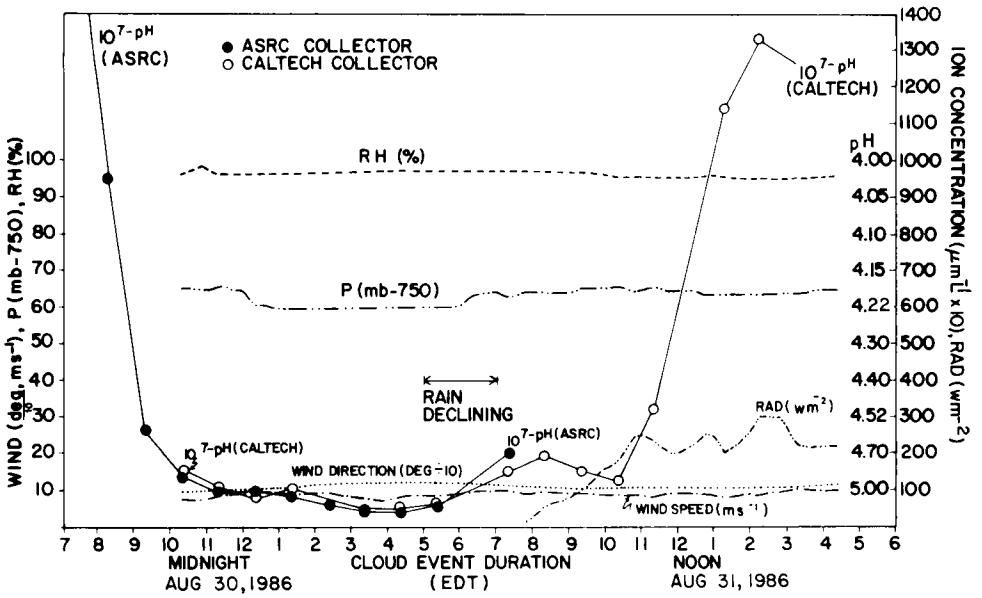


*Fig. 3.* Ion concentration, radiation (units on the right hand side ordinate), wind direction and speeds, relative humidity, and barometric pressure (units on the left, side ordinate) are shown plotted as a function of eastern daylight savings time (EDT) for the cloud event of 30–31 August 1986. The event was associated with a frontal passage.

and long duration episodes (lasting more than 1/3 day). Cloud water was sampled hourly for a total of 360 h.

### *3.2. Case studies of cloud episodes: pH trends*

During each cloud episode, meteorological parameters namely, temperature, pressure, relative humidity, solar radiation (direct plus diffuse), and wind speed and direction were continuously monitored. Using ASRC passive and Caltech active collectors, cloud water samples were collected hourly atop the tower. The collectors were located more than 7.6 m above the surrounding forest canopy. Hourly averages of meteorological parameters are shown plotted for two representative long episodes in Figs. 3 and 4, and one short episode in Fig. 5. An analysis of these representative plots and our observational record shows that:

- The pH value and the volume of the cloud water collected by the passive as well as active collectors agree within experimental error (~5%).
- The minimum pH = 2.20 was recorded during a sort cloud event on the morning of 26 July 1986.
- During long cloud episodes, the pH of the cloud water was more acidic at the onset (see evening hours of 30 August and 10 September 1986, in Figs. 3 and 4) and dissipative (afternoon of 31 August and evening of 11 September 1986) stages of clouds than that during the middle of the event. One possible explanation of such occurrence lies in the fact that during cloud formation on the site, diffusional condensation, being the primary growth mechanism for cloud droplets, produces smaller but concentrated solution droplets (Saxena and Fisher, 1984). During the dissipative stages, mixing with the surrounding dry air causes evaporation of cloud droplets thus producing concentrated solution droplets once again.
- The short cloud episode (Fig. 5) was characterized by more acidic cloud water than the long ones. A shift in the wind direction at 08:00 EDT in the morning of 9 September 1986 was accompanied by further reduction in the pH value. The cloud water collected during the middle of the event did not show any trend of decreasing acidity as was the case during long episodes.
- Solar radiation plotted in Figs. 3 and 4

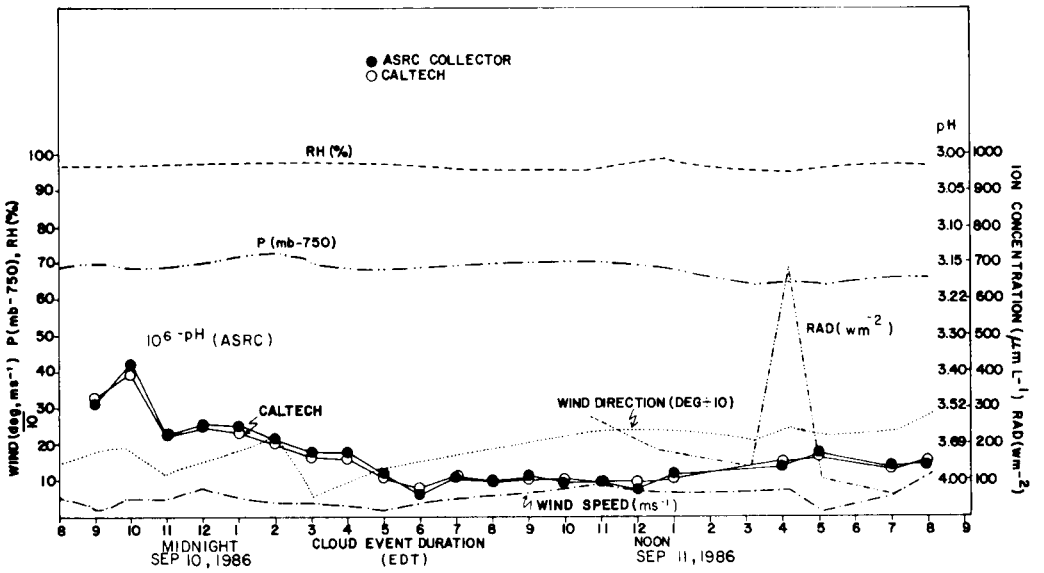


*Fig. 4.* The legend is the same as in Fig. 3 except the cloud event continued from 10–11 September 1986. The peak in radiation at 04:00 p.m. EDT is caused by the patchiness of clouds during dissipating stages.

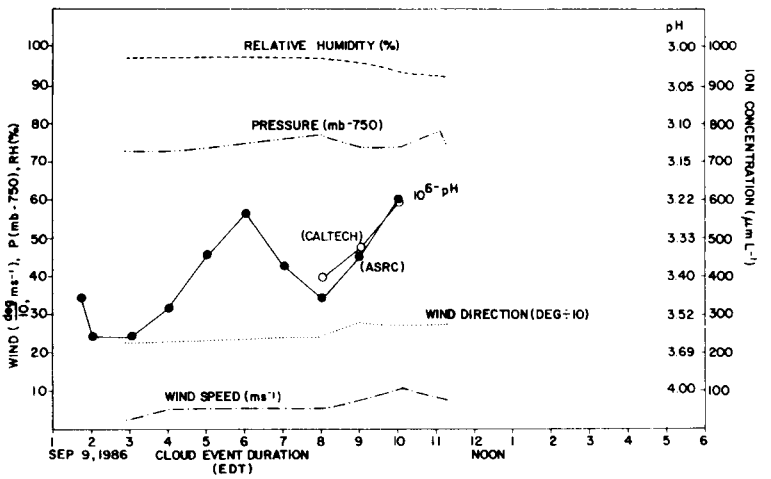


*Fig. 5.* The legend is the same as in Fig. 3 except the cloud event is a short one associated with orographic lifting and it occurred on 9 September 1986.

showed a dramatic increase during the cloud dissipative stages thus signaling the clear skies overhead. Changes in solar radiation during the short episode of 9 September 1986, were rather small and did not warrant graphical presentation.

The agreement between the ASRC passive and Caltech active collectors regarding the cloud water pH is also confirmed recently in a field study (Hering et al., 1987) of 5 types of fogwater collectors deployed at Henninger Flats, a mountain site at 777 m MSL overlooking the Los Angeles basin.

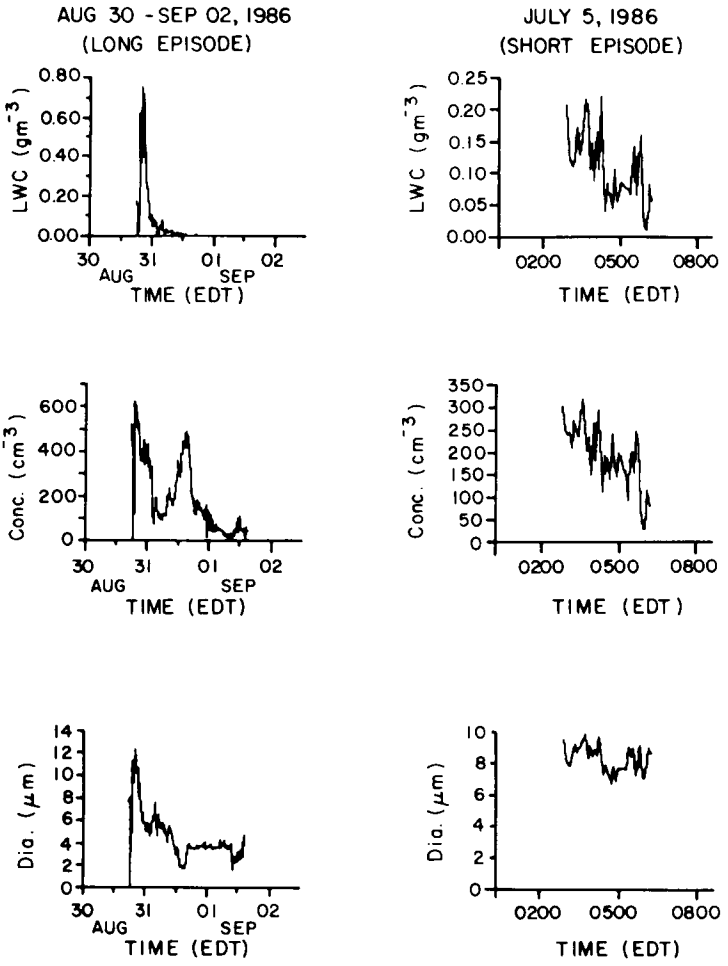


*Fig. 6.* Microphysical parameters measured at the experimental site. Values shown are based on 5-min averages of one second data recorded by Forward Scattering Spectrometer Probe (FSSP).

### *3.3. Cloud microstructure: long versus short episodes*

In Fig. 6, cloud droplet concentration, size, and liquid water content are shown plotted for the short episode of 5 July and the long episode of 30 August 1986 based on the FSSP data. The following is perceived as a result of the analysis of these observations:

- Variation in the cloud droplet sizes for the 5 July event is smaller than for the 30 August event.
- Total droplet concentration is lower for the 5 July event in comparison to the 30 August event indicating more continental microstructure of the latter clouds. This is exactly what was expected based on prevailing windfields (5 July: southwesterly and light winds; 30 August: southeasterly and moderate winds). Initial droplet size distribution evolves as a result of interactions between cloud dynamics and nucleating characteristics of the aerosol content of the cloud forming air.
- Liquid water content (LWC) is highly variable beginning from the onset of both the cloud events.

It is well understood (e.g., Lovett et al., 1982) that cloud droplet size distribution and liquid water content are two significant parameters in

estimating the wet deposition of atmospheric pollutants on the forest canopy resulting from direct capture of droplets. Exchange of cloud droplets and water vapor between the canopy and the atmosphere encompasses two aerodynamic regimes. The first regime is the crown space of the canopy, where air is mixed by turbulent eddies. The second aerodynamic regime encompasses the boundary layers surrounding the individual canopy surfaces where water vapor moves primarily by molecular diffusion and cloud droplets penetrate by inertial impaction. For example, in the windy environment usually encountered at Mt. Mitchell, sedimentation may account for less than five percent of the total amount of cloud water delivered. Our FSSP data shows that:

- Clouds and fogs are highly inhomogeneous and consequently continuous monitoring of liquid water content is desirable.
- Droplet size distribution should be monitored in addition to LWC in order to arrive at reasonable estimates of wet deposition due to direct cloud/fog interception.

### 3.4. *Windfield and pH dependence*

The station wind speeds and directions were continuously monitored for all of the cloud events. Clouds are most frequently associated with northwesterly and southeasterly winds. In Fig. 7, cloud water pH is plotted as a function of wind direction. Number of hourly cloud water samples are shown in parenthesis for each wind direction. The minimum pH value of the samples is shown by broken circle. For the average wind direction of 210°, the minimum cloud water pH is about 3.0. Our records show that this wind direction is not very frequent. For easterly (90°) winds, average cloud water pH is about 4.5. Considering the site location and topography, it becomes evident that involvement of marine air in the cloud forming process produces less acidic clouds. Directional dependence of cloud water pH suggests that back trajectory analysis for the air parcel giving rise to cloud episodes would yield revealing information about source (of acidic pollutants)—receptor (mountaintop forest) relationships based on models of terrain-induced mesoscale systems (e.g., see Pielke, 1984). It is found that speeds associated with 90° and 210° winds do not exceed 10 m $s^{-1}$ and are consequently moderate in comparison to speeds associated with 300° winds. Cloud episodes do frequently occur in association with 300° winds when the speed ranges from 5–19 m $s^{-1}$. Let it be pointed out that at speeds exceeding 15 m $s^{-1}$, manual collection of cloud water atop the tower poses occupational hazard. This was clearly realized at our site when such winds during the 1987 winter took place and caused heavy riming of the tower and its subsequent collapse under its own weight. The site becomes frequently inaccessible during winter months as the public thoroughfares are closed. However, the above cloud-base forests are subjected to pollutant/nutrient deposition fluxes during wintertime also in addition to climatological stresses. Characterization of such episodes is currently a significant challenge in the logistics of our site.

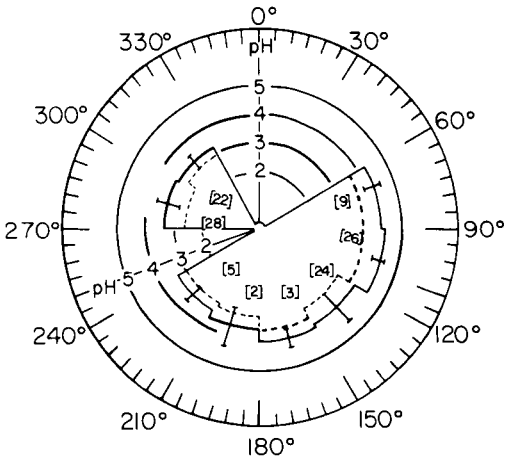


*Fig. 7.* Dependence of cloud water pH on the prevailing wind direction. Numbers in parenthesis represent number of hourly cloud water samples considered in averaging the pH. Broken circle represents the minimum pH values, error bars on the average pH are also shown.

### 3.5. *Neutralization of cloud water acidity*

The ratio of $[H^+]/[NO_3^- + SO_4^=]$ shown plotted in Fig. 8 is an indicator of the degree to which ambient acids are neutralized in the atmosphere following their formation. For comparison, the ratio for Los Angeles stratus cloud water was found (Waldman et al., 1985) to be 0.5 which indicates that in such cloud water about half of the acidic anions are not neutralized. As can be

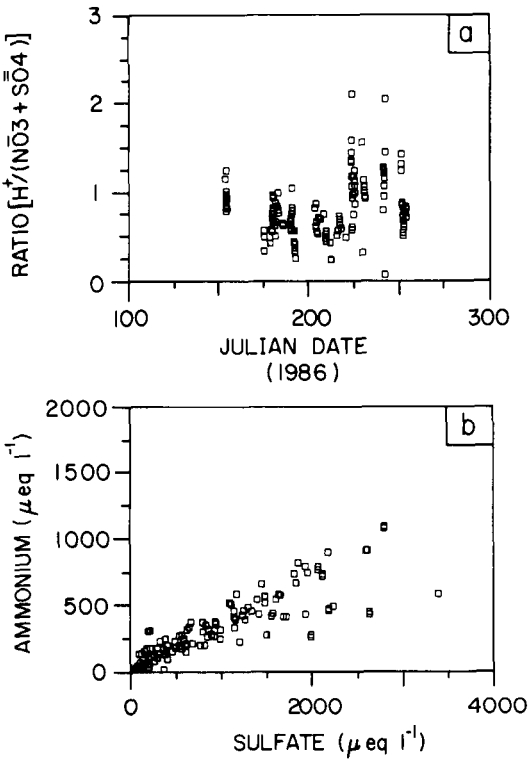


*Fig. 8.* (a) Plot of ratio $[H^+]/(NO_3^- + SO_4^=]$ as a function of Julian date showing the extent of neutralization of acidic anions. The concentrations of ions are in $\mu$ eq $l^{-1}$. (b) Plot of ammonium vs sulfate ion concentration indicating the excess of a major acidic anion in the cloud water.

seen in Fig. 8, for clouds at our site, the ratio did often assume a value of 0.5 and even less. It is also evident that the ratio is highly dependent upon the processes leading to cloud formation and shows a trend towards higher values thus pointing out better acidic neutralization toward the end of the summer (Julian date: 225–250, corresponding to late August and early September). Since model computations demonstrate (Jacob and Hoffmann, 1983) that gaseous ammonia should be completely scavenged by acidic cloud droplets, the plot of ammonium vs sulfate in Fig. 8 clearly indicates that not enough ammonia is present in the cloud forming airmasses to neutralize high acidic anion concentrations. Jacob et al. (1984) have investigated sites with very high ammonia emissions and found that fogwater with similarly high acidic anion concentrations was largely neutralized.

Model computations have also demonstrated (Walcek and Taylor, 1986) that ozone concentrations play a crucial role in determining the cloud water acidity as ozone is highly soluble in water and aqueous conversion of $SO_2$ and $NO_x$ is helped by ozone considerably. As in seen in Fig. 9, ozone concentration at our site showed dramatic decrease during cloudy events. Toward the end of the summer, 1986 when the drought period was ending, ozone concentrations, in general, receded to background levels.

### *3.6. Diurnal pattern and peak ozone concentrations*

Heggestad and Bennett (1984) have pointed out that background $O_3$ concentrations at the earth's surface are in the range of 20–30 ppb. In the NAPAP (1987) report, background ozone concentrations are inferred to be $50 \pm 10$ ppb.

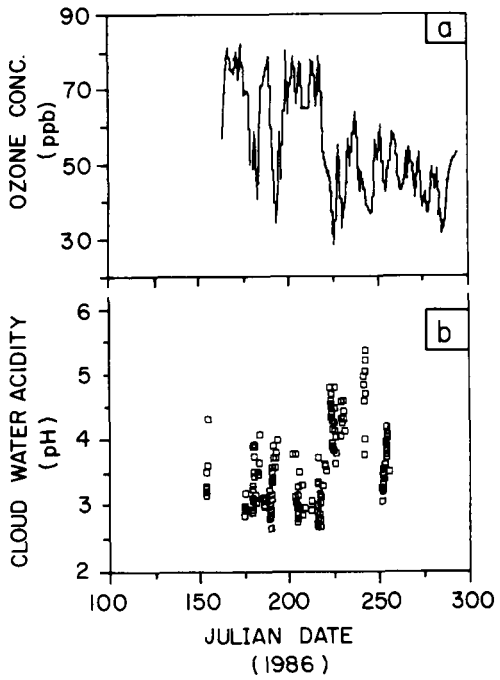


*Fig. 9.* (a) Plot of ozone concentration (in ppb) monitored above the forest canopy as a function of Julian date showing substantial decrease during cloudy days. (b) Cloud water pH plotted as a function of Julian date showing a trend toward higher pH at the end of summer, 1986, when long duration cloud episodes were frequently realized and severity of the drought was on the decline.

Ozone concentrations higher than 50 ppb have been demonstrated (e.g., see NAPAP, 1987) to cause decreased growth of seedlings in controlled experiments. In field studies, however, such concentrations are not found to cause any growth retardation. In San Bernardino Mountains, where peak ozone concentrations exceed 200 ppb for 10 to 20 days per growing season, tree vigor is reported (NAPAP, 1987) to be significantly reduced. This may eventually cause tree mortality from secondary causes.

It is pointed out by Heggestad and Bennett (1984) that meterological parameters accompanying the high ozone days in eastern United States may be summarized as having:

- ambient temperatures in the range 25–35°C
- high intensities of solar radiation
- low relative humidities and the absence of precipitation
- low or moderate wind speeds in the range 0–4 m $s^{-1}$.

They also suggested that ozone concentrations show a maximum during summer months on an annual basis and a peak around midday on a diurnal basis. Nocturnally, ozone destruction by dust, reactive hydrocarbons, nitric oxide, and other atmospheric pollutants occurs.

In the light of the above conventional knowledge about ozone, an analysis of the findings for our site (Fig. 10) during summer of 1986 reveal the following information, some of which is contradictory:

- At midday, the average ozone concentration was minimum around 60 ppb.
- The average maximum in ozone concentration was about 75 ppb and occurred after sunset. It was preceded by a peak in the water-vapour mixing ratio thus pointing out that the ozone maximum is caused by mixing mechanisms which cause the transported ozone to approach an altitude of 2006 m MSL.
- The ozone maximum was also preceded by the maximum diurnal temperature which occurred in the afternoon.
- At the maximum ozone concentration, the wind speeds were moderate, usually less than 8 m $s^{-1}$, and wind direction was around 260° indicating, generally, a westerly flow.

The above features suggest that ozone is transported to our site and as the mixing of the air aloft proceeds, the ozone concentrations register

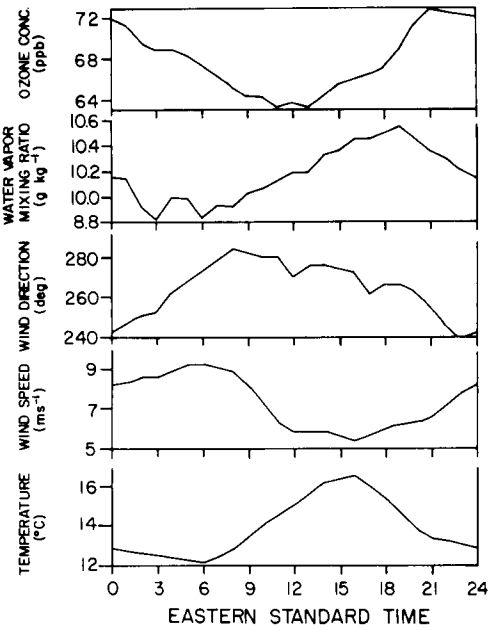


*Fig. 10.* Plots of average values of temperature, wind speed and direction, mixing ratio, and ozone concentration as a function of eastern standard time (EST). The nocturnal maximum in ozone concentration is evident.

a rising trend throughout the afternoon. The nocturnal decoupling of the boundary layer after sunset causes the onset of a decreasing trend. At sunrise, the incident solar radiation starts to lift the inversion and mixing of the ozone deficient air from below causes the midday minimum. There are no anthropogenic ozone sources in the vicinity of our station, but the transport of ozone from urban-industrial areas is a well-documented fact (see, e.g., Cleveland et al., 1976).

Five episodes of ozone concentration equal to or exceeding 100 ppb were detected. On June 14, 1986, ozone concentration peaked at 100 ppb at 2303 EDT and stayed there for 36 minutes. On June 16, 1986, the ozone concentration exceeded 100 ppb at 2200 EDT, peaked to a value of 117 ppb at 2336 EDT and stayed above 100 ppb until 0200 EDT on 17 June 1986. The latter episode lasted for 204 min. A much shorter ozone episode occurred on 9 June 1986, when ozone concentration reached 100 ppb level at 2300 EDT. It is noteworthy that in all these episodes, ozone concentration has registered a maximum around midnight. This demonstrates that at high

elevations, unusual ozone concentrations may prevail and if such phenomena occur during the growing season, consequences may be severe for the health of the forest.

### *3.7. Estimation of deposition flux resulting from direct cloud capture*

As pointed out by Lovett and Reiners (1983), the method used to estimate deposition flux due to direct cloud capture by trees may be classified into three categories. First, surrogate surfaces have been used (Schlesinger and Reiners, 1974, Vogelmann et al., 1968, Scherbatskoy and Bliss, 1983). Second, water balance in the forest canopy can be used if volumetric measurements of stemflow and throughfall are available. Thirdly, micrometeorological models (e.g., Lovett, 1984) could be used if the input parameters such as cloud water gradient and the canopy characteristics are known. The model output is particularly sensitive to wind speed, liquid water content of clouds, and cloud immersion time. In addition to these three methods, deposition flux can also be estimated by analyzing the hydrologic fluxes of the whole watersheds in conjunction with the flow-weighted concentration of a "tracer" element in precipitation, cloud water, and streamwater. In modeling the acidification of lakes, which are catchments for the directly captured cloud water, the importance of the canopy (e.g., Chen et al., 1982, 1983) has been recognized in the Integrated Lake Watershed Acidification Study (ILWAS).

The cloud deposition on the forest canopy is mechanistically more similar to dry deposition although the process is wet. It indeed is a hybrid between wet and dry deposition processes because for in-cloud interception, the main delivery mechanisms are impaction and sedimentation. Both dry and wet deposition result from particle sedimentation, although the dry deposition is frequently dominated by inertial impaction and turbulent diffusion. No direct methods are available to measure the fluxes due to dry and cloud deposition. We have used the one dimensional cloud deposition model (CDM) developed by Lovett (1984) for estimating the chemical input to the forest canopy at Mt. Mitchell. The choice is made based on the fact that during short duration cloud/fog episodes, no measurable stemflow and throughfall are collected and it is unlikely to simulate the forest canopy by surrogate collection surfaces.

The CDM assumes steady state conditions, assuming for example that the wind has sufficient upwind fetch to reach equilibrium before encountering the canopy. The canopy is divided into layers one meter in height. Deposition of cloud droplets is modeled using an analogy to Ohm's law for direct currents, namely V = IR. The flux of cloud water for each layer, $I_i$, is computed as the ratio of the potential difference for that layer, $V_i$, (concentration of cloud droplets in this case) and the turbulent resistance, $R_i$. The turbulent resistance is calculated from the turbulent diffusivity for cloud droplets $K_d$ and using similarity theory, it is given by

$$K_d = K_m = ku_*(z-d) \tag{1}$$

where $K_m$ is the diffusivity of momentum, $k$ is von Karman's constant (0.41), $u_*$ is the friction velocity, $d$ is the zero plane displacement and $z$ is the height within the canopy. Equation (1) assumes neutral conditions within the canopy and that the diffusivity of momentum is equal to that of cloud droplets. The friction velocity, $u_*$, may be calculated from the well known logwind equation

$$u(z) = (u_*/k)\ln\{(z-d)/z_o\}, \tag{2}$$

where $z_o$ is the roughness length. Lovett (1984) found $z_o$ and $d$ to be 0.911, 7.885 m, respectively. He assumed an exponential decrease of momentum and hence of $K_d$, within the canopy of the form:

$$K_d(z) = K_d(h)\exp(a_k CSA I_z) \tag{3}$$

where $h$ is the height at the canopy top, $CSA I_z$ is the cumulative surface area index at height $z$ and $a_k$ is a parameter assumed to be $-0.14$. From these equations, $R_i$, can be calculated as

$$R_i = 0.5(dz_i/K_{di} + dz_{i-1}/K_{di-1}), \tag{4}$$

$V_i$ may subsequently be calculated assuming a droplet size distribution (e.g., of the form given by Best, 1951) or preferably determined from the FSSP measurements.

Capture efficiency (CE) of cloud droplets by the canopy was modeled empirically and found to be of the form (Thorne et al., 1982),

$$CE = \exp[-1.84 + 0.90(\ln S_t) - 0.11(\ln S_t)^2 - 0.04(\ln S_t)^3], \tag{5}$$

where $S_t$ is the well-known Stokes number, a non-dimensional inertial parameter. The canopy components have been assumed perfect sinks for cloud water.

The model accepts as input four meteorological parameters and two microphysical parameters, namely; temperature, wind speed, solar radiation, relative humidity, liquid water content (LWC) and droplet mode size. All parameters were readily available from data recorded by the electronic weather station at our site and by the FSSP.

Our tests, based on cloud water samples collected with the ASRC collector, during 37 h, showed that for wind speeds ($u$) greater than 2.0 m s$^{-1}$, the liquid water content (LWC) of clouds (g m$^{-3}$) is empirically related to the volume ($V$ in ml) of the collected cloud water during the time period (d$t$ in minutes) of collection:

$$\mathrm{LWC} = m\left(\frac{V}{u\ \mathrm{d}t\ 60}\right) + b. \qquad (6)$$

We determined:

$m = 18.74 \pm 1.16$ m$^{-2}$,

$b = 0.027 \pm 0.015$ g m$^{-3}$.

In eq. (6), a factor of 60 appears in the denominator because $dt$ is expressed in min while $u$ is in m s$^{-1}$. Eq. (6) was found to estimate LWC within 20% of the average value directly determined with the help of a filter assembly technique provided by the Tennessee Valley Authority. In Table 1 are shown the estimated values of LWC based on eq. (6). For the sake of brevity, only three points are tabulated. These values are compared with those obtained by integrating the cloud droplet size distribution as recorded by FSSP. Evidently, an extremely good agreement exists. We have therefore used eq. (6) to estimate LWC in the CDM for estimating the cloud deposition flux.

Table 1. *Comparison between liquid water content (LWC) of a cloud episode, observed from integration of forward scattering spectrometer probe (FSSP) data (in g m$^{-3}$) and computed using an empirical formula (Eq. 6) based on the collected volume of cloud water*

| Period (EDT) | FSSP observed | Eq. (6) estimated | Difference |
|---|---|---|---|
| 0410–0510 | 0·150 | 0·159 | 6.0% |
| 0510–0610 | 0·092 | 0·095 | 3.3% |
| 0610–0710 | 0·082 | 0·076 | 7.3% |

We have analyzed 87 h of cloud episode observations in order to estimate deposition to Mt. Mitchell area forests. The average duration of short episodes was 3.6 h, while long episodes averaged 16.23 h. For running the model, we selected observations covering the period from 24 June through 18 August 1986. During this period, 7 long and 16 short cloud episodes were observed, their average span being 13.13 h and 3.65 h, respectively.

Wind speeds were measured at the tower-top (16.5 m above ground level) while the CDM requires as input the wind speed at the top of the tallest tree (about 10 m) and consequently the model input parameter was estimated. Runs were made with observed winds, since this represents an upper bound on the cloud deposition. Runs were also made using estimated winds for the 10 m level using the logwind equation.

$$u(10) = u(16.5)[\ln(10 - d)/z_0)/\ln((16.5 - d)/z_0)]. \qquad (7)$$

The values of $d$ and $z_0$ were taken as the same as reported by Lovett (1984).

We have performed 174 runs of CDM. The input parameters, and cloud water deposition rates are summarized in Table 2. Rate of cloud water deposition is plotted as a function of liquid water content and wind speed in Fig. 11 for short cloud episodes, and in Fig. 12 for long cloud episodes. These figures indicate that estimated cloud deposition is well correlated with the liquid water content of clouds. Such a correlation is not evident with wind speed, indicating that cloud deposition is most sensitive to liquid water content and cloud droplet size. There is, however, a slight hint that the maximum deposition occurs around 10 m s$^{-1}$.

While these conditions do not represent winter environment at Mt. Mitchell, it is useful to extend the deposition rates on an annual basis. Based upon climatological data, the relative frequency of short to long episodes, and the average length of each type of cloud episode, cloud deposition represents between 35.7 and 76.5 cm yr$^{-1}$ of wet deposition. When combined with the increased acidity of cloud droplets over precipitation, this represents an even larger wet

Table 2. *Statistical summary of cloud deposition model runs for Summer 1986 cloud episodes*

| Parameter | Mean | | Maximum | | Minimum | |
|---|---|---|---|---|---|---|
| | short | long | short | long | short | long |
| liquid water content (g $m^{-3}$) | 0.16 | 0.22 | 0.33 | 0.51 | 0.05 | 0.04 |
| temperature (°C) | 12.64 | 13.67 | 15.62 | 16.09 | 10.13 | 11.95 |
| pressure (mb) | 810.30 | 811.40 | 822.00 | 821.00 | 801.00 | 806.00 |
| wind speed at 10 m (m $s^{-1}$) | 3.34 | 3.57 | 6.53 | 5.86 | 0.97 | 1.15 |
| wind speed at 16 m (m $s^{-1}$) | 8.67 | 9.27 | 16.95 | 15.21 | 2.51 | 2.99 |
| deposition rate at 10 m (mm $h^{-1}$) | 0.14 | 0.27 | 0.51 | 0.79 | 0.004 | 0.01 |
| deposition rate at 16 m (mm $h^{-1}$) | 0.36 | 0.53 | 0.90 | 1.30 | 0.011 | 0.05 |

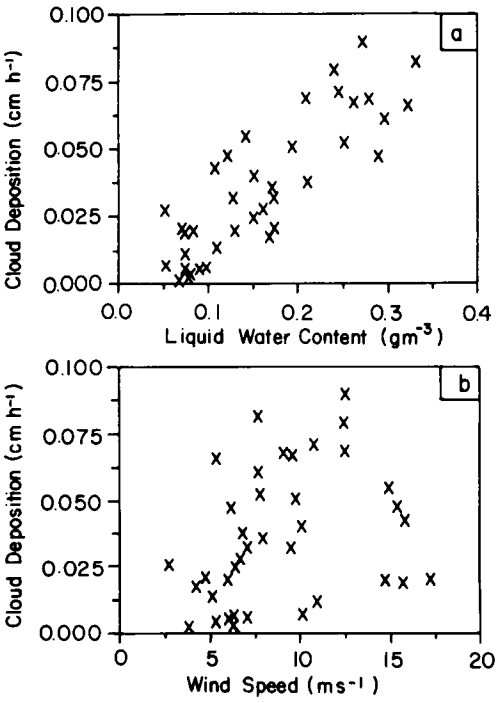


*Fig. 11.* Cloud water deposition from short duration cloud episodes (less than 8 h) using observed winds (a) deposition versus liquid water content (lwc). (b) deposition versus observed windspeed.

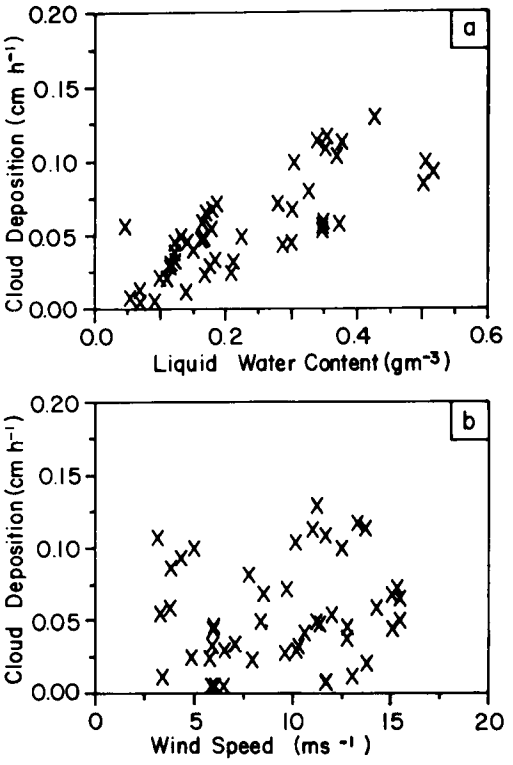


*Fig. 12.* The legend is the same as in Fig. 17, except that the cloud deposition is from long duration cloud episodes.

deposition contribution to Mt. Mitchell area forests. A statistical summary of the episodes used is given in Table 3. The table indicates that short episodes are slightly more acidic than their longer synoptic counterparts. Both types of episodes, however, are considerably more acidic than precipitation in the Mt. Mitchell area, the pH of which is only around 4.4. The latter, is most probably less acidic because dilution processes contribute to the development of precipitation-size particles. Thus, clouds are nearly ten times as acidic as precipitation in the Mt. Mitchell area. The acidity experienced by leaf

Table 3. *Chemical analysis of cloud samples used in deposition analysis, all concentrations are sample weighted and in mg $l^{-1}$ unless otherwise noted*

| Species | Short episodes | Long episodes |
|---|---|---|
| pH* | 3.34 | 3.41 |
| pH | 3.27 | 3.41 |
| $NH_4^+$ | 7.33 | 4.63 |
| $Na^+$ | 0.57 | 0.51 |
| $K^+$ | 0.36 | 0.18 |
| $Ca^{+2}$ | 2.32 | 1.07 |
| $Mg^{+2}$ | 0.38 | 0.18 |
| $Cl^-$ | 1.36 | 1.11 |
| $NO_3^-$ | 22.15 | 13.15 |
| $SO_4^{-2}$ | 51.54 | 41.22 |

* Volume weighted.

surfaces may even be higher still, once evaporation is considered (Unsworth, 1984).

Combining the results of chemical analysis with those of model runs, one can calculate ionic deposition to Mt. Mitchell area forests. The mean hourly ionic deposition rates for the events studied are presented in Table 4. The table shows that although long episodes deposit more water, due to their higher relative liquid water content and wind speed, the ionic deposition for the two types are approximately the same due to the higher acidity of the shorter episodes. Again it is useful to extend the results on an annual basis, assuming these depositions to be typical of average annual values. This extrapolation is done in Table 5, which also displays the values found by Lovett et al. (1982).

Table 4. *Hourly mean ionic deposition rates resulting from direct cloud droplet capture by Mt. Mitchell area forests; all depositions in kg $ha^{-1}$ $h^{-1}$; wind speeds are given above ground level (AGL)*

| | Deposition (for wind speeds at 10 m AGL) | | Deposition (for wind speeds at 16 m AGL) | |
|---|---|---|---|---|
| Ion | short | long | short | long |
| $H^+$ | $0.872 \times 10^{-3}$ | $0.144 \times 10^{-2}$ | $0.221 \times 10^{-2}$ | $0.316 \times 10^{-2}$ |
| $NH_4^+$ | $0.790 \times 10^{-2}$ | $0.931 \times 10^{-2}$ | $0.201 \times 10^{-1}$ | $0.215 \times 10^{-1}$ |
| $Na^+$ | $0.545 \times 10^{-3}$ | $0.784 \times 10^{-3}$ | $0.146 \times 10^{-2}$ | $0.189 \times 10^{-2}$ |
| $K^+$ | $0.336 \times 10^{-3}$ | $0.344 \times 10^{-3}$ | $0.929 \times 10^{-3}$ | $0.782 \times 10^{-3}$ |
| $Ca^{+2}$ | $0.168 \times 10^{-2}$ | $0.197 \times 10^{-2}$ | $0.459 \times 10^{-2}$ | $0.458 \times 10^{-2}$ |
| $Mg^{+2}$ | $0.283 \times 10^{-3}$ | $0.332 \times 10^{-3}$ | $0.763 \times 10^{-3}$ | $0.773 \times 10^{-3}$ |
| $NO_3^-$ | $0.207 \times 10^{-1}$ | $0.256 \times 10^{-1}$ | $0.543 \times 10^{-1}$ | $0.593 \times 10^{-1}$ |
| $SO_4^{-2}$ | $0.542 \times 10^{-1}$ | $0.825 \times 10^{-1}$ | 0.140 | 0.190 |
| $Cl^-$ | $0.143 \times 10^{-2}$ | $0.214 \times 10^{-2}$ | $0.369 \times 10^{-2}$ | $0.492 \times 10^{-2}$ |

Table 5. *Annual ionic deposition rates resulting from direct cloud droplet capture by Mt. Mitchell area forests; all depositions are in kg $ha^{-1}$ $yr^{-1}$*

| Species | Deposition (for wind speeds at 10 m AGL) | Deposition (for wind speeds at 16 m AGL) | Lovett et al. (1982) Mt. Moosilauke (New Hampshire) |
|---|---|---|---|
| $H^+$ | 2.01 | 4.59 | 2.4 |
| $NH_4^+$ | 14.45 | 34.60 | 16.3 |
| $Na^+$ | 1.14 | 2.84 | 5.8 |
| $K^+$ | 0.56 | 1.38 | 3.3 |
| $Ca^{+2}$ | 3.06 | 7.57 | — |
| $Mg^{+2}$ | 0.52 | 1.28 | — |
| $NO_3^-$ | 39.0 | 94.7 | 101.5 |
| $SO_4^{-2}$ | 118.0 | 282.0 | 275.8 |
| $Cl^-$ | 3.07 | 7.31 | — |

Table 5 shows good agreement between values estimated for Mt. Mitchell (North Carolina) and those for Mt. Moosilauke (New Hampshire). The table shows the relative importance of cloud deposition, as a source of wet deposition. For example, wet deposition of $H^+$ from precipitation sources at Mt. Mitchell can be calculated as follows. Mt. Mitchell received 201 cm of rainfall per year, at a average pH of 4.4. This represents only 0.81 kg $ha^{-1}$ $yr^{-1}$ of $H^+$ ion deposition by conventional wet deposition. Table 5, however, indicates that between 2.01 to 4.59 kg $ha^{-1}$ $yr^{-1}$ of $H^+$ ion may be deposited by cloud droplet interception, or 2 to 5 times as much as from precipitation sources. Such mechanisms for wet deposition must be included in areas such as Mt. Mitchell and Mt. Moosilauke if accurate wet deposition amounts are to be obtained. Furthermore, in watersheds that are catchments for cloud water deposition, the latter should be included in modeling their acidification as suggested by Chen et al. (1982, 1983).

## 4. Concluding remarks

Our investigations have resulted, for the first time, in quantitative assessment of the chemical climate to which above cloud-base forests in Mt. Mitchell State Park are subjected. The potential of tree damage due to cloud water acidity and high ozone concentrations was found to be real. Our findings are summarized below. These should not be considered as concrete conclusions because the reported results are based on the 1986 summer data only. To assert the causes of forest decline, a broader data base is obviously needed. Nevertheless, the following remarks will prove useful in furthering the goals of the study.

(1) Mount Mitchell, being the highest peak east of the Mississippi river, experiences unusually high number of cloudy days and the forest has a potential of accumulating considerable deposition of acidic substances due to direct capture of cloud droplets. Ionic deposition may be 2 to 5 times the deposition received due to precipitation.

(2) Frequency of cloudiness exhibits a diurnal pattern and is maximum during early morning hours. Short-term cloud episodes, are frequently observed at Mt. Mitchell. Such episodes usually have low liquid water content but are more acidic than the long episodes associated with upper level disturbances.

(3) Windfield plays an extremely important role in evolving the cloud water acidity and in inducing evaporation, thereby acidifying the residues of cloud droplets on the forest canopy. Generally, low cloud water pH was associated with the westerly flow.

(4) The cloud water pH varies over a wide range. During short episodes, it could be as low as 2.2 and during long episodes, as high as 5.4. The average pH of precipitation is about 4.4. During the onset and dissipation stages of clouds, the pH is usually low.

(5) We used the cloud deposition model (CDM) due to Lovett (1984) and performed 174 model runs for 23 cloud episodes. The cloud episodes, classified by duration of their sustenance, showed no difference in ionic deposition with respect to their duration. Long ($\frac{1}{2}$ day or longer) and short duration episodes were found to have water deposition rates in the range 0–0.90 mm $h^{-1}$ and 0.01–1.30 mm $h^{-1}$ respectively. Ionic deposition rates were demonstrated to be a major contributor to annual deposition caused both by precipitation and direct cloud capture. These rates were of similar magnitude as the ones reported by Lovett et al. (1982) for Mt. Moosilauke (New Hampshire) forest. The CDM is sensitive to liquid water content, cloud droplet size distribution and windfield. These input parameters should be precisely monitored in future work. The CDM is also sensitive to canopy parameters such as leaf surface area index (LSAI), which was not measured in our experiments.

(6) In order to accurately assess the role of cloud immersion on Mt. Mitchell forests, more work is needed to characterize the winter deposition rates. The capture efficiency of the forest canopy drastically changes when snow crystals are involved (e.g. Pruppacher and Klett, 1980).

(7) Episodes of unusually high ozone concentrations (exceeding 100 ppb) were detected at Mt. Mitchell during summer of 1986. The southeastern United States was under the spell of a severe drought during this period. The causes and frequency of occurrence of these high ozone episodes warrant further careful monitoring since

these episodes occurred nocturnally, and this is contrary to conventional knowledge that ozone peaks out around midday.

(8) An agreement between the deposition rates estimated for Mt. Mitchell (North Carolina) and Mt. Moosilauke (New Hampshire) does not guarantee the validity of the micrometeorological method used here. We recommend that there is a dire need for carefully designed experiments in which the cloud deposition model is validated and tested against direct observations of stemflow and throughfall. These experiments should also examine the role of windfield and associated evaporation on the forest canopy. Measurements of canopy parameters such as surface LSAI should also be undertaken.

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