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# Factors governing cloud water composition in the Appalachian mountains

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ABSTRACT

Cloud events collected during the summers of 1986–1988 at 5 sites in the Appalachian Mountains of the eastern USA were classified on the basis of meteorology. The data consisted of cloud water chemical concentrations, liquid water content (LWC), mixed-layer air trajectories, synoptic type from weather maps, and whether or not the cloud was precipitating. An analysis of variance (ANOVA) supported the hypothesis that the meteorological variables describe the cloud water chemical composition ($p < 0.001$); there were differences between precipitating and non-precipitating events (>few hours duration) and among synoptic-trajectory classes. The highest $H^+$, $SO_4^{2-}$, $NH_4^+$ and $NO_3^-$ concentrations occur when a site is in the warm sector of the cyclone or in a cap cloud; lower concentrations occur during easterly (marine) flow or post-cold-frontal cloud events. The difference among classes was similar when cloud LWC was accounted for; this supports the hypothesis that the synoptic-trajectory classes describe differences in the transport and mixing of aerosol and gases rather than LWC differences. The chemical concentrations for non-monitored cloudy hours were predicted from the meteorological classes and the resulting mean concentrations for the entire growing season were compared to the sampled cloud events. Insufficient data exists for examining annual variability but, when all 3 years of data were used together, differences between sampling sites could be observed. Two southern sites received cloud water with higher solute concentrations than two northern sites. Differences in solute concentrations between 2 sites at different elevations on the same mountain were observed, with higher solute concentrations observed near cloud base.

## 1. Introduction

Cloud water acidity represents a potential stress to high elevation forests of the Appalachian Mountains in the eastern USA. The extent of forest canopy exposure to airborne chemicals and the amount of acidic deposition to a mountain site depend on meteorological and chemical factors such as cloud frequency, wind speed and direction, liquid water content (LWC) and cloud droplet size distribution, and the concentration of solutes in the cloud water. We present data for the chemical composition and LWC of cloud water collected near the crest of the Appalachian Mountain range. These data consist of hourly samples collected over three summers at five ground-based sites, and they represent a cloud chemical climatology for high elevation spruce-fir forests.

Cloud water concentrations of $SO_4^{2-}$, $NO_3^-$, $NH_4^+$, and $H^+$ are extremely variable in time and space; aqueous $SO_4^{2-}$ concentrations can vary over three orders of magnitude. Our conceptual model of this variation is that aqueous phase $SO_4^{2-}$ concentrations reflect the concentrations of the aerosol particle and gaseous sulfur species that enter the cloud, the availability of oxidants such as $H_2O_2$ and $O_3$ in the cloudy air, scavenging processes in the cloud, and cloud LWC. In our conceptual model the variation in

$SO_4^{2-}$ concentration that occurs over time scales of less than a few hours is due to variation in LWC and the oxidation of $SO_2$ to $SO_4^{2-}$. However, it was our hypothesis that, when averaged over time scales of a few hours or more, the chemical composition of clouds is governed by large scale transport (>100 km) and vertical mixing of gases and aerosol particles. In addition we hypothesized that the location of a monitoring site relative to synoptic scale features could be used to characterize this transport and mixing when supplemented with air trajectories. We also expected to find differences in LWC among synoptic types and, therefore, additional variability in those solute concentrations that result from aerosol nucleation scavenging (Junge, 1963; Vong et al., 1988a). Easter and Luecken (1988), using a deterministic cloud scavenging and chemistry model, found that cloud water solute concentrations and LWC were higher behind a warm front than prior to warm frontal passage.

We examine the variation in the chemical concentrations and LWC as a function of synoptic meteorology. Cloud events were characterized according to a site's location relative to surface weather map features such as frontal systems. Mixed-layer air trajectories based on rawinsonde measurements were calculated from a model. Meteorological classes describing frequently occurring synoptic types, air trajectories, and whether the cloud was precipitating were used to stratify the cloud water composition and LWC data. Cloud water composition for hours when cloud occurred, but samples were not collected, was predicted from meteorology and the association between cloud water composition and the synoptic-trajectory classes.

Synoptic types with winds that correspond to transport from high emission density areas (e.g., Ohio Valley, USA) or that represent relatively stagnant conditions (e.g., the influence of a Bermuda high and orographic clouds) should have relatively large concentrations of cloud water solute precursors (aerosol and gases) while synoptic types that advect marine air (e.g., an "easterly surface flow" synoptic type) should contain substantial amounts of water. Because the aqueous concentrations resulting from any cloud events that contain high aerosol and LWC are not obvious, and because these events have the potential to deliver substantial chemical fluxes to mountain ecosystems, we analyze cloud water chemical composition, LWC, and the relationship of LWC to concentration. The goal of this analysis was to understand better the meteorological situations that influence cloud water chemistry in mountaintop environments in the eastern USA. In this manner we can identify key processes for modeling studies and, at the same time, understand the limits on extrapolation of the data to other high-elevation spruce-fir forests.

A complete characterization of the chemical composition of cloud droplets requires, at a minimum, determination of the partitioning of each species of interest among the various phases (Morgan, 1982) and as a function of size in the condensed phase (Noone et al., 1988). For forest cloud climatology both temporal and spatial resolution of the data are critical. Considering the difficulty in sampling clouds, it is not surprising that such a complete characterization has not yet been performed. The present study of cloud water composition is based on bulk cloud water samples that represent a weighted average droplet composition. Often referred to as the Mountain Cloud Chemistry Program (MCCP), this project includes more sites and collection hours than previously published for montane cloud chemistry. The MCCP used a part-time, non-random sampling protocol (every cloudy hour was sampled during multiple week sampling intensives and then no clouds were sampled for other multiple week periods). It was our expectation that the cloud water samples might not completely characterize cloud chemical climatology during the growing season because not all synoptic types were sampled in proportion to their true frequency over all cloud events.

Cloud droplet nucleation on preexisting aerosol, condensation of diffusing water vapor, and droplet growth occur with vertical motion of clouds overrunning mountaintops. The Junge (1963) formulation for nucleation scavenging implies that the concentration of cloud water solute varies as 1/LWC. Since LWC typically increases with height above cloud base (Prupacher and Klett, 1980), the concentration of any solute with a substantial aerosol phase precursor should decrease with height above cloud base. We examine cloud water concentration collected at two different locations on one

mountain to gain information on elevational differences in composition.

Only growing season (April through September) clouds are discussed here. These "warm clouds" are in the form of liquid water at the elevation of the sampling sites (1000 to 2006 m) but they can contain an ice phase aloft. Other than Kadlecek et al. (1988), very few data exist to describe a chemical climatology of eastern USA forests for "cold clouds" (in the winter) because of sampling problems. Differences are expected between summer and winter clouds such that extrapolation of the data presented here to true annual values is not advised. Thus, only differences between growing seasons are implied when we refer to annual variation in cloud water composition.

## 2. Experimental methods

Standardized sampling, analysis, and quality assurance (QA) protocols have been employed to insure data comparability among sites and years.

### *2.1. Sites*

The MCCP consists of sampling sites in the Appalachian Mountain Range in the northeastern and southeastern United States. Five sites located at high elevations experience frequent cloudiness and cloud water samples are collected for chemical analysis: Whiteface Mtn, NY, Mt Moosilauke, NH, Shenandoah, VA, Whitetop Mtn, VA, and Mt Mitchell, NC. Experimental details and data for two years (1986–87) for four MCCP sites have been described previously (Mohnen and Kadlecek, 1989; Reisinger and Imhoff, 1989; Sigmon et al., 1989; Saxena et al., 1989). The MCCP sites are depicted in Fig. 1 along with synoptic types that are used later in this paper.

Two MCCP sites are located in the northern Appalachians: Whiteface, NY, and Moosilauke, NH. Three sites are located in the southern Appalachians: Mitchell, NC, Whitetop, VA, and Shenandoah, VA. At Whiteface, Whitetop, and Mitchell, the main sites are located on the summits near the crest of the Appalachian Mountains, while the main sites at Shenandoah and Moosilauke are located at lower elevations along a ridgeline.

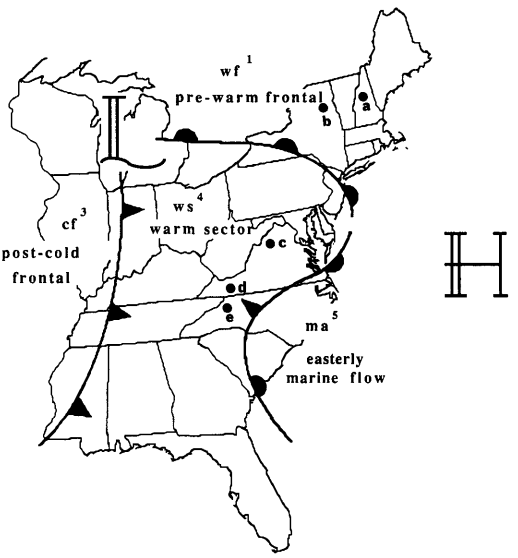


*Fig. 1.* Mountain Cloud Chemistry Program cloud water collection sites (a = Mt Moosilauke, NH; b = Whiteface Mtn, NY; c = Shenandoah, VA; d = Whitetop Mtn, VA; e = Mt Mitchell, NC, USA) and weather map illustration of four synoptic cloud types 1 (pre-warm-frontal), 3 (post-cold-frontal), 4 (warm sector), and 5 (marine flow).

Whiteface Mountain (44°23′N, 73°5′W) is located in the northeastern Adirondack Mountains in New York; subsite 1 is on the 1483 m summit. Whiteface Mtn subsite 2 is a mobile trailer which is located near a spruce-fir canopy at 1245 m elevation. Mt Moosilauke, New Hampshire (40°01′N, 71°50′W), is in the southern portion of the White Mountains, located about 50 km southwest of Mt Washington. The cloud water collection site (at 962 m) does not experience the high frequency of orographic clouds that can be seen on the summit (1465 m).

The Shenandoah, Virginia, site (37°72′N, 78°20′W) is located in the north-central section of the Shenandoah National Park at 1014 m. Whitetop Mtn (36°39′N, 81°36′W) is located in southwestern Virginia, 6 km southwest of the highest peak in Virginia, Mount Rogers at 1686 m. The Mt Mitchell, North Carolina collection site (35°44′05″N, 82°17′15″W) is located 2 km southwest of Mt Mitchell (the highest peak in the eastern USA) at an elevation of 2006 m.

*2.2. Sampling protocol*

The sites collect cloud water only during the growing season, the onset of which varies with site location. At most sites, sampling is conducted during intensive campaigns of approximately 3 to 6 weeks duration, during which nearly every cloudy hour is sampled. During other multiple week periods of the growing season no clouds are sampled. Three sampling campaigns were conducted during each growing season (approximately April–October) of 1986 through 1988, except at two sites (Moosilauke and Whiteface, subsite-2) that started during 1987.

Cloud water collection was begun as soon as possible after the start of a cloud event, which is defined by both visibility and volume. When a stationary object 1 km away is obscured from view for more than 15 min, a cloud event is defined to have started. Collection is discontinued either when the object is no longer obscured from view or when less than 10 ml of sample has been collected over a 20-min period. At night a greater degree of operator judgement is necessarily involved in estimating the start of a cloud event; the end of an event is determined from collection volume. Gases ($O_3$, $SO_2$, sometimes $H_2O_2$ or $NO_x$), liquid water content, and aqueous phase chemical composition are monitored during these cloud events. Gaseous measurements are not discussed here.

Hourly liquid water content (LWC) was determined during 1987 and 1988 using a filter collection method (Valente et al., 1989). A metered air volume is drawn over a cartridge filled with polypropylene mesh. Anisokinetic sampling errors are reduced by matching inlet air velocity with wind speed. A rain shield reduces contamination from precipitation-sized droplets for wind speeds less than 10 m/s.

*2.3. Chemical analysis*

Cloud water samples were analyzed at five laboratories {Dartmouth College (DC), State University of New York at Albany—Whiteface Mtn (SUNY-WF), Tennessee Valley Authority—Whitetop Mtn (TVA-WT), North Carolina State University (NCSU), or the University of Virginia (UVa)}. When more than 125 ml was collected, the sample was split with one aliquot sent to the site-associated analytical laboratory and the other aliquot sent to the Illinois State Water Survey (ISWS) Central Analytical Laboratory (CAL) that also analyzes National Atmospheric Deposition Program (NADP) precipitation samples. Split samples demonstrated the precision among the laboratories.

Volume permitting, cloud water samples are analyzed for the aqueous concentrations of $SO_4^{2-}$, $NO_3^-$, $NH_4^+$, $H^+$ (from pH), $Cl^-$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Na^+$ and conductivity. All laboratories use the electrometric method with a combination electrode for pH. $[NH_4^+]$ was determined by colorimetry (UVa and NCSU) and ion chromatography (IC). IC was used for $[SO_4^{2-}]$, $[NO_3^-]$, and $[Cl^-]$ analyses. Either IC or flame atomic absorption spectroscopy (AAS) was used for $[K^+]$, $[Ca^{2+}]$, $[Mg^{2+}]$, and $[Na^+]$ analyses.

*2.4. Uncertainties*

Standardized sampling, analysis, and quality assurance (QA) protocols insure data comparability among sites. Interlaboratory split sample comparisons indicate that the precision between ISWS-CAL and the MCCP laboratories is generally between 0.07 to 0.11 pH units, 6 to 33 $\mu$eq/l $NO_3^-$, and 9 to 34 $\mu$eq/l $NH_4^+$, approximately 5 to 20% of solute concentrations. Further details on QA procedures and the interlaboratory comparisons are provided elsewhere (Mohnen, 1988, 1990; Vong et al., 1990).

Two types of cloud water collectors are used at MCCP sites, a passive string collector and an active string collector. The passive cloud water collectors (Falconer and Falconer, 1980) depend on ambient wind speed to impact droplets onto 0.4-mm diameter wires strung between two circular disks. The active collectors have a blower to provide the velocity difference for droplet impaction (Daube et al., 1987). Mohnen and Kadlecek (1989) simultaneously deployed a passive string collector and an active collector at Whiteface Mtn, NY; the two samplers produced samples with equivalent chemistry for a range of wind speeds (about 3 to 30 m/s).

LWC uncertainties were investigated by Valente et al. (1989) by simultaneously operating two filter devices (used by MCCP), a Gerber LWC instrument (Gerber, 1984), a forward scattering spectrometer probe (FSSP-100) (Pinnick et al., 1981), and several prototype instruments at Whitetop Mtn, VA. Regression

analysis suggested that the filter instrument provided LWC that was similar to the other instruments; the precision for the filter technique was estimated to be $\pm 0.04$ gm/m$^3$ (Valente et al., 1989).

The characterization of each cloud hour as precipitating or non-precipitating was done by on-site observers. Both the LWC and cloud water concentration measurements for precipitating clouds are subject to contamination by rain drops at high wind speeds, despite attempts to shield the collectors. Therefore, while data for non-precipitating clouds are subject primarily to analytical imprecision and size-dependent collection uncertainties, the data for precipitating clouds contain still larger uncertainties due to possible mixing of cloud droplets with precipitation-sized droplets; the concentrations in the precipitating cloud droplets are underestimated. However these data have been included in this analysis because they represent additional forest canopy exposure to airborne chemicals beyond what occurs from precipitation alone. Our analysis tends to support this decision in that precipitating and non-precipitating clouds are shown to vary similarly with meteorology.

## 3. Data analytical methodology

Here we describe data sources, data preprocessing, and statistical analysis methodology.

### *3.1. Meterological data*

Meteorological data consisted of local winds, cloud presence, and relative humidity (RH) measured at the individual sites, mixed-layer trajectories estimated from a model, and synoptic type evaluated from surface weather maps.

*3.1.1. Synoptic types.* Fig. 1 illustrates four of eight synoptic types obtained from surface weather maps; types 1, 3 and 4 are associated primarily with the main sectors of an extratropical cyclone, while type 5 is the result of easterly flow off of the Atlantic Ocean. Three infrequently occurring synoptic types were eventually pooled into an "other" category (#2); six synoptic categories were used to classify cloud water samples.

(1) Pre-warm-fronted clouds are marked by low-level easterly winds, low cloud bases, and a likelihood of precipitation. The mountain summit is often in warm overrunning air, while its lower slopes are in cool easterly flow.

(2) Three infrequently occurring synoptic types are referred to as "other" synoptic types. Northwest-sector-of-cyclone clouds occur in direct response to intensifying circulation at low levels with the lowest cloud bases associated with strong storms. Stationary-front cloudiness is found along previous cold- or warm-frontal zones that have ceased moving forward. A cut-off low aloft synoptic type was occasionally observed at the southern sites.

(3) Post-cold-frontal clouds result from destabilization of the atmosphere due to cold advection with cloud bases between 1200 m and 1800 m.

(4) Warm-sector clouds include the southeast sector of the cyclone and stagnant conditions often found during summer under the influence of a Bermuda high, particularly in the southern Appalachians. Some characteristics of these air masses are high dewpoints, evening convection, and a higher potential for orographic cloud at night.

(5) Easterly (marine) surface flow results from circulation around high pressure that advects low-level moisture inland from the Atlantic Ocean. Low cloud bases ($<600$ m) and light rain are characteristic of these clouds.

(6) Cap cloud describes mountain cloudiness in which no important synoptic scale features were apparent within several hundred kilometers of the site, while local airport observations had clear skies or high cloud bases. This is a narrower definition of "orographic cloud" than was used by Reisinger and Imhoff (1989).

*3.1.2. Mixed-layer air trajectories.* Trajectories were obtained from an isobaric, mixed-layer model that uses rawinsonde measurements to define the transport field (Heffter, 1980; Kahl and Samson, 1988). The back-trajectory information consisted of end points calculated every 3 hours back to 36 hours before an air parcel arrived at the sampling site; this was converted to three variables describing the fraction of hours that the air was located in each of three sectors (NW/N, E, SW) and a variable that describes the length of the trajectory path. Samson and Moody (1986) used similar trajectories to describe the variability in precipitation chemistry at 2 continental sites.

*3.1.3. Synoptic type-trajectory association.* The 3-dimensional wind flow field associated with large scale systems, as well as their temporal variation, precludes a priori specification of a single trajectory for each synoptic type.

Due to the large number of post-cold frontal, warm-sector, and marine synoptic types (Table 1), we further sub-divided each based on mixed-layer trajectory. This was intended to resolve pollutant transport during the cloud event while retaining a sufficient number of samples in each class for statistical analysis. The "marine" easterly-flow synoptic type was divided by separating the expected easterly trajectories from all other trajectories. The post-cold frontal synoptic type was subdivided by separating northwesterly trajectories from all other trajectories. The warm-sector synoptic type was divided into two classes consisting of transport from one high emissions area (Ohio Valley) or all other trajectories. In order to maintain consistency between northern and southern sites, the separation was based either on southwesterly (northern sites) or northwesterly (southern sites) trajectories. Thus the division for warm-sector events reflects either transport from the Ohio Valley region of the USA or transport from any other direction.

As described above, 9 synoptic-trajectory classes were selected to classify the cloud water chemical concentrations of $H^+$, $NH_4^+$, $SO_4^{2-}$, and $NO_3^-$:

(1) Pre-warm-frontal, all trajectories.

(2) "Other" synoptic types, i.e., those due to large-scale features but that did not occur frequently (NW sector of the cyclone, stationary front, cut-off low aloft), all trajectories.

(3a) Post-cold-frontal synoptic type, NW/N trajectory.

(3b) Post-cold-frontal synoptic type, all trajectories other than (3a).

(4c) Warm-sector synoptic type, trajectory from Ohio Valley (defined as SW sector for northern sites but NW sector for southern sites).

(4d) Warm-sector synoptic type, all trajectories other than (4c).

(5e) Marine-flow synoptic type, E trajectory.

(5f) Marine-flow synoptic type, all trajectories other than (5e).

(6) Cap cloud, all trajectories (summit sites only).

*3.1.4. Winds and cloud presence.* Local wind speed and direction initially were used in the multivariate statistical modeling (see PLS, below)

Table 1. *Cloud frequencies during the growing season stratified by synoptic type at five Appalachian Mountain sites (range from different growing seasons)*

| Site: | Moosilauke | Shenandoah | Mitchell | Whiteface | Whitetop |
|---|---|---|---|---|---|
| Elev. (m) | 1000 | 1014 | 2006 | 1483 | 1686 |
| Cloudy hours[1] | 19% | 11% | 29% | 37% | 30% |
| Synoptic type[2]: | | | | | |
| 1 | 25.5 (23–31) | 6.5 (1–10) | — | 16.5 (9–24) | — |
| 2* | 11.5 (2–18) | 4.5 (1–18) | 2.5 (1–3) | 5.8 (1–9) | 4.2 (1–9) |
| 2† | 0.1 | 3.2 (0–8) | 2.5 (1–3) | 0.3 | 1.5 (1–2) |
| 2‡ | 2.0 (1–2) | 1.8 (0–5) | 2.9 (0–4) | 3.4 (0–6) | 5.0 (0–13) |
| 2§ | 2.2 (0–6) | 5.1 (0–15) | — | 1.4 (0–2) | 0.1 |
| 3 | 11.0 (8–15) | 23.9 (16–35) | 15.2 (13–17) | 32.4 (29–36) | 16.0 (12–20) |
| 4 | 31.8 (25–50) | 11.3 (7–16) | 41.9 (39–43) | 30.7 (21–41) | 45.4 (39–57) |
| 5 | 15.9 (1–22) | 43.7 (18–61) | 26.8 (21–34) | 4.0 (0–6) | 23.1 (20–28) |
| 6 | — | — | 8.2 (1–10) | 5.5 (1–10) | 4.6 (2–6) |

[1] % of total hours with cloud.
[2] % of cloudy hours for each synoptic type.
* NW sector of cyclone.
† Stationary front.
‡ Cut-off low aloft (NW to SW).
§ Cut-off low aloft (NE to SE).

but were dropped because they did not provide additional information for classifying cloud water composition.

Cloud presence was estimated from on-site observers (see above for a definition of cloud events), relative humidity (absolute RH and its slope near 95% were used to estimate saturated conditions), and a cloud detector that utilizes forward scattering of an IR beam (Mohnen, 1988; Vong et al., 1990). The last two methods were used to determine which non-monitored hours (no chemical samples were collected) required synoptic type and trajectory information for the prediction step of our ANOVA modeling. Non-monitored cloudy hours at Mt Mitchell were more difficult to characterize than for the other sites because the RH trace under saturated conditions was somewhat more variable than at the other sites for unknown reasons.

*3.1.5. Uncertainties.* There are substantial uncertainties associated with estimating mixed-layer trajectories and with determining synoptic type from surface weather maps. The synoptic weather types were determined by a meteorologist and independently verified by a second meteorologist but there is necessarily some subjectivity involved. In particular, the transition from pre-warm-frontal synoptic type (#1) to warm-sector synoptic type (#4) was difficult to distinguish from surface weather maps.

The mixed-layer trajectories have considerable uncertainties associated with the failure to account for vertical air motions (Rodhe, 1974); these uncertainties are increased in complex terrain. Thus "analytical error" in the meteorological variables adds to natural variability in the association of trajectory with synoptic type.

### *3.2. Cloud water composition data*

The chemical data consisted of hourly cloud water samples collected during the growing seasons of 1986, 1987, and 1988. The large number of hourly cloud water samples for five sites and three years was reduced to a smaller number of event averages which were transformed to satisfy necessary assumptions for subsequent statistical modeling steps. Here we describe why and how the data were preprocessed before the statistical modeling.

*3.2.1. Data preprocessing.* Our hypothesis was that synoptic meteorology can be used to describe the substantial variation in cloud chemistry that occurs over time scales of around a few hours but that LWC drives additional short-time variation (<few hours) in cloud water composition. Because this conceptual model implies that the hourly samples display serial correlation by virtue of common meteorology (the concentration for an hour is more correlated to the next few hours than later hours), the hourly chemical data were aggregated into "sub-events".

Cloud events were divided into "sub-events" during data analysis; a new sub-event started when the synoptic type changed (e.g., a front passed the site), a change in trajectory occurred, precipitation occurred, or nine hours had passed. Trajectory changes were defined as shifts out of the SW (180° to 269°), NW/N (270° to 44°), or E sector (45° to 179°) from the previous hour. The 9-h upper limit on sub-event duration was designed to avoid unduly downweighting synoptic categories with long durations. Each sub-event covers a continuous cloudy period when a single meteorological condition persists (synoptic type, trajectory, and "cloud type").

The "sub-events" averaged 4-h duration (range 1 to 9 h). Data analysis confirmed that this definition of sub-events significantly reduced ($p < 0.05$) the serial correlation in the data for short (1 to 3 h) time intervals. Removal of this autocorrelation allows a better estimate of the true number of "independent samples" (663 sub-events for 5 main sites plus Whiteface subsite-2) of cloud water chemistry for the 2337 hours of sampling at the six sites. We refer to these "sub-events" as cloud "events" for convenience.

*3.2.2. Data transformation.* The chemical data were cube-root transformed before analysis to homogenize variance among the classes (sites, synoptic type, trajectories, and cloud type) and to keep extreme samples from dominating the modeling results. Comparison of synoptic class means with their variance confirmed that a cube-root transformation of the sub-event chemical means would achieve the necessary independence (Box et al., 1978). The cube-root transformation resulted in normally distributed model residuals that were independent of the predicted value. Analyses conducted in untransformed, square-root-transformed and log-transformed units produced similar synoptic class rankings but the differences between synoptic-trajectory classes

can only be tested for the cube-root transformed chemical data. Cube-root transformations were previously applied to rainwater data by Vong et al. (1988c). Sampson and Guttorp (1989) discuss the relationship between transformed and untransformed data analyses.

### 3.3. Statistical modeling

Given the uncertainties in mixed-layer trajectory, synoptic type, and chemical composition, 2 contrasting approaches were used to classify cloud water composition:

(1) a PLS model determined associations between trajectory, synoptic type, and cloud water composition;

(2) the frequency of each synoptic type and trajectory defined classes with only the most frequently occurring classes being modeled with ANOVA.

*3.3.1. Partial least squares regression (PLS).* Similar to principal component regression, PLS calculates orthogonal components which describe covariance structure in a data matrix ($X$) while predicting a second set of orthogonal components derived from the covariance structure of another matrix ($Y$) (Lorber et al., 1988). Colinearity in the $X$ variables presents problems for techniques such as multiple linear regression, but with PLS correlated predictor ($X$ variables) or response ($Y$ variables) are combined into PLS components (Geladi and Kowalski, 1985). In the present analysis the meteorological variables synoptic type, trajectory, and cloud type are employed as $X$ while the chemical and liquid water concentrations form $Y$. The PLS $X$ components are similar to what would be obtained from a principal component analysis of the same meteorological variables except that the PLS components can be thought of as the rotation of the $X$ components that optimizes their ability to predict the $Y$ components (Vong et al., 1988b). PLS is being increasingly used for multivariate calibration of non-selective analytical chemistry instrumentation (Martens, 1985).

The significance of each PLS component was determined by calculating an F-ratio for the regression (variance explained by that component divided by variance remaining) and by cross-validation (a portion of the data are left out and predicted from the remaining data). A component which passes cross-validation explains significant variation in the data and has good predictive power for the $Y$ variables (Wold, 1978).

PLS, as used here, is an exploratory data analysis tool in that no meteorological classes (of the 24 possible synoptic type-trajectory classes plus stratification by cloud type) or chemical species (six species plus LWC were investigated) are pre-selected for analysis. With PLS covariates are allowed as predictor variables and any intervariable relationships are revealed. Because the second statistical technique used here, ANOVA (described below), necessitates a preselection of the meteorological classes, the two techniques are complementary; if consistent results are obtained from these techniques one has added confidence in the interpretation of the results.

*3.3.2. Analysis of variance (ANOVA).* The second statistical model, analysis of variance (ANOVA), was used to test the hypothesis that a small number of meteorological variables would describe variability in cloud water chemical composition. The ANOVA model (Box et al., 1978; Vong et al., 1988c) tested for chemical differences among nine synoptic/trajectory classes, sites, and cloud type. The ANOVA model corresponds to our conceptual model of event-to-event variation in cloud water composition. The GLM procedure in the SAS Statistical package was used because it is not sensitive to unbalanced designs, i.e., unequal occurrences of different meteorological classes (SAS, 1985). Initially the fixed effects ANOVA model included the full set of possible interactions among synoptic-trajectory classes, cloud type, and different sampling sites. After eliminating non-significant interactions the ANOVA model was:

$$Y(ijkl) = m + S(i) + Sy(j) + Ty(k) + S(i)*Sy(j) + e(ijkl), \quad (1)$$

where:

$Y$ = transformed concentration ($SO_4^{2-}$, $H^+$, $NO_3^-$, or $NH_4^+$)

$m$ = overall data mean of 663 sub-events

$S(i)$ = site mean, all synoptic types ($i = 1, 6$ sites)

$Sy(j)$ = synoptic-trajectory class mean, all sites ($j = 1, 9$ types)

$Ty(k)$ = precipitating or non-precipitating cloud type ($k = 1, 2$)

$S(i)*Sy(j)$ = synoptic-trajectory class mean for each site ($i*j = 54$)

$e(ijkl)$ = residual for each of 663 observations.

ANOVA was repeated for two alternate formulations of eq. (1) to investigate the role of LWC in the variation of cloud water solute composition. The equivalent air concentrations for $SO_4^{2-}$ (obtained by multiplying $SO_4^{2-}$ concentration by LWC) were modeled according to eq. (1) while aqueous concentrations were studied by modifying eq. (1) to include LWC and its interactions (e.g., $Sy(j)*LWC(j)$) as covariates. If the effect of synoptic-trajectory class was due solely to *LWC* class differences, the class effect for $SO_4^{2-}$ would not be significant when modeling equivalent air concentration or when *LWC* was used as a covariate.

## 4. Results

The analysis and modeling was performed on the cloud water solute concentration and *LWC* data for 5 ground-based cloud water collection sites located near the crest of the Appalachian Mountains. The results of those analyses are presented as a function of site, synoptic-trajectory class, and cloud type. Also we present elevational differences at one mountain and describe the covariance among the meteorological and chemical variables.

### *4.1. Synoptic type frequency*

A site-cloud climatology for a 3-year period (1986–1988) is given in Table 1. At Whiteface Mtn, the post-cold-frontal and warm-sector synoptic types comprised almost two-thirds of total cloud hours. The pre-warm frontal class was the third most frequent. Moosilauke experienced more frequent "easterly (marine) flow" clouds than Whiteface Mtn but fewer pre-warm-frontal clouds. At Whitetop Mtn and Mt Mitchell the warm-sector type was most frequent because the normal storm track during summer is through the Great Lakes region (Barchet and Davis, 1984). The second most frequent synoptic type during cloudy conditions at Whitetop Mtn and Mt Mitchell was a result of "easterly (marine) flow". This was substantially more than that observed at Whiteface Mtn, NY. Shenandoah experienced fewer warm sector clouds, and fewer total cloudy hours, than the other sites.

### *4.2. Elevational variation at Whiteface Mountain*

Simultaneous observations of entire events were performed at two sites on the same mountain: Whiteface summit (1483 m) and Whiteface-2 (1250 m). The concentrations of $SO_4^{2-}$, $NO_3^-$, $H^+$, and $NH_4^+$ for 108 hourly cloud water samples have been compared to determine whether cloud water composition varies with height above cloud base.

The $SO_4^{2-}$, $NO_3^-$, $H^+$, and $NH_4^+$ concentrations for samples collected at a mid-elevation (subsite-2) site are nearly twice those recorded at the summit (subsite-1). However, the relative standard deviations at each site are larger than 100%; meteorological variation related to synoptic type and air trajectory tends to obscure any differences between the two Whiteface Mtn sites. Fig. 2 presents the differences in $SO_4^{2-}$ concentration from the two Whiteface sites (calculated as $[SO_4^{2-}]$ at WF-2 minus $[SO_4^{2-}]$ at WF-1). During 92% of the sampled hours, the site at lower elevation received cloud water with higher concentrations of $SO_4^{2-}$ than the summit (similar results are obtained by stratifying for precipitation, i.e., "cloud type").

### *4.3. Variation in cloud chemistry with synoptic type*

*4.3.1. PLS results.* For each sampling site, a 3-component PLS model was calculated from the "sub-event" data; the 1st component was always significant (passed cross-validation) while the 2nd and 3rd components probably were not (passed *F*-test but failed cross-validation).

At the two northern sites, long southwesterly trajectories accompanying warm-sector clouds resulted in higher concentrations of $H^+$, $NH_4^+$, $NO_3^-$, and $SO_4^{2-}$ than did post-cold-frontal (Whiteface) and marine (Moosilauke) synoptic types which occur with northerly and easterly trajectories. For warm-sector clouds no relationship between solute concentrations and LWC was indicated at Whiteface while a positive correlation with LWC was observed for Moosilauke. At Whiteface, cap clouds had high concentrations of $H^+$, $NH_4^+$, $NO_3^-$, and $SO_4^{2-}$ that were negatively correlated with LWC during easterly

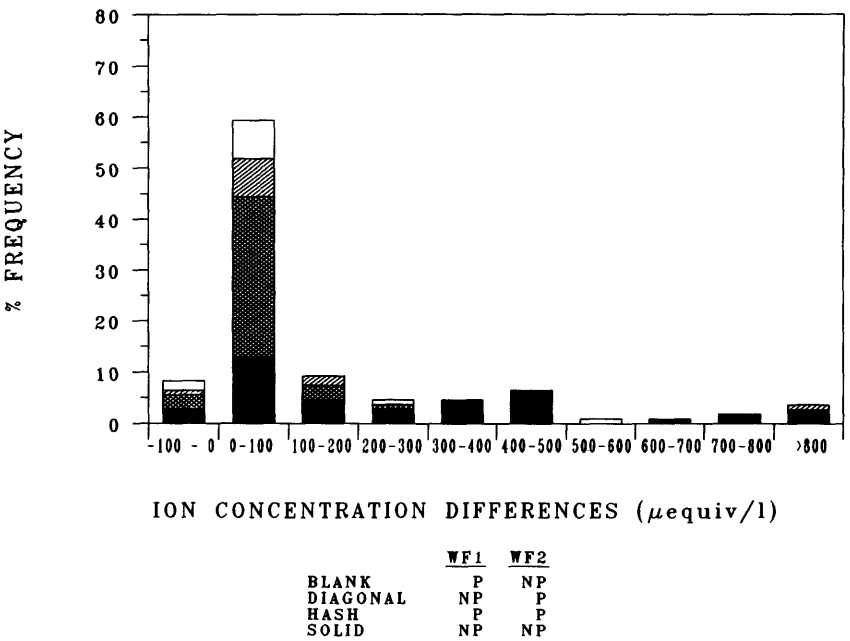


*Fig. 2.* Frequency of occurrence for the differences in $SO_4^{2-}$ concentrations between Whiteface Mtn, NY, subsite 1 (summit, elevation 1486 m) and subsite 2 (1250 m) for simultaneous samples collected during 1987–88; bars are coded for precipitating (P) and non-precipitating (NP) cloud types at the two sites (calculated as $[SO_4^{2-}]$ at WF2 minus $[SO_4^{2-}]$ at WF1).

trajectories but were not related to LWC under long southwest trajectories.

Warm-sector clouds at Whitetop Mtn and Mt Mitchell with northerly trajectories have higher concentrations of all species than do marine clouds with easterly trajectories; LWC and concentration are negatively correlated. At Shenandoah, post-cold-frontal clouds with northerly trajectories have higher concentrations of all species than pre-warm-frontal and "other" synoptic types with long southwest trajectories.

PLS identified significant covariance in the chemical data. $H^+$, $NH_4^+$, $SO_4^{2-}$, and $NO_3^-$ always were correlated and sometimes were negatively correlated to liquid water content (LWC). The correlation among the ions was stronger than their collective relationship with LWC. The covariance in the chemical data strongly suggests that $H^+$, $NH_4^+$, and $NO_3^-$ (and sometimes total cations or $Cl^-$) have a similar dependence upon synoptic type, trajectory, and cloud type as $SO_4^{2-}$ does. Subsequently we focus our analysis on $SO_4^{2-}$.

*4.3.2. ANOVA results.* The ANOVA model (described in eq. (1)) accounted for 43% of the variance in the cube-root transformed $SO_4^{2-}$ concentrations and was highly significant ($p < 0.001$). Similar results were obtained for $H^+$, $NH_4^+$, and $NO_3^-$ concentrations. The three main effects ($S(i), Sy(j), Ty(k)$) were significant; there were differences between (1) sites, (2) cloud types, and (3) synoptic-trajectory classes. Differences are tested in ANOVA by comparing mean values and their variances. In Table 2 ($SO_4^{2-}$) and Table 3 (LWC) the mean values associated with these three significant effects are expressed as: (1) "mean overall" for each of 5 sites, (2) "cloud type mean" for precipitating versus non-precipitating clouds, and (3) "all sites *p* and *np* clouds" for each of 9 synoptic-trajectory classes.

Cloud type was highly significant with non-precipitating clouds having higher concentrations than precipitating clouds. The effect of cloud type was the same for all sites and synoptic classes.

The site-synoptic type interaction $(S(i)*Sy(j)$ in eq. (1) was significant indicating that the synoptic-trajectory class effect varies from site-to-site (expressed in Tables 2 and 3 as synoptic-trajectory class means for individual sites). To understand how important the site*class interaction is to the interpretation of the results, we inspected the class means and their ranking for the individual sites. Tables 2 through 4 suggest that, while the magnitude of the effect of synoptic-trajectory class varies from site-to-site, the synoptic-trajectory classes rank in the same order for the different sites (except at Shenandoah where no significant class effect was found with ANOVA; there was less data at this site). Figs. 3 and 4 illustrate the synoptic-trajectory class effect for non-precipitating clouds at Whiteface Mtn, NY. Compared to all cloud events, the warm sector cloud water $SO_4^{2-}$ distributions (cube root scale) are shifted towards higher concentrations while the post-cold frontal distributions are shifted towards lower concentrations.

Table 4 presents synoptic-trajectory class differences as evaluated using a Bayesian estimator (Waller and Duncan, 1969) to control for chance differences when making multiple comparisons. Synoptic-trajectory classes are ranked in 3 groups (A, B or C) for each site; 2 classes in the same group are not significantly different from each other; 2 classes in different groups are significantly different.

Cap clouds (class 6) and warm-sector (classes 4c and 4d) events have higher cloud water concentrations than post-cold frontal (classes 3a, 3b), pre-warm-frontal (class 1), and "other" (class 2) clouds. Warm-sector cloud events with trajec-

Table 2. *$SO_4^{2-}$ concentration in cloud water: mean values ($\mu eq/L$) and number of hours for synoptic-trajectory classes and cloud types (data were back-transformed from the cube-root scale)*

| Location | Synoptic-Trajectory Class** | | | | | | | | | Mean Overall No. Hours (NP & P)* | Cloud type* mean | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | wf[1] | o[2] | cf[3,a] | cf[3,b] | ws[4,c] | ws[4,d] | ma[5,e] | ma[5,f] | cap[6] | | P clouds | NP clouds |
| Whiteface-1 | 110 | 16 | 20 | 76 | 286 | 218 | 60 | 281 | 537 | 128 | 77 | 165 |
| NY | 175 | 72 | 59 | 217 | 258 | 67 | 24 | 17 | 23 | 912 | 327 | 585 |
| Moosilauke | 146 | 47 | 178 | 45 | 266 | 257 | 94 | 62 | - | 158 | 96 | 249 |
| NH | 133 | 25 | 2 | 4 | 104 | 11 | 37 | 9 | 0 | 325 | 166 | 159 |
| Whitetop | - | 237 | 147 | 136 | 434 | 226 | 133 | 591 | 1043 | 231 | 134 | 263 |
| VA | 0 | 95 | 44 | 54 | 47 | 112 | 147 | 44 | 19 | 562 | 119 | 443 |
| Mitchell | - | 679 | 291 | 562 | 964 | 285 | 123 | 302 | 1036 | 281 | 71 | 359 |
| NC | 0 | 46 | 22 | 20 | 12 | 140 | 144 | 21 | 12 | 417 | 78 | 339 |
| Shenandoah | 84 | 94 | 308 | 140 | - | 57 | 378 | 103 | - | 130 | 69 | 287 |
| VA | 24 | 25 | 13 | 33 | 0 | 7 | 7 | 12 | 0 | 121 | 75 | 46 |
| All Sites | 121 | 144 | 94 | 105 | 308 | 243 | 121 | 333 | 799 | 178 | N.A. | N.A. |
| P and NP clouds | 332 | 263 | 140 | 328 | 421 | 337 | 359 | 103 | 54 | 2337 | | |
| All Sites | 93 | 77 | 36 | 48 | 186 | 109 | 59 | 89 | 244 | N.A. | 87 | N.A. |
| only P clouds | 204 | 96 | 42 | 114 | 128 | 63 | 96 | 21 | 1 | | 765 | |
| All Sites | 178 | 196 | 132 | 149 | 373 | 285 | 152 | 432 | 815 | N.A. | N.A. | 239 |
| only NP clouds | 128 | 167 | 98 | 214 | 293 | 274 | 263 | 82 | 53 | | | 1572 |

*P, precipitating; NP, nonprecipitating

**Synoptic Trajectory Classes: wf[1] - pre -warm- frontal; o[2] - "other" synoptic types; cf[3,a] - post-cold-frontal; NW/N trajectory; cf[3,b] - post-cold-frontal; not NW/N trajectory; ws[4,d] - warm sector; Ohio trajectory; ws[4,c] - warm sector; not Ohio trajectory; ma[5,e] - marine flow, E trajectory; ma[5,f] - marine flow, not E trajectory; cap[6] - cap cloud.

Table 3. *Cloud liquid water content (LWC): mean values [$g/m^3$] and number of hours for synoptic-trajectory classes and cloud types*

| Location | Synoptic-Trajectory Class** | | | | | | | | | Mean Overall No. Hours (NP & P)* | Cloud type* mean | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | wf[1] | o[2] | cf[3,a] | cf[3,b] | ws[4,c] | ws[4,d] | ma[5,e] | ma[5,f] | cap[6] | | P clouds | NP clouds |
| Whiteface-1 NY | 0.49 25 | 0.41 28 | 0.54 13 | 0.50 57 | 0.46 61 | 0.39 18 | 0.72 6 | 0.23 3 | 0.32 11 | 0.46 222 | 0.57 46 | 0.44 176 |
| Moosilauke NH | 0.20 100 | 0.14 7 | 0.09 1 | 0.17 5 | 0.27 81 | 0.20 6 | 0.17 25 | 0.18 11 | - 0 | 0.21 236 | 0.21 109 | 0.22 127 |
| Whitetop VA | - 0 | 0.23 71 | 0.17 47 | 0.22 35 | 0.21 41 | 0.20 65 | 0.24 105 | 0.22 34 | 0.16 19 | 0.22 417 | 0.22 111 | 0.21 306 |
| Mitchell NC | - 0 | 0.20 30 | 0.46 16 | 0.34 15 | 0.15 14 | 0.24 82 | 0.40 84 | 0.40 10 | 0.11 10 | 0.30 261 | 0.41 37 | 0.28 224 |
| Shenandoah VA | 0.34 18 | 0.14 18 | 0.15 7 | 0.21 7 | - 0 | - 0 | - 0 | 0.25 8 | - 0 | 0.23 58 | 0.24 44 | 0.17 14 |
| All Sites P and NP clouds | 0.27 143 | 0.24 154 | 0.28 84 | 0.36 119 | 0.31 197 | 0.24 171 | 0.31 220 | 0.25 66 | 0.19 40 | 0.28 1194 | N.A. | N.A. |
| All Sites only P clouds | 0.24 97 | 0.26 66 | 0.31 31 | 0.40 30 | 0.30 34 | 0.23 31 | 0.36 42 | 0.24 16 | - 0 | N.A. | 0.29 347 | N.A. |
| All Sites only NP clouds | 0.32 46 | 0.22 88 | 0.26 53 | 0.35 89 | 0.31 163 | 0.24 140 | 0.29 178 | 0.25 50 | 0.19 40 | N.A. | N.A. | 0.28 847 |

*P, precipitating; NP, nonprecipitating

**Synoptic Trajectory Classes: wf[1] - pre -warm- frontal; o[2] - "other" synoptic types; cf[3,a] - post-cold-frontal; N trajectory; cf[3,b] - post-cold-frontal; E/SW trajectory; ws[4,d] - warm sector; Ohio trajectory; ws[4,c] - warm sector; not Ohio trajectory; ma[5,e] - marine flow, E trajectory; ma[5,f] - marine flow, not E trajectory; cap[6] - cap cloud.

Table 4. *Differences between synoptic-trajectory classes when sites were treated in separate ANOVA models (cube-root transformed, sub-event mean $SO_4^{2-}$ concentration in cloud water)*

| Group: Site: | A (Highest) | B (Second highest) | C (Lowest) |
|---|---|---|---|
| Whiteface | 6 | 4c 4d 5f | 1 2 3a 3b 5e |
| Whitetop | 6 | 4c 5f | 2 3a 3b 4d 5e |
| Moosilauke | 4c 4d | 1 3a 5e 5f | 2 3b |
| Mitchell | 4c 6 | 2 3b | 3a 4d 5e 5f |
| Shenandoah* | 3a 5e | 1 2 3b 5f | 4d |

* *Note: the synoptic-trajectory class effect was not significant for the Shenandoah model; results for this site should be interpreted with caution.*

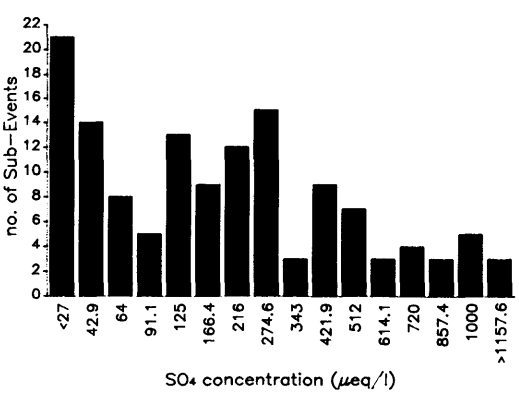


*Fig. 3.* Frequency of occurrence for the sub-event mean $SO_4^{2-}$ in cloud water collected at Whiteface Mtn, NY, summit site, 1986–88. Data are for non-precipitating clouds for all synoptic-trajectory classes.

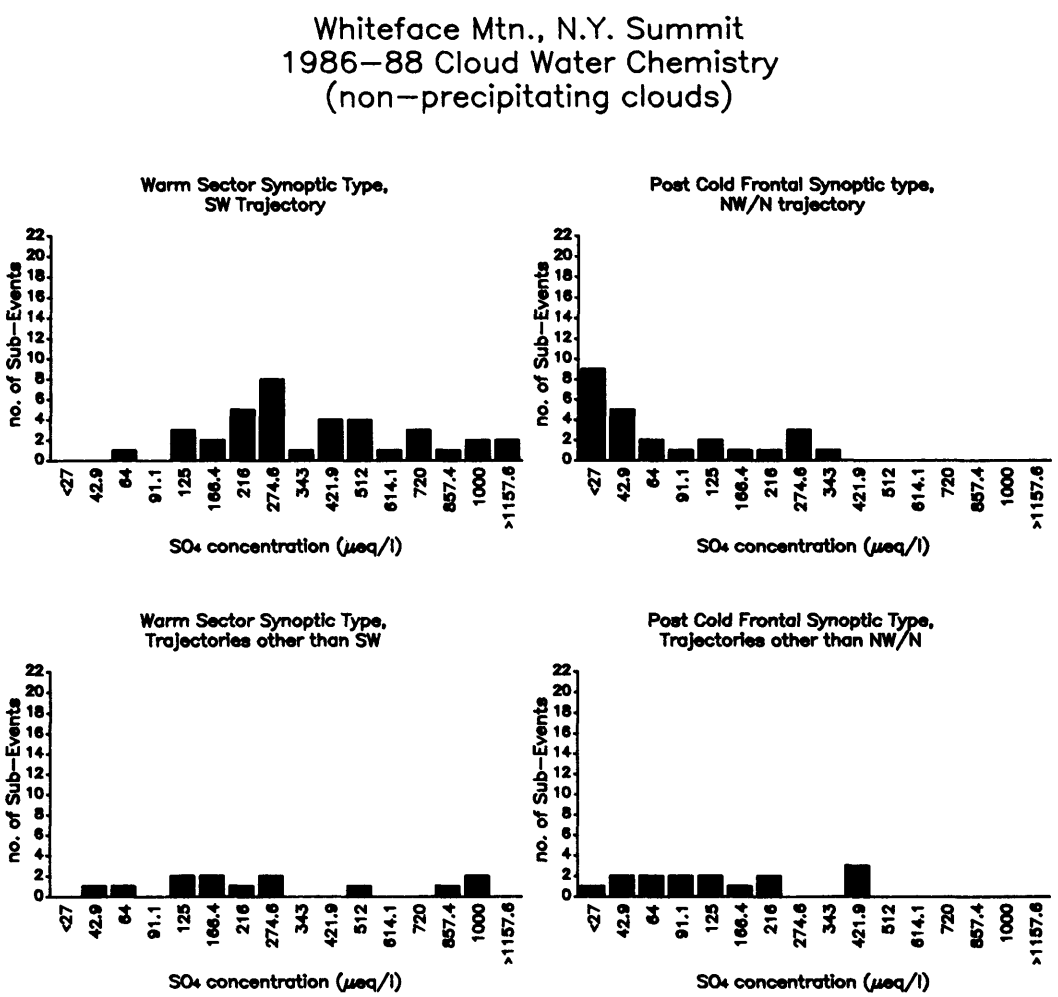


*Fig. 4.* Frequency of occurrence for the sub-event mean $SO_4^{2-}$ in cloud water collected at Whiteface-1, NY (summit site), 1986–88. Data are for non-precipitating clouds for two warm sector (SW = 4c, "other" = 4d) and two post-cold-frontal (NW/N = 3a, and "other" = 3b) synoptic-trajectory classes.

tories from the Ohio Valley (4c) are consistently in groups A and B in Table 4 (the classes with the highest concentrations) while warm sector events with any other trajectories (4d) are in group A or B for two sites but in group C (lowest concentrations) for 3 sites. The differences in the ranking of class 4d for different sites is a SITE*CLASS interaction. The marine synoptic type displays a strong dependence on air mass trajectory with the class restricted to easterly trajectories (5e) having relatively low concentrations while the class (5f) comprised of other trajectories has high concentrations (similar to the warm-sector classes). Apparently, the easterly flow for class 5f was too shallow to characterize pollutant transport.

We compared this classification approach with two that have been suggested elsewhere. These classifications, as we tested them, are:

(1) cloud event duration and cloud type;

(2) mixed-layer trajectory (without synoptic type) and cloud type.

The duration model described only 20% of the variance in these data, the trajectory model accounted for 30% of the variance, while the synoptic-trajectory model that we used here described 43% of the variance. In fact, the event duration model (that Saxena et al., 1989 used to stratify Mt Mitchell data) described only 11% of the variance if cloud type (precipitating/non-precipitating) is not used in the classification. The synoptic-trajectory model described here better describes the data than simple trajectory or duration classifications.

We also applied eq. (1) to the equivalent air concentration of $SO_4^{2-}$ (concentration times LWC) and found similar class effects as are described in Tables 2 and 4 while describing 38%

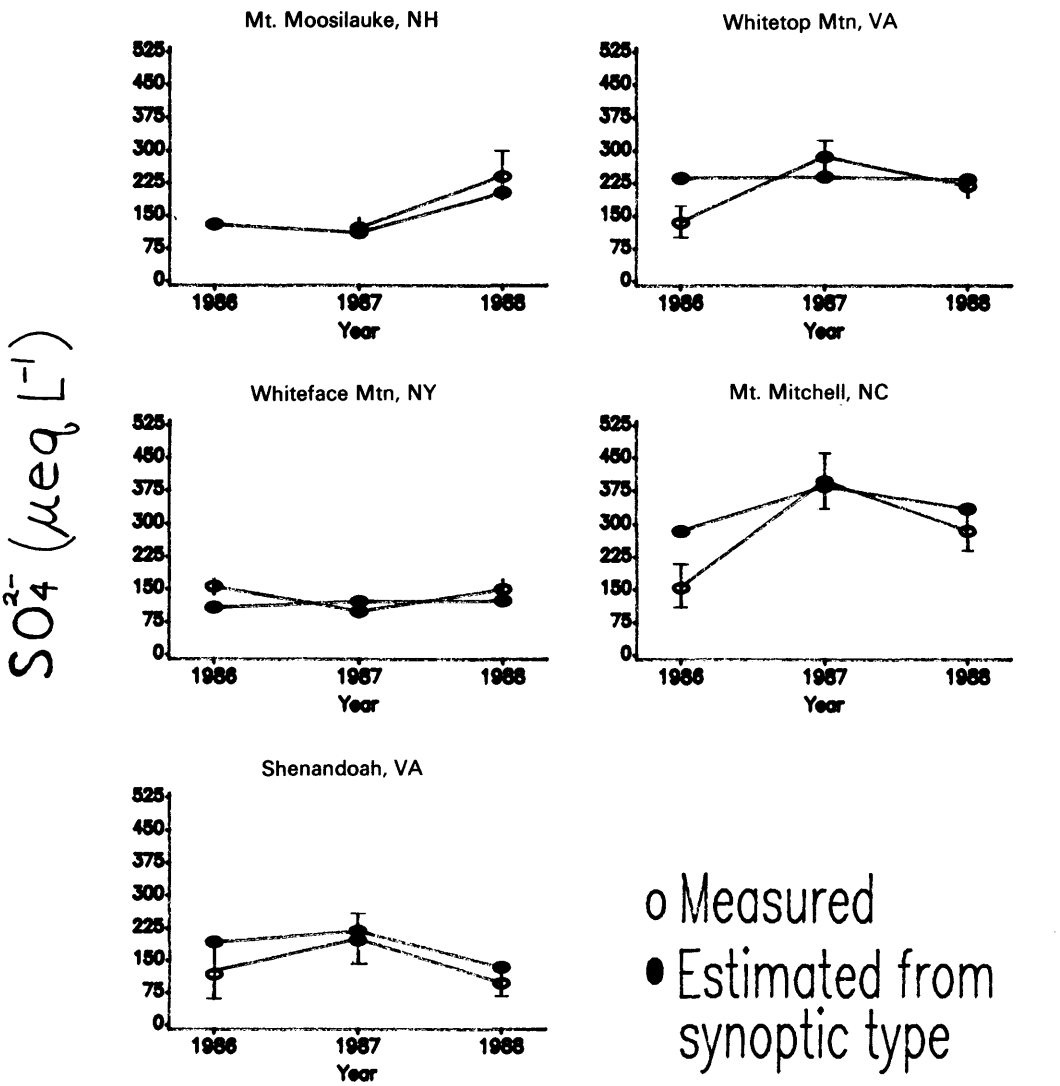


*Fig. 5.* Interannual variation in growing season mean cloud water $SO_4^{2-}$ concentrations for both precipitating and non-precipitating clouds. Measured (hours with cloud collection) and estimated population means (from synoptic type) are back-transformed from a cube-root scale. Bars indicate the 95% confidence intervals within which the sample means are predicted to fall.

of the variance. To assess quantitatively any role of LWC in the $SO_4^{2-}$ concentration differences between synoptic-trajectory classes, we added LWC to eq. (1) as a covariate. We were able to describe 46 to 60% of the variance in the $SO_4^{2-}$ concentrations with this last ANOVA model, depending upon which interactions are specified between LWC and the terms in eq. (1). This last exercise, while not useful for estimating non-monitored hours, established 2 key points:

(1) differences in $[SO_4^{2-}]$ between classes are not associated with LWC;

(2) our conceptual model describes the variation in solute concentration better than our statistical results (43% variance) alone would indicate, but some potentially useful predictor variables (such as LWC or height above cloud base) cannot be specified a priori.

### 4.4. *Prediction for non-monitored hours*

The results of the synoptic-trajectory classification were used to predict cloud water chemistry for non-monitored hours. In this manner, any bias in seasonal means related to the part-time, nonrandom nature of the sampling strategy (every cloud hour is sampled for multiple-week periods and then no events are sampled for a number of weeks) can be accounted for. When RH or cloud detector data suggested that the site was in cloud, trajectory and synoptic type information were assembled. Each non-monitored hour was assigned a $SO_4^{2-}$ concentration from Table 2 based on its synoptic-trajectory class and site. In effect cloud type, which could not be predicted, was assumed to occur in the same proportion in the non-monitored hours as it did during cloud water collection (765 hours precipitating, 1572 hours non-precipitating). These predicted $SO_4^{2-}$ concentrations for 7607 non-monitored cloudy hours were averaged with measured $SO_4^{2-}$ concentrations (representing 2337 h of cloud) as the best estimate of the population means for each site (representing 9944 total hours of cloud for five sites over three growing seasons).

Fig. 5 displays the interannual variation in growing season mean $SO_4^{2-}$ concentration for the samples actually collected during that year and the expected population means for that year. The interannual variation displayed by the sample means was greater than the variation predicted in the population means. This reflects the persistence of one or several meteorological regimes during any sampling period such that a fully representative sample of the meteorology for that growing season may not be realized. Fig. 5 indicates no systematic differences between the sample and population means. These data are appropriately used as a single data set comprised of samples from all three years (1986–1988); there are not adequate data to resolve ianterannual variation but there appears to be adequate data to estimate the $3 - y$ means and associated data distributions (Fig. 6).

Differences between sites for $[SO_4^{2-}]$ are apparent in Fig. 6, both for the 3-year sample means (open points with bars indicating the 95% CI)

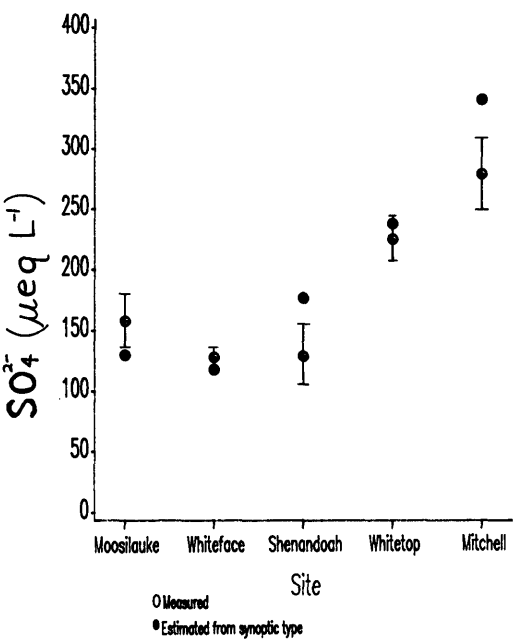


*Fig. 6.* Intersite variation in growing season 3-year mean cloud water $SO_4^{2-}$ concentrations for both precipitating and non-precipitating clouds. Measured (hours with cloud collection) and estimated population means (from synoptic type) are back-transformed from a cube-root scale. Bars indicate the 95% confidence intervals within which the sample means are predicted to fall.

and our best estimate of the population means (solid points). We accounted for synoptic-trajectory class mean value and frequency differences (between monitored and non-monitored hours) in the predictions in Figs. 5 and 6. Therefore, we conclude that the southern sites at Mt Mithcell, NC, and Whitetop, VA, did have higher concentrations than the northern sites, Whiteface, NY, and Moosilauke, NH. $SO_4^{2-}$ at Moosilauke, NH, was within a range defined by Whiteface-1 and Whiteface-2.

## 5. Discussion

Overall, the PLS and ANOVA modeling described significant variation ($p < 0.001$) in cloud water chemistry with synoptic type, cloud type, and sometimes for different trajectories within a single synoptic type. PLS and ANOVA results were mutually consistent in that both derived and pre-selected classes were similar and described the variation in the cloud water chemical data in a similar manner. Substantial variation remained within each synoptic-trajectory class (see Figs. 3 and 4). This was expected because the air mass history (e.g., upwind precipitation), gas-phase and aqueous-phase chemical processing, cloud scavenging, and site micrometeorology could not be described in the synoptic-trajectory classification scheme. For example, the height of the monitoring site above cloud base would be expected to affect the amount of available liquid water and, therefore, aqueous phase concentrations, but a test of that effect was not possible because cloud base data were not available for all sites.

However, the comparison of two sites at Whiteface Mtn suggests that height above cloud base is one determinant of cloud water solute concentration. Substantial spatial (vertical) variation in cloud water concentrations at Whiteface Mtn is explained by increased dilution of pre-existing aerosol if one assumes that LWC increases with height above cloud base (Pruppacher and Klett, 1980). Cloud and rain water data from hill and mountain sites in Europe present mixed indications. Kins et al. (1988) reported significantly higher concentrations near the cloud base in stratus and stratocumulus clouds in a study near Deuselbach, West Germany. However, Fowler et al. (1988) reported that precipitation concentrations and amount sometimes increased with elevation at Great Dunn Fell, Great Britain. The latter study, while not measuring cloud water composition, points out the necessity of understanding site-specific transport and scavenging processes before attempting to extrapolate elevational differences from one mountain to another.

The use of LWC for examination of long-term (time scales > few hours) variations suggested that it is a secondary effect compared to synoptic-trajectory class and cloud type. Short-time variation in LWC (time scales < a few hours) is likely related to patchiness within a cloud and evaporation near the cloud edge that is associated with entrainment of dry air; we were not able to observe any consistent relationship between LWC and solute concentration within events (after accounting for synoptic type).

Our conceptual model of cloud water $SO_4^{2-}$ concentration is supported by this analysis. The differences in solute concentration between cloud water events (time scales > a few hours) are governed by synoptic type and mixed-layer trajectory. Cap clouds and warm sector cloud events were more concentrated than other clouds; these synoptic types often correspond to stagnant air masses where cloud water solute precursors would achieve higher air concentrations and have more time for gas-to-particle conversion than otherwise would occur. Additionally we note that air temperature, $O_3$, and $H_2O_2$ concentrations are generally higher during these warm sector events than other synoptic types (Mohnen, 1990) suggesting that more rapid conversion of $SO_2$ to $SO_4^{2-}$ might occur for warm sector clouds than for other synoptic types.

The covariation between synoptic types and trajectories revealed by PLS is realistic from a physical perspective. Lazrus et al. (1983) obtained warm sector trajectories from an isentropic surface which are consistent with the isobaric trajectories reported here. For example, the "marine" synoptic type occurred with easterly trajectories while the post-cold-frontal synoptic type occurred with NW/N trajectories. This agreement added confidence to the use of the two types of meteorological variables (synoptic

type and mixed-layer trajectory), given their uncertainties.

The influence of air mass orign on solute concentrations is apparent from the analyses described here. The covariance between trajectory and synoptic type demonstrates that different synoptic types occur preferentially with certain trajectories, i.e., synoptic type serves partially as a surrogate for air trajectory. A model which accounted for trajectories but not synoptic type did not describe the cloud water composition as well as the synoptic-trajectory classes did. The same mixed-layer trajectory sector might result in very different cloud water solute concentrations depending on synoptic type. Two possibilities exist for these differences: (1) synoptic type better describes horizontal air movement (therefore emission source regions) than the trajectories, or (2) synoptic type describes horizontal air motion plus other aspects of air mass history such as vertical mixing, temperature, and time for chemical processing of the cloud water solute precursors.

It is not possible to state with certainty which of the above explanations are more valid but it is our conclusion that the synoptic-trajectory class model used here accounts for both transport and mixing in the atmosphere and thus better describes the movement of storm systems than mixed-layer trajectories alone. This is consistent with our hypothesis that large scale (>100 km) transport and vertical mixing of precursor gases and aerosol particles governs cloud water solute composition.

The approach outlined here allows the prediction of mean cloud water solute composition at the same sites for years without monitoring data if cloud presence and synoptic type are documented. Such predictions require that emission sources and oxidant availability are the same for the prediction period as for the modeled 1986–88 period. Note that while high solute concentrations occur more frequently for warm sector and cap cloud events than for other synoptic types, substantial remaining variability (ca. 50%) exists within each class. Thus, our synoptic-trajectory class model can provide a reasonable estimate for an ensemble of events or a seasonal mean concentration (Fig. 6 displays the prediction intervals that are calculated for the number of samples, mix of synoptic types, and sampling sites given in Table 2) but it would not be appropriate for estimating the cloud water solute concentration during a single event.

## 6. Conclusions

We used meteorology to classify the cloud water composition and LWC data for Whiteface Mtn, NY, Mt Moosilauke, NH, Whitetop Mtn, VA, Mt Mitchell, NC, and Shenandoah, VA. Because synoptic type characterizes the cloud water $SO_4^{2-}$ concentration better than was achieved with trajectories alone, we conclude that synoptic-trajectory classes describe both air mass origin and mixing of sulfur species in the troposphere. Results for ions other than $SO_4^{2-}$ indicated a similar dependence on synoptic-trajectory class and cloud type. The classes have consistent ranking with respect to chemical concentration at all sites (e.g., warm-sector events had higher concentrations than post-cold-frontal events).

We conclude that the sampling protocol prevents examination of interannual variability and that the data should be used as 3-year means. The southern sites at Mt Mitchell, NC, and Whitetop, VA, had higher concentrations than the northern sites at Whiteface, NY, and Moosilauke, NH. $SO_4^{2-}$ at Moosilauke, NH, was within a range defined by Whiteface-1 and Whiteface-2. There were consistent differences in cloud water $SO_4^{2-}$ concentration between two Whiteface Mtn collection sites with higher concentrations at the lower elevation site. The differences between southern and northern sampling sites principally are attributable to different frequencies of occurrence for the various synoptic types.

## 7. Acknowledgements

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## REFERENCES


Barchett, W. R. and Davis, W. E. 1984. A weather pattern climatology for the United States. *PNL-4889*, Battelle Pacific Northwest Lab, Richland, WA.

Box, G. E. P., Hunter, W. G. and Hunter, J. S. 1978. *Statistics for Experimenters*. John Wiley, New York. 635 pp.

Easter, R. C. and Luecken, D. J. 1988. A simulation of sulfur wet deposition and its dependence on the inflow of sulfur species to storms. *Atmos. Environ. 22*, 12, 2715–2739.

Fowler, D., Cape, J. N., Leith, I. D., Choularton, T. W., Gay, M. J. and Jones, A. 1988. The influence of altitude on rainfall composition at Great Dunn Fell. *Atmos. Environ. 22* (7), 1355–1371.

Falconer, R. E. and Falconer, P. D. 1980. Determination of cloud-water acidity at a mountain observatory in the Adirondack Mountains of New York State. *J. Geophys. Res. 85C*, 7465–7470.

Geladi, P. and Kowalski, B. R. 1985. Partial least squares regression: a tutorial. *Anal. Chim. Acta 185*, 1–32.

Gerber, H. 1984. Liquid water content in fogs and hazes from visible light scattering. *J. Clim. Appl. Met. 23*, 1247–1252.

Heffter, J. L. 1980. Air Resources Laboratory Atmospheric Transport and Dispersion Model (ARL-ATAD) NOAA Tech. Mem. ARL-81 Silver Spring, MD.

Junge, C. 1963. *Air Chemistry and Radioactivity*. Academic Press, New York.

Kahl, J. D. and Samson, P. J. 1988. Trajectory sensitivity to rawindsonde data resolution. *Atmos. Environ. 22* (7), 1291–1299.

Kadlecek, J. A., Arons, T., Cohen, I., McLaren, S. and Pratt, R. 1988. Wintertime trace gas and cloudwater chemistry studies. Report to Empire State Electric Energy Research Corporation, Atmos. Sci. Res. Center, SUNY-Albany, NY.

Kins, L., Mueller, K. P. and Meixner, F. X. 1988. Experiment Alsdan (1985): Some preliminary results of height resolved measurements of trace gases, aerosol composition, cloud- and precipitation water. In: *Acid Deposition at High Elevations. NATO ASI Series, Vol. 252* (eds. M. H. Unsworth and D. Fowler). Kluwer Academic Publishers, Boston, pp. 375–394.

Lazrus, A. L., Haagenson, P. L., Kok, G. L., Huebert, B. J., Kreitzberg, C. W., Likens, G. E., Mohnen, V. A., Wilson, W. E. and Winchester, J. W. 1983. Acidity in air and water in a case of frontal precipitation. *Atmos. Environ. 17* (3), 581–591.

Lorber, A., Wangen, L. E. and Kowalski, B. R. 1987. Theoretical basis for partial least squares regression. *J. Chemometrics* 1, 19.

Martens, H. 1985. Multivariate calibration: quantitative interpretation of non-selective chemical data, PhD thesis, Norwegian Inst. of Technology, University of Trondheim, Norway, 522 pp.

Mohnen, V. A. 1988. Exposure of forests to air pollutants, clouds, precipitation and climatic variables. *EPA AREAL Report. Contract No. CR 813934-01-2*. Research Triangle Park, NC.

Mohnen, V. A. 1990. An assessment of atmospheric exposure and deposition to high elevation forests in the eastern United States, report to U.S. EPA AREAL, MD-76, Research Triangle Park, NC.

Mohnen, V. A. and Kadlecek, J. A. 1989. Cloud chemistry research at Whiteface Mountain. *Tellus 41B*, 79–91.

Morgan, J. J. 1982. Factors governing the pH, availability of $H^+$, and oxidation capacity of rain. In: *Atmospheric Chemistry* (ed. E. D. Goldberg). Dahlem Konferenzen 1982, Springer-Verlag, New York, pp. 17–40.

Pinnick, R. G., Garvey, D. M. and Duncan, L. D. 1981. Calibration of Knollenberg FSSP light scattering counters for measurement of cloud droplets. *J. App. Meteor. 20*, 1049–1057.

Pruppacher, H. R. and Klett, H. R. 1980. *Microphysics of clouds and precipitation*. D. Reidel Publ., Dordrecht, Holland, p. 18.

Reisinger, L. M. and Imhoff, R. E. 1989. Analysis of summertime cloud water measurements made in a southern Appalachian spruce forest. *Water, Air, and Soil Poll. 45*, 1–15.

Rodhe, H. 1974. Some aspects on the use of trajectories for the computation of large scale dispersion and fallout patterns. *Advances in Geophysics 18B*, 95–109.

SAS Users Guide and STAT Guide, 1985, version 5. Available from SAS Institute, Inc., Box 8000, Cary, NC 27511.

Sampson, P. and Guttorp, P. 1990. Testing interaction in $2 \times 2$ designs using transformed data. *American Statistician*.

Saxena, V. K., Stogner, R. E., Hendler, A. H., DeFelice, T. P., Lin, N. J. and Yeh, R. J. 1989. Monitoring the chemical climate of the Mt Mitchell State Park for evaluation of its impact on forest decline. *Tellus 41B*, 92–109.

Sigmon, J. T., Gilliam, F. S. and Partin, M. E. 1989. Precipitation and throughfall chemistry for a montane hardwood ecosystem: potential for contributions from cloud water. *Canad. J. For. Res. 19*, 1240–1247.

Valente, R. J., Mallant, R. A. M., McLaren, S., Schemenauer, R. and Stogner, R. 1989. Field intercomparison of ground based cloud physics instruments at Whitetop Mountain, Virginia. *J. Atmos. Oceanic. Technol. 6*, 396–406.

Vong, R. J., Mohnen, V., Kadlecek, J., Bailey, B., Mueller, S., Meagher, J. and Baumgardner, R. 1990. Network Measurements of Droplet Deposition of Atmospheric Pollutants. In: *NAPAP State of Science&Technology Report #6* (ed. D. Sisterson). National Acid Precipitation Assessment Program, Washington, DC, June 1990.

Vong, R. J., Hansson, H.-C., Covert, D. S. and Charlson, R. J. 1988a. Acid rain: simultaneous observations of a natural marine background and its acidic sulfate aerosol precursor. *Geophys. Res. Lett. 15* 4, 338–341.

Vong, R. J., Geladi, P., Wold, S. and Esbensen, K. 1988b. Source contributions to ambient aerosol calculated by discriminant Partial Least Squares (PLS). *J. Chemometrics 2*, 281–296.

Vong, R. J., Moseholm, L., Covert, D. S., Sampson, P., O'Loughlin, J. F., Stevenson, M., Charlson, R. J., Zoller, W. H. and Larson, T. V. 1988c. Changes in rainwater acidity associated with closure of a copper smelter. *J. Geophys. Res. 93D6*, 7169–7179.

Waller, R. A. and Duncan, D. B. 1969. A Bayes Rule for the Symmetric Multiple Comparison Problem. *J. Amer. Stat. Assoc. 64*, 1484–1499.

Wold, S. 1978. Cross-validatory estimation of the number of components in factor and principal components analysis. *Technometrics 20*, 198–200.