IONIC AND TRACE ELEMENT COMPOSITION OF CLOUD WATER COLLECTED ON THE OLYMPIC PENINSULA OF WASHINGTON STATE

RICHARD J. VONG,*† BRADLY M. BAKER,‡ FREDRICK J. BRECHTEL,*
ROBERT T. COLLIER,* JOYCE M. HARRIS,§ ANDREW S. KOWALSKI,*
NOREEN C. MCDONALD* and LYNN M. MCINNES‡

*College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, OR 97331, U.S.A.;
‡Department of Chemistry, University of Washington, Seattle, Washington 98195; and §NOAA Environmental Research Lab, Boulder, CO 80303, U.S.A.

Abstract—Field measurements of the chemical composition of boundary-layer clouds that formed in clean, marine air are presented as a background reference point for comparison to cloud water composition in more polluted regions. An impaction-based sampler was used to simultaneously collect cloud water on two stages, where the ratio of droplet diameter was ~ 1.1 for the two droplet size fractions. Analysis revealed that large droplets were more concentrated than smaller cloud droplets by a factor of 1.5 for sea-salt-derived species.

Cloud water concentrations of ionic species were generally five times greater the concentrations of the same ions in rain water. Aqueous-phase solute concentrations in cloud varied over two orders of magnitude but generally were quite low, correlated to each other and to aerosol (CN) concentration, but negatively correlated to LWC. Air-equivalent solute concentrations were calculated, allowing the detection of the influence of air-mass trajectory on cloud-water composition. A multivariate statistical analysis of the cloud water data suggested sea salt, biogenic, crustal, and anthropogenic emission source contributions; the last two sources existed only for continental air-mass trajectories. Coastal and oceanic trajectories were selected for the purpose of estimating a northern hemisphere, mid-latitude, marine, background cloud water composition of 8 neq m^{-3} non-sea salt SO$_4^{2-}$ and 4 neq m^{-3} NO$_3^-$. © 1997 Elsevier Science Ltd.

Key word index: Acid rain, size-dependent composition, organic acids, PLS regression.

1. INTRODUCTION

Few thorough investigations of the heterogeneous nature of marine cloud water composition have been performed despite the critical importance of this subject to the in-cloud oxidation of SO$_2$ (Collett *et al.*, 1994; Pandis *et al.*, 1990) and resulting effects on the marine aerosol size distribution (Hegg *et al.*, 1992; Hoppel *et al.*, 1990). Cloud water composition and solute concentrations vary over minutes-to-days time scales and across the droplet-size spectrum (Ogren *et al.*, 1989; Ogren and Charlson, 1992). Cloud water composition is affected by environmental factors such as long-range transport, local emission sources, phase partitioning and aqueous-phase reaction rates, and cloud microphysical properties (e.g. liquid water content—LWC). In fact, sampling clouds at a "clean", marine site is likely to represent a relatively simple set

of environmental factors compared to many other sampling sites (Charlson *et al.*, 1983). However, it can be difficult to distinguish concentration differences that are related to these types of environmental factors from those related to sampling technique itself.

In fact, the size of cloud droplets sampled for chemical analysis varies among published studies because cloud water samplers employ a variety of collection methods (Schell *et al.*, 1992; Collett *et al.*, 1995; Hering *et al.*, 1987; Mohnen and Kadlacek, 1989). Since solute composition is expected to vary across the droplet size spectrum, it is important to characterize a cloud water sampler in terms of its size-dependent collection properties (e.g. aspiration and impaction efficiencies) so that reported results may be understood in that context.

The purpose of the present study was to characterize and deploy a cloud water sampler under a sampling protocol that will produce high-quality data on the heterogeneous nature of maritime cloud water chemical composition. This sampler relies on

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† Author to whom correspondence should be addressed.

impaction of droplets onto cylindrical rods. The 150 collected cloud water samples consisted of the simultaneous collection of two different droplet size fractions, each of which was chemically analyzed for major ionic species.

The present work presents and applies a comprehensive set of data analytical methods that are appropriate for evaluation of many of the environmental and methodological factors that could influence cloud water composition. A widely neglected factor, the sampler inlet, or aspiration, efficiency was modeled in order to understand the dependence of solute concentration on mean droplet size. Air-equivalent solute concentrations were calculated as the most appropriate means for examining emission source influences on the cloud water composition. A multivariate statistical model (partial least-squares regression) was introduced and applied to the data to help identify factors controlling marine cloud water composition.

The results of this investigation, besides providing a methodology for collecting and evaluating cloud water chemical composition at any site, also have implications for understanding marine CCN chemical composition and, therefore, cloud albedo over the oceans (Charlson et al., 1987). Furthermore, at windy sites interception of cloud droplets by vegetation can result in substantial chemical fluxes (Vong et al., 1991; Lovett and Kinsman, 1990; Kowalski, 1996) and both the turbulent and sedimentary deposition processes are likely to be size-dependent (Beswick et al., 1991; Vong and Kowalski, 1995). Such fluxes can be determined from simultaneous water flux (e.g. by eddy correlation) and cloud water composition measurements such as are presented herein.

2. EXPERIMENTAL METHODS

2.1. Field measurements

From 5 to 25 May 1993, cloud water was collected at the Cheeka Peak Observatory (460 m elevation) located 4 km from the Pacific Ocean on the Olympic Peninsula of Washington State (Fig. 1) as part of the first cloud and aerosol chemistry experiment (CACHE-1). Previously collected rain and aerosol demonstrate the clean, marine background character of the upwind North Pacific air masses (Vong et al., 1988a; Covert, 1988; Basabe et al., 1989); local emissions are negligible and contribute very little to sampled cloud water composition.

Cloud water was collected at 10 m a.g.l. from a tower over 20–200 min intervals using an active sampler. The sampler was "active" in that a high-capacity blower, rather than ambient wind speed, aspired the cloudy air. Sampled air at $250 \ell s^{-1}$ passes through a cylindrical sampling section which contains impaction rods. An existing sampler (Pade et al., 1987) was modified by adding a top stage consisting of 1.02 cm diameter collection rods to a bottom stage consisting of 0.167 m diameter rods. Six radially oriented, 60° sections each presented either one large rod (top stage) or nine small rods (bottom stage) to the air flow. Each stage of the sampler received "ambient" cloud in that no sequential removal by the two stages was attempted. The sampler inlet was oriented 90° to the mean wind. Thus, the cloud water

sampler's impaction cut sizes, d_{50} (droplet diameters impacted at 50% efficiency for each stage), are independent of ambient wind speed.

Collected droplets drained down the rods into separate, precleaned vials for each droplet size fraction (rod size). Typically, a sample of $\geqslant 5$ ml could be collected in 30 min. The entire sampler was acid-washed before deployment, rinsed with deionized water between cloudy periods, and covered during sunny weather. The periodic cloud water sampler rinses were analyzed to determine the overall experimental limits of detection for each species. Cloud water collection vials consisted of 30 or 60 ml PE and PP bottles that had been acid washed by soaking in 1 N HNO$_3$ (reagent grade for IC, Ultrex for ICP-MS aliquots) for $\geqslant 24$ h. The acid-washed vials were repeatedly rinsed with distilled, deionized (millipore) water and soaked in deionized water overnight. The conductivity of the last rinse water was required to be within 10% of the $\leqslant 1 \mu S\, cm^{-1}$ makeup water.

The cloud sampler did not have a rain shield and the representativeness of cloud water collected during precipitation is unknown; thus we only consider samples collected during non-precipitating or lightly drizzling cloud. Drizzle indicates precipitation rates too small (< 1 mm/h) to register on a tipping bucket rain gauge or for a person to get wet when standing in an open area. In this study, drizzle was defined subjectively and detected as precipitation that produced ripples on a pool of still water.

Rain-water samples were collected over 3-day periods and analyzed for Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, and K^+ by ion chromatography (IC) and pH. Rainwater samplers consisted of acid-washed and rinsed 1ℓ PE bottles and 15 cm diameter PE "powder funnels". The rain samplers were deployed at 3 m a.g.l.; duplicates verified that any contamination was not detectable, similar to earlier experience with this type of sampler (Vong et al., 1988a).

A number of other measurements were performed and are utilized for interpreting cloud water chemical composition. Cloud microphysical measurements were performed continuously from a boom extending upwind of the tower and ~ 3 m. crosswind from the cloud water chemical sampler (Vong and Kowalski, 1995), including: cloud droplet-size spectra from a forward scattering spectrometer (PMS FSSP-100) liquid water content (LWC) from a particle volume monitor (GSI PVM-100). Additional measurements included three-dimensional winds (sonic anemometer; ATI SWS-211-3K), ozone concentration (Dasibi 1003PC, UV absorbance) and aerosol number concentration (TSI 3760) sampled downstream of an inlet which aspires and evaporates most cloud drops and senses aerosol as the approximate sum of CCN and interstitial aerosol (diameter > 10 nm).

2.2. Cloud water sampler characterization

The cloud water sampler performance was characterized for both aspiration and impaction efficiencies for the two rod sizes (stages). The impaction characteristics for the same sampler, but containing only the small rods (0.167 cm diameter), were investigated by Pade et al. (1987), including efficiency calibrations using fluorescein-tagged droplets. Since our sampler modifications were minor (the addition of an impaction stage and small changes in the flow cross-sectional area associated with a new sample delivery system), we measured air velocity profiles within the sampling sections (pitot tube and manometer) and calculated the impaction d_{50}'s for the two rod sizes based on air velocities as a function of position within the sampler. Impaction efficiencies calculated according to the approach of Langmuir and Blodgett (1961) indicate that the sampler top stage rods intercept primarily large droplets (impaction $d_{50} = 12 \mu m$) while the bottom stage was efficient at intercepting nearly all droplet sizes ($d_{50} = 5 \mu m$) and are in agreement with calculations by Mohnen and Kadlecek (1989).
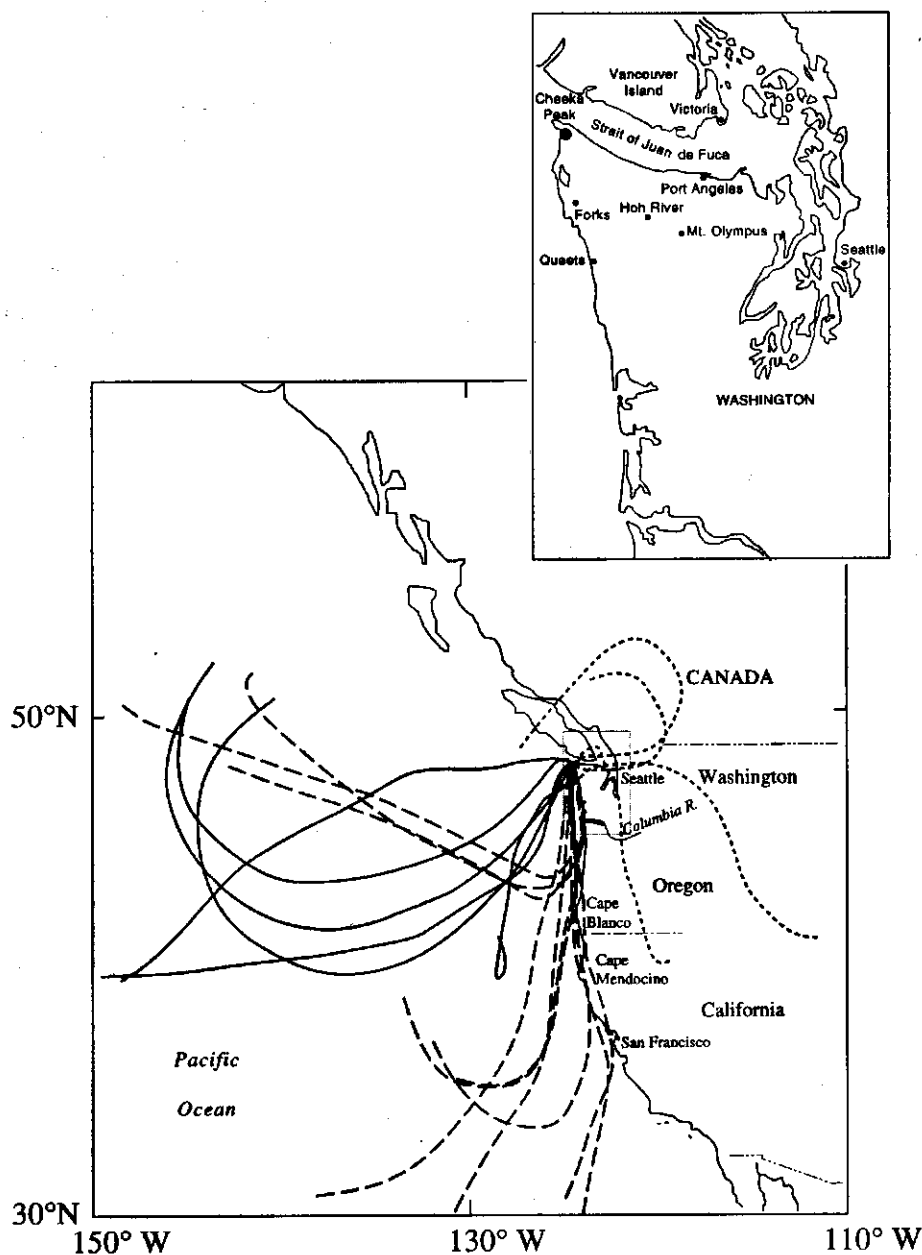
Fig. 1. Maps of the Olympic Peninsula in western Washington State, U.S.A., and the Cheeka Peak sampling site with three day isentropic air mass trajectories traced for continental (short dashes), oceanic (solid), and coastal (long dashes) classes.

For a fixed sampler geometry, aspiration efficiency for 90° sampling depends on droplet size and the ratio of sampler to ambient wind speed, according to Vincent (1989) and Schell et al. (1992) as

$$E_{asp} = \frac{1}{1 + 4kSR^{0.5}}$$

where $R = U_a/U_S$, U_a is the ambient mean wind speed, U_S the sampler air velocity at the inlet, k the empirical parameter ($k \sim 2$), S the inlet Stokes number (dimensionless), ($= \rho d_d^2 U_a/18\eta L_c$), L_c the inlet diameter (22 cm) d_d, ρ and η are droplet diameter, water density, and air viscosity, respectively.

Measurements by Noone et al. (1992) for a 90° sampling in a wind tunnel support the validity of this aspiration efficiency equation. The probabilities of aspiring 10, 20 and 30 μm droplets into the 90° cloud water sampler inlet are 0.98, 0.92, and 0.83, respectively, at 4 m s^{-1} ambient wind speed and decrease to 0.94, 0.80, and 0.64 at 8 m s^{-1}. Though inefficient for large droplets, the proportion of large-to-small droplets that are aspired is similar for different wind speeds.

The droplet size that characterizes each fraction collected by the sampler is constrained by the fact that the sampled clouds have narrow droplet-size distribution; cloud events typically had half of the liquid water mass below 15 μm but less than one-tenth below 10 μm diameter (Vong and Kowalski, 1995). Considering aspiration and impaction efficiencies and the ambient droplet-size distribution together, the large rods typically collected 13 μm droplets (mass- or volume-mean diameter—vmd) while the smaller

rods typically collected 12 μm drops. Thus, any differences in solute concentration from the two stages of the sampler correspond to a ~ 1 μm difference in the mean diameter in the collected droplets or a ratio of droplet diameters of ~ 1.1.

2.3. Laboratory methods

After field collection, the cloud water samples were divided into aliquots inside a class-100 clean bench, and refrigerated until analysis (typically 1 month except for pH which was measured within 24 h of sample collection). When sufficient cloud water was collected, aliquots were separated for the determination of acid-soluble trace elements via inductively coupled plasma mass spectrometry (ICP-MS), pH, ion chromatography (IC) analysis of anions (Cl^-, NO_3^-, SO_4^{2-}), cations (NH_4^+, Na^+, Mg^{2+}, Ca^{2+}, and K^+), and organic acids (methane sulfonate, formate, and acetate). The IC analysis for organics was performed on a 2 ml aliquot that had 40 μl of chloroform added at the time of field collection to inhibit microbial degradation. The ICP-MS aliquots were acidified in their collection vials to a pH of ~ 1.5 with teflon-redistilled HNO_3. All storage of individual cloud water aliquots consisted of new, 2 ml PE centrifuge tubes that had been previously acid washed, as described above for the collection vials, except for pH aliquots which were simply rinsed in deionized water.

The pH measurements were performed with a glass probe that was calibrated using pH 4 and 7 commercial buffers. Probe performance and drift were checked continually using a low ionic strength H_2SO_4 solution (pH = 4.66). Duplicate analyses suggested that the pH measurements during CACHE-1 were precise to ~ 0.1 pH unit.

The IC measurements of inorganic anion concentrations were performed using a Dionex AS4A column (Na_2CO_3/$NaHCO_3$ eluent). The IC measurements of monovalent inorganic cations were performed using a Dionex CS3 column (HCl/diaminopropionic acid monohydrochloride eluent). The IC measurements of of organic anions were performed using a Dionex AS4A column ($NaHCO_3$ eluent; 200 μl sample loop).

Trace element analyses were carried out using an inductively coupled plasma mass spectrometer (ICP-MS; VG/Fisons PQ2 +) following standard methods (Jarvis et al., 1992). Peak integrations were performed for Mg, Al, Ti, V, Mn, Ni, Cu, Zn, Br, Sr, Cd, I, Ba, and Pb; results for only seven elements are presented because the others were often below the ICP-MS analytical detection limits.

Each ICP-MS analysis run was calibrated against mixed-element standard curves prepared daily. Samples and standards were spiked with an internal monitor containing Be, In, and Bi for determination of a mass-specific correction curve for each acquisition set. A series of replicate blanks and standards were analyzed periodically and all data were "drift corrected" (Cheatham et al., 1993) to these consistency standards.

The overall experimental limits of detection for Mg, Al, and Mn were 20, 8, and 0.8 $\mu g\,l^{-1}$, respectively, with values of 0.5 $\mu g\,l^{-1}$ for V, Ni, Cu, and Pb. These values were defined from observed mean concentrations in blanks (deionized water sprayed into the sampler) and their variability (Currie, 1968). Concentrations for undetected species were set at a random number between zero and the experimental detection limit before further data analyses to preserve the information that certain samples had very low concentrations (Vong, 1993).

3. DATA ANALYSIS METHODOLOGY

3.1. Trajectory method

An isentropic transport model (Harris and Kahl, 1994), based on 2.5° latitude–longitude gridded meteorology and

topography (European Centre for Medium Range Weather Forecasts), was used to determine air-mass trajectories for this study. The details of techniques employed in the trajectory model and their uncertainties are discussed elsewhere (Merrill et al., 1985; Harris, 1992).

For the present analysis, the isentropic trajectories were grouped into three classes based on their passage over open ocean, coastal areas of North America, or the North American continent itself during the 3 d period immediately prior to arrival at Cheeka Peak, WA (Fig. 1).

3.2. Air-equivalent solute concentration

For defining background solute concentrations and for multivariate statistical analyses involving air-mass trajectories, the cloud water chemical data were expressed as air-equivalent concentrations (Ogren and Rodhe, 1986; Leaitch et al., 1992) calculated as the product of aqueous-phase solute concentrations and LWC; individual samples were arithmetically composited to form 2 to 3 h values. This calculation of air-equivalent concentrations for cloud water composition reduced the strong influence of LWC on species concentrations that existed within many, but not all, continuous cloud events, see Fig. 2. Since the variation of cloud water solute concentration over time scales of minutes-to-hours (Winkler, 1986; Vong et al., 1990) often is controlled by LWC, a statistical analysis of short-term aqueous-phase concentration data generally will indicate that all species are somewhat correlated to each other and to LWC. In contrast, 2–3 h averages for air-equivalent concentrations in cloud more nearly reflect concentrations of aerosol and gas-phase species, themselves indicators of transport and emission source influences which might be expected to vary over time scales of several-hours-to-days at a marine site.

3.3. PLS regression methodology

A partial least-squares regression (PLS) model was used to examine the dependence of cloud water chemical composition on both microphysical influences and air-mass trajectory. Microphysical influences considered were the occurrence of precipitation, cloud LWC, and aerosol (CN) number concentration.

PLS describes correlated chemical species in cloud water (X matrix) as chemical factors that are in turn related to physical factors (Y matrix) consisting of air mass trajectories and microphysical measurements. Details of the PLS method and its application to atmospheric data have been presented elsewhere (Vong et al., 1988a, b; Vong, 1993; Geladi and Kowalski, 1985). The PLS components describe the "chemical fingerprints" associated with the three selected trajectory classes and the microphysical measurements. In addition, PLS can identify individual samples as multivariate outliers, thus pinpointing any unusual samples that were collected during a particular trajectory type. The composition of each cloud water sample is used with the PLS model to determine how well each sample "fit" its trajectory class (Vong, 1993) based on a calculated residual in the model's multivariate chemical space (the distance of a sample from its class model is compared to the variance of the samples for that same class). Outlier samples may contain errors or simply be unusual samples. The use of outlier rejection with PLS allows one to describe the sources of variability in typical samples.

3.4. Evaluation of droplet-size-dependent concentration

A size-dependence in cloud water solute composition can arise from the well-known site-dependence in aerosol composition (Seinfeld, 1986) and an inverse dependence of droplet growth rate on droplet radius (Pruppacher and Klett, 1978). Thus, the analysis of variations in composition with droplet size is treated as a multiplicative problem, consistent with condensational growth as the main determinant of droplet size. Variations in composition across the droplet

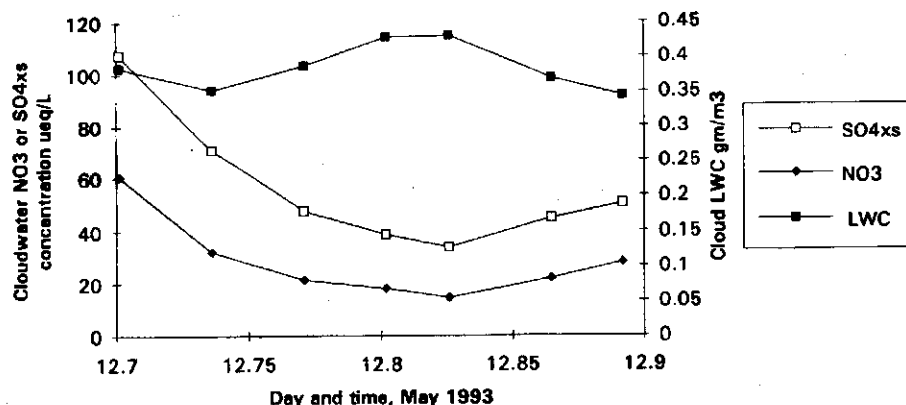**Cloudwater solute and liquid water concentrations through a single event**

Fig. 2. Cloud water chemical composition and LWC through a single cloud event on May 12, 1993. Points are located at the start times for continuous collection periods. This event had 9 m s^{-1} winds from the SSW, a droplet volume mean diameter (vmd) of 12.5 μm a LWC of 0.37 g m^{-3}, and a LW turbulent flux [15] of 9 mg m^{-2} s^{-1} (Vong and Kowalski, 1995).

spectrum are examined by comparing simultaneous cloud water collections for different mean droplet sizes (sampler stages) where the ratio of droplet diameters is ~ 1.1 for the present study (see above). Droplet-size dependence in solute concentrations are evaluated for non-precipitating cloud only; precipitation would be expected to reduce or eliminate any size dependence through mixing of drops of different sizes during the collision–coalescence process.

A size dependence for a particular species is indicated when a comparison of simultaneous data, expressed as aqueous-phase solute concentration for each of the two rod sizes, results in a regression slope that is significantly different from 1.0. When the (slope − 1.0) $\geqslant$ 1 standard error (SE) of the regression slope, a size dependence is said to have been demonstrated ($t \geqslant 1.1$, thus, for a single-ended t-test one is ~ 85% confident, or more, that a size dependence exists (Box et al., 1978)). Mean differences in concentration averaged across all simultaneous sample pairs also are determined for illustrative purposes.

4. RESULTS AND DISCUSSION

Aqueous-phase solute concentrations in cloud sampled at Cheeka Peak during CACHE-1 varied over two orders of magnitude but generally were quite low, correlated to each other and to aerosol (CN) concentration, negatively correlated to LWC (Fig. 2) and mean droplet size. Concentrations were lower in drizzling cloud than for non-precipitating cloud for all species; data for precipitating cloud are excluded here because the cloud sampler collection characteristics for rain is unknown and probably highly variable. Light drizzle (see above) is included in the data except when evaluating droplet-size dependence.

4.1. Data quality

Data quality was examined by comparing independent measures of the same quality, sample charge balance and sea-salt ion ratios. Cloud- and rain-water

samples displayed reasonable charge balances in that the sum of anions and cations differed by < 20% for individual samples with no particular bias evident. Similarly, the sum of anions as nitrate, non-sea-salt sulfate, and organic acids was quite similar to the sum of ammonium and hydrogen ions (a "mini-charge balance") that excludes the dominating sea-salt species. A comparison of Mg concentrations (slope = 1.0, $r^2 = 0.87$) from the contrasting IC and ICP-MS techniques confirmed the compatibility of data from these analytical methods. The accuracy and precision of the ICP-MS results is estimated to be on the order of 10–20% (except for Al, Section 4.3), based on analysis of standards and replicate sample analyses. Measured Mg/Cl and Mg/Na mass ratios of 0.065 and 0.138 compared favorably with sea-salt values of 0.067 and 0.120, respectively, providing further confirmation of data quality.

Two measures of LWC from the FSSP-100 and PVM-100 were in excellent agreement (Vong and Kowalski, 1995). Finally, the smooth time evolution of cloud water solute composition within some, but not all, individual cloud events (Fig. 2) suggests that the precision of the data is sufficient to resolve the low ion concentrations experienced at Cheeka Peak.

4.2. Cloud- and rain-water mean ionic concentrations

During CACHE-1, Cheeka Peak received clean air during cloud episodes, as evidenced by low CN (< 500 cm^{-3}) and ozone (~ 30 ppbv) concentrations as well as low-aqueous-phase solute concentrations. Rain-water concentrations are a factor of five smaller than the concentrations for the same ions in cloud droplets sampled from non-precipitating and drizzling clouds, see Table 1, and are similar to northern hemisphere marine background rain-water values (Vong et al., 1988a; Vong, 1990). Cloud pH averaged

4.2 while rain pH averaged 5.0. Cloud water composition varied over a broad range; the standard deviations in short-term aqueous-phase concentrations were similar in magnitude to mean values.

4.3. Trace elements from ICP-MS

The application of ICP-MS to collected cloud water detected seven elemental concentrations in most of the 89 samples analyzed. One element, Mg, was used only to establish the comparability between the ICP-MS and IC results. The remaining elements serve as tracers for specific emission source categories.

Generally, any apportionment of observed concentrations in air or aqueous samples relies on the use of

Table 1. Chemical comparison of the species that were measured in both rain and cloud samples ("all droplets", see text) at Cheeka Peak, WA, during May 1993 ($N_{cloud} = 102$; $N_{rain} = 9$) for all trajectory classes

Cloud:	small	rods		Rain:
	Mean	SD	Units	Mean
SO_4^{2-}	84	66	$\mu eq\ \ell^{-1}$	13
Cl^-	478	554	$\mu eq\ \ell^{-1}$	62
Na^+	316	340	$\mu eq\ \ell^{-1}$	46
K^+	9	10	$\mu eq\ \ell^{-1}$	3
NH_4^+	15	15	$\mu eq\ \ell^{-1}$	5
$SO_4^{2-}XS$	42	35	$\mu eq\ \ell^{-1}$	7
NO_3^-	28	30	$\mu eq\ \ell^{-1}$	5
H^+	57	51	$\mu eq\ \ell^{-1}$	10
pH	4.2		pH units	5.0

Data for non-precipitating or drizzling cloud are included but data for precipitating cloud are not.

mass ratios (enrichment factors) or multiple correlations (Vong et al., 1988a, b) in the chemical data. Data correlations are examined in Section 4.5 using the PLS regression model. Mass ratios for average continental crust (Taylor, 1964) suggest that either the cloud water is enriched in Mn, Ni, and V (i.e., that non-crustal sources are active) or that our Al concentrations are biased low. Since Mn, V, and Ni themselves are present in crustal proportions, and the cloud water V/Ni ratio is much smaller than that for fuel oil combustion (Kowalczyk et al., 1978) (the dominant anthropogenic source of these elements according to Gordon, 1988), it is likely that Al is underestimated by a factor of 2 in the data reported here, for unknown analytical reasons. Pb is undetected in the cloud water more frequently than other ICP-MS analytes, suggesting few, if any, important emission source influences.

4.4. Size dependence

Table 2 presents the size dependence in cloud water composition for ionic species during non-precipitating cloud only. Large droplets (13 μm diameter) are more concentrated for sea-salt-derived species (e.g. for Na^+, Cl^-, Mg^{2+}, K^+, and Ca^{2+}, but not NH_4^+, three organics, or non-marine SO_4) than bulk cloud water (12 μm diameter) by a factor of about 1.5, depending on species. Here non-marine, or "excess", SO_4^{2-} is calculated on a mass basis as $[SO_4^{2-}\ xs] = [SO_4^{2-}] - 0.252\ [Na^+]$. Sampling in marine locations by Ogren et al. (1989), Munger et al. (1989), and Noone et al., (1988) suggested size dependences

Table 2. Size dependence in cloud water aqueous-phase solute concentrations, expressed as the regression slope for {"large" drop conc = slope * "smaller" drop conc} where "large" drops are from the upper stage and "smaller" drops are from the bottom sampler stage and in terms of mean concentration difference for {large–small} drops, i.e. Δ mean (all units are $\mu eq\ \ell^{-1}$ except for pH)

Species	Mean 12	SD	Mean 13	SD	Δ Mean	No. of Pairs	Regression slope b	SE(b)	Size dep[a]
Na	194.0	163.0	302.0	291.0	109.0	33	1.6	0.5	yes
Cl	328.0	375.0	498.0	519.0	169.0	33	1.4	0.4	yes
Mg	51.0	53.0	74.0	77.0	23.0	33	1.5	0.5	yes
Ca	35.0	45.0	54.0	92.0	19.0	34	1.8	0.7	yes
K	8.0	10.0	12.0	20.0	4.0	35	1.8	0.5	yes
SO₄	75.0	62.0	87.0	72.0	12.0	33	1.1	0.3	no
SO₄xs	46.0	41.0	45.0	41.0	− 0.7	33	1.0	0.3	no
NH₄	13.0	14.0	13.0	12.0	0.0	34	0.9	0.3	no
NO₃	33.0	36.0	43.0	51.0	10.0	34	1.3	0.5	no
H⁺	37.0	50.0	41.0	65.0	4.0	21	1.2	0.2	weak
MSA	1.7	2.2	1.8	2.4	0.1	10	1.0	0.1	no
Formate	6.4	4.9	6.5	3.0	0.1	10	0.8	0.3	no
Acetate	2.9	2.1	2.6	1.7	− 0.3	10	0.8	0.2	no

SE(b) is the standard error of regression slope.

$$SE(b) = \left\{ \frac{1}{N-1} \frac{\sum (y_{meas} - bx_{meas})^2}{\sum x_{meas}^2} \right\}^{0.5}$$

where $X_{meas} = 12\ \mu m\ d_{50}$, i.e.—lower stage concentration (referred to as "small" or "all" drops) $Y_{meas} = 13\ \mu m\ d_{50}$, i.e. upper stage concentration (large drops).

[a] Size dependence ("yes" implies that large droplets were more concentrated than smaller drops at the 85% confidence level).

similar to these from CACHE-1 in that large droplets and more concentrated than small drops for total solute mass and for sea salt.

4.5. *Data correlations and PLS modeling*

The aqueous-phase concentrations of five sea-salt species were highly correlated ($0.81 \leqslant r \leqslant 0.96$; for various pairs) in cloud water. These sea-salt-derived species also display the strongest negative correlation ($0.42 \leqslant |r| \leqslant 0.48$) to LWC of all the species measured in cloud water. Non-sea-salt sulfate (SO_4^{2-}xs) was correlated ($0.72 \leqslant r \leqslant 0.93$) with NO_3^-, H^+, and N_d (droplet number concentration as measured by the FSSP-100). All solute concentrations were correlated to CN concentration ($0.61 \leqslant r \leqslant 0.92$ for SO_4^{2-}xs, NO_3^-. H^-, Al, Mn, V, and Pb).

A five-component PLS model related 74% of the variance in air-equivalent cloud water composition for 18 species to three air mass trajectory classes (Fig. 1), cloud LWC, precipitation status (drizzling or not), and CN concentration. Table 3 presents PLS loadings (analogous to the correlation between the variable and the PLS component) for the chemical and physical variables for the first three PLS components, i.e. those that dominate the variability in the data (two-thirds of the modeled variance). The samples were sorted by PLS to identify two "outliers" (different than the other data for the same trajectory

class at 95% CI) and discarded as either unreliable or unusual. Thus, the PLS components described in Table 3 reflect the typical sources of variability in the bulk of the collected samples.

The PLS loadings have been interpreted in terms of possible emission source influences ("factors") on the collected samples. Continental trajectories had a strong association with CN (aerosol number), Pb, Ni, V, SO_4^{2-}xs, and NO_3^- concentrations (component #1, Table 3) consistent with an anthropogenic influence such as combustion (Gordon, 1988; Kowalczyk *et al.*, 1978) and with crustal contributions (Al, Mn) (component #4, not shown). Cloud water samples collected when the site was influenced by coastal trajectories tended to have higher values for both cloud LWC and the concentrations of three organic anions and H^+ compared to samples with oceanic trajectories (component #2, Table 3), suggesting biogenic influences on pH and a tendency for thick cloud to occur under this flow pattern (up to the coast of Oregon and Washington to the sampling site). Both oceanic and coastal trajectories occurred when samples had high Na^+, Mg^{2+}, Cl^-, Ca^{2+}, and K^+ concentrations but low CN concentrations (component #3, Table 3), consistent with sea-salt aerosol.

Overall, the PLS model identified separate seasalt, anthropogenic (presumably "pollution"-related), biogenic, and crustal source contributions that are each

Table 3. Sources of variability in cloud water chemical composition identified from PLS regression

	x: chemistry		y: trajectory and microphysics	
	Variable beta[a]		Variable beta[a]	
Component 1	V	− 0.33	CN	− 0.41
30% X variance	Ni	− 0.33	Continental	− 0.38
	Pb	− 0.33	Precip	0.56
	Cu	− 0.31	LWC	0.37
	Al	− 0.32	Coastal[b]	0.31
	SO_4xs	− 0.23		
	NO_3	− 0.24		
Component 2	Formate	− 0.42	Coastal[b]	− 0.62
19% X variance	Acetate	− 0.38	LWC	− 0.52
	NH_4	− 0.38	Oceanic	0.55
	MSA	− 0.37		
	SO_4xs	− 0.31		
	NO_3	− 0.28		
	H^+	− 0.25		
Component 3	Na	− 0.46	LWC	− 0.28
12% X variance	Cl	− 0.44	Coastal	− 0.23
	Mg	− 0.42	Oceanic	− 0.27
	Ca	− 0.39	Continental	0.85
	H^+	− 0.36	CN	0.27

The PLS X-components (cloud chemistry) are related to the Y-components through a regression coefficient (not shown). The variables comprising the Y-matrix were three air mass trajectory classes (Fig. 1), CN concentration, cloud LWC, and precipitation status[c] at the site. The listed variables all have strong associations with the first three PLS components and with the other variables listed for the same PLS component.

[a] The strength of the associations between the measurements and the individual PLS components is described by the listed variable loadings (beta).

[b] continental, coastal, and oceanic refer to air mass trajectory classes.

[c] A negative association with precipitation means that concentrations are higher in non-precipitating than in drizzling clouds.

related to specific transport patterns and cloud LWC. PLS components #1 and #4 were not important for coastal or oceanic trajectories.

4.6. Background cloud water composition

Table 4 presents our best estimate of a northern hemisphere, mid-latitude, background ("clean air") for marine cloud water based on springtime sampling during CACHE-1. While the data represent but 1 month's sampling, they still represent the largest available data base (102 different sample collection periods generated 48 2–3 h samples for clean, marine, North Hemisphere, mid-latitude cloud water composition that have been published to date). Mean cloud water data are presented both as time-weighted

Table 4. Estimates of northern hemisphere background composition from cloudy periods at Cheeka Peak, WA (CACHE-1: May 1993) N refers to number 2–3 h periods

LWC, ozone, aerosol, and wind speed during cloud

	Mean	SD	Units	N
LWC	0.3	0.2	$gm\,m^{-3}$	48
O_3	30.0	5.0	ppbv	48
CN	471.0	173.0	cm^{-3}	48
vmd	14.0	3.0	μm	48
N_d	217.0	97.0	cm^{-3}	48
U	7.0	2.0	$m\,s^{-1}$	48

Cloud water solute composition (N refers to 2–3 h periods) expressed as both aqueous-phase and air-equivalent concentrations

Major Ions

| | Aqueous phase as $\mu eq\,\ell^{-1}$: | | Air-equivalent conc as $neq\,m^{-3}$ | |
	Mean	SD	Mean	N
SO_4^{2-}	63.5	38.9	16.2	47
Na^+	290.6	236.9	68.3	45
Cl^-	432.9	369.6	96.9	47
Mg^{2+}	66.4	55.5	15.9	39
Ca^{2+}	36.1	37.0	9.2	39
K^+	8.1	5.8	2.0	48
NH_4^+	11.1	10.1	3.3	48
$SO_4 xs^{2-}$	27.9	19.8	8.0	47
NO_3^-	15.1	12.9	4.2	47
H^+	35.0	16.5	10.0	46
$CH_3SO_3^-$	3.4	3.5	1.0	36
$HCOO^-$	6.4	7.3	2.3	36
CH_3COO^-	2.9	4.5	1.1	36

Trace Elements

| | Aqueous phase as $\mu g\,\ell^{-1}$ (ppb): | | Air-equivalent conc as $ng\,m^{-3}$ | |
	Mean	SD	Mean	N
Al	9.7	8.2	2.9	37
V	1.3	1.5	0.4	37
Mn	1.1	1.0	0.3	37
Ni	0.5	0.4	0.2	37
Cu	1.7	1.6	0.5	37
Pb	0.5[a]	0.5	0.1[a]	37

[a] Experimental limit of detection.

aqueous-phase cloud water concentrations and as air-equivalent concentrations. LWC-weighted mean aqueous-phase concentrations can be obtained by dividing air-equivalent values by the mean LWC $(0.3\,g\,m^{-3})$.

These cloud water background concentrations are quite low compared to other measurements (Jacob et al., 1985; Ogren and Rodhe, 1986; Weathers et al., 1988; Mohnen and Kadlecek, 1989; Basabe et al., 1989; Fuzzi et al., 1992; Collett et al., 1993; Mohnen and Vong, 1993; Schumenauer et al., 1995), suggesting that our goal of estimating background values has been met. The cloud water (non sea salt) SO_4^{2-} and NO_3^- values from CACHE-1 (Table 4) compare well to "clean-air" cloud water mean air-equivalent concentration of 5.3 and 2.7 neq m^{-3}, respectively, derived from selected aircraft flights over eastern Canada in a study by Leaitch et al. (1992).

4.7. Discussion

The overall mean concentrations of major ions and trace elements measured during CACHE-1 for non-precipitating clouds are low. As expected, rain water was found to be more dilute than cloud water. The stoichiometry of the cloud water samples is similar to that for marine rain water (see Table 1). The air-equivalent $SO_4^{2-}xs$ value of $0.38\,\mu g\,m^{-3}$ for the CACHE-1 cloud water data is quite similar to aerosol data for clean marine locations worldwide (Leaitch et al., 1992; Savoie, 1984).

Non-sea-salt, or "excess", sulfate contributes about one-half of the measured non-sea-salt anion equivalents followed by nitrate and three organic acids (see Table 4) while H^+ dominates the sum of non-sea-salt cations for the cloud water samples. The measured $SO_4^{2-}xs/NO_3^-$ equivalent ratio of 2 is similar to values for clean rain. The measured $MSA/SO_4^{2-}xs$ ratio is consistent with values for atmospheric aerosol from mid-latitude and tropical sites (Saltzman et al., 1986) but lower than values observed for colder regions such as the Arctic (Li and Barrie 1993). The three analyzed organics account for one-fourth of the non-sea-salt anion equivalents, suggesting that clean, marine areas have a substantial organic contribution to cloud water solute. Both aerosol, as suggested by Novakov and Penner (1993), and gas-phase (Keene et al., 1995) contributions to cloud water organic species are likely.

Ogren and Charlson (1992) showed theoretically that droplet condensation growth leads to a situation where large droplets, while acquiring more water than small droplets, actually dilute more slowly than do the smaller droplets in the same cloud. As moist air is lifted to a mountaintop, coarse mode (diameter $> 2\,\mu m$) sea-salt aerosol nucleate readily and form large cloud droplets while the sub-μm aerosol are more likely end up in the smaller cloud droplets (Pruppacher and Klett, 1978). Since the large droplets experience proportionally less dilution, coarse mode

species such as sea salt should be more concentrated in large droplets. This, the most obvious of predicted size dependences (Ogren and Charlson, 1992), corresponds quite well to the pattern that emerges from CACHE-1 measurements in that soluble species derived from coarse mode aerosol (Na^+, Ca^{2+}, Cl^-, K^+, Ca^{2+}) are shown to be more concentrated in the large drops while species with substantial gas phase partitioning in clear air (formate, acetate) have a tendency to be more concentrated in the smaller cloud droplets. Species with likely sources in both fine mode aerosol and gas phase (SO_4^{2-} xs and NH_4^+) displayed no measurable size dependence in cloud water concentrations observed during CACHE-1. Data presented elsewhere (Collett et al., 1993, 1994; Ogren et al., 1992) sometimes describe higher concentrations in smaller drops than in large cloud droplets. However, when published results are stratified in order to examine only the simpler system represented by liquid phase, marine clouds (Collett et al., 1994: Munger et al., 1989; Noone et al., 1988), the large droplets are more concentrated for sea-salt species (i.e. those derived from hygroscopic "coarse mode" aerosol).

Both ambient cloud droplet size and sampler aspiration efficiency serve to sharply reduce differences in droplets collected by the two sampler stages from a 7 μm change in characteristic droplet size (Δvmd), as expected from impaction principles alone, to ~ 1 μm Δvmd for actual conditions in the field. Thus, the measured "significant differences" (at 85% CI) in certain solute concentrations correspond to very small differences in mean collected droplet size for the two sampler stages.

According to the model of condensational growth of hygroscopic aerosol examined by Ogren and Charlson (1992), the typical CACHE-1 measured ratio in solute concentrations for sea-salt-derived species of ~ 1.5 is entirely consistent with the 1.1 ratio in collected droplet diameter for the two sampler stages. The lack of any observed size dependence for the other species likely reflects a more complicated set of processes governing the cloud water solute concentrations for non-sea-salt species, for example, aqueous-phase production of sulfate in the clouds.

Air-equivalent cloud water chemical species concentrations varied over time scales of a few hours and were shown to relate to air-mass trajectories, whereas aqueous-phase concentrations varied over time scales of minutes (within individual events) and were more likely to correlate to LWC.

ICP-MS was successfully used to detect seven trace elements in the cloud water samples and these species proved useful in defining a cloud water background reference point. The mean CACHE-1 trace element concentrations from ICP-MS are similar to the very lowest reported values, for example trace metals in cloud water observed near the coast of Chile by Schemenauer and Cereceda (1992); these low levels of trace species lend further credence to the notion that CACHE-1 data represent the best available

estimate of a true marine background cloud water composition.

The PLS model provided a convenient means by which to simultaneously consider correlated variables for the 20 chemical and microphysical variables that were measured precisely during cloud events. The PLS analysis was able to discern differences in the degree of anthropogenic influence on the two marine trajectories compared to cloud collected under continental trajectories, in part, because of the inclusion of the trace element measurements from ICP-MS. Although the coastal and oceanic classes differed in their LWC and organic acid concentrations, and to a smaller extent NH_4^+ and SO_4^{2-} xs, no differences between these two trajectory types for any species normally associated with "pollution" or continental sources (e.g. NO_3^-, Pb, V, Ni, Al, Mn) were identified. We have chosen to use samples from both oceanic and coastal air mass trajectories in defining a marine background cloud water composition.

Inspection of the PLS-identified outlier samples revealed high CN concentrations (CN > 800 cm^{-3}) and elevated trace metal concentrations during coastal or oceanic trajectories. This "chemical-meteorological criteria" selected samples for the background definition based upon a consistent composition–air-mass trajectory relationship and only when the cloudy air was sampled under marine (either coastal or oceanic) flow. In effect, our PLS-based "meteorological–statistical" sample screening criteria for identifying "background samples" achieved a similar result to that which would be obtained by stratifying the chemical data by trajectory and CN concentration (CN < 800 cm^{-3}). However, PLS provided an added benefit in that groups of correlated species in the chemical and physical data were determined and samples that did not fit those correlation patterns were easily identified and eliminated from our definition of a background.

Specific "chemical fingerprints" associated with samples collected during continental air-mass trajectories were utilized to differentiate relatively "polluted" air from cloud collected during "clean" air. On this basis, coastal and oceanic air-mass trajectories were selected for the purpose of estimating the northern hemisphere's mid-latitude, marine, background cloud water composition from samples collected on the Olympic Peninsula of Washington State.

5. CONCLUSIONS

Sampler characterization and sample collection and analysis revealed the heterogeneous nature of non-precipitating cloud droplets that were sampled at Cheeka Peak, Washington during May 1993. Large droplets (~ 13 μm diameter) were found to be ca. 1.5 times as concentrated as smaller droplets (~ 12 μm diameter) for five sea-salt species but not for non-sea salt SO_4^{2-} and pH. Preprocessing of this cloud water

chemical data to form air-equivalent solute concentrations, along with the application of a multivariate statistical model (PLS), allowed the determination of the dependence of composition on air-mass trajectory. The results of this PLS modeling formed the basis for a "meteorological–statistical" method for selecting a consistent set of "clean" cloud water samples that subsequently were averaged in order to characterize a suite of typical background concentrations for northern hemisphere, mid-latitude, maritime cloud water.

REFERENCES

Basabe, F. A., Chang, W. L., Larson, T. V. and Edmunds, R. L. (1989) Fog and cloud water chemistry in Western Washington. In *Effects of Air Pollution on Western Forests*, eds R. K. Olsen and A. S. Lefohn, pp. 33–49. Transactions of the Air and Waste Management Assoc., Pittsburgh, Pennsylvania.

Beswick, K. M., Hargreaves, K., Gallagher, M. W., Choularton, T. W. and Fowler, D. (1991) Size-resolved measurements of cloud droplet deposition velocity to a forest canopy using an eddy correlation technique. *Q. Jl R. Met. Soc.* 117, 623–645.

Box, G. E. P., Hunter, W. G. and Hunter, J. S. (1978) *Statistics for Experimenters*, p. 459. Wiley, New York.

Charlson, R. J., Vong, R. J. and Hegg, D. A. (1983) Sources of sulfate in precipitation. II. Sensitivity to chemical variables. *J. geophys. Res.* 88, 1375–77.

Charlson, R. J., Lvelock, J. E., Andreae, M. O. and Warren, S. G. (1987) Oceanic phytoplankton, atmospheric sulfur, cloud albedo, and climate. *Nature* 326, 655–661.

Cheatham, M. M., Sangrey, W. F. and White, W. M. (1993) Sources of error in external calibration, ICP-MS analysis of geological samples and an improved non-linear drift correction procedure. *Spectrochim. Acta* 48B, E487–E506.

Collett, J. L. Jr., Oberholzer, B. and Staehelin, J. (1993) Cloud chemistry at Mt. Rigi Switzerland: dependence on droplet size and relationship to precipitation chemistry. *Atmospheric Environment* 27A, 33–42.

Collett, J. L. Jr., Iovinelli, R. and Demoz, B. (1995) A three-stage cloud impactor for size-resolved measurements of cloud drop chemistry. *Atmospheric Environment* 29, 1145–1154.

Collett, J. L. Jr., Bator, A., Rao, X. and Demoz, B. B. (1994) Acidity variations across the cloud drop size spectrum and their influence on atmospheric sulfate production rates. *Geophys. Res. Lett.* 21, 2393–2396.

Covert, D. S. (1988) North Pacific marine background aerosol: average ammonium to sulfate molar ratio equals 1. *J. geophys. Res.* 93, 8455–8458.

Currie, L. A. (1968) Limits for qualitative detection and quantitative determination, application to radiochemistry. *Anal. Chem.* 40, 586–590.

Fuzzi, S. et al. (1992) The Po valley fog experiment, an overview. *Tellus* 44B, 448–468.

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

Gordon, G. E. (1988) Receptor models. *Envir. Sci. Technol.* 22, 1132–1142.

Harris, J. M. and Kahl, J. D. W. (1994) Analysis of 10-day isentropic flow patterns for Barrow, Alaska: 1985–1992. *J. geophys. Res.* 99, 25,845–25,855.

Harris, J. M. (1992) An analysis of 5-day mid-tropospheric flow patterns for the South Pole: 1985–89. *Tellus* 44B, 409–421.

Hegg, D. A., Yuen, P. and Larson, T. V. (1992) Modeling the effects of heterogeneous cloud chemistry on the marine particle size distribution. *J. geophys. Res.* 97, 12,927–12,934.

Hering, S. A. et al. (1987) Field intercomparison of five types of fogwater collectors. *Envir. Sci. Technol.* 21, 654–663.

Hoppel, W. A., Fitzgerald, J. W., Frick, G. M., Larson, R. E. and Mack, E. J. (1990) Aerosol size distributions and optical properties found in the marine boundary layer over the Atlantic Ocean. *J. geophys. Res.* 95, 3659–3686.

Jacob, D. J., Waldman, J. M., Munger, J. W. and Hoffmann, M. R. (1985) Chemical composition of fogwater collected along the California coast. *Envir. Sci. Technol.* 19, 730–736.

Jarvis, K. E., Gray, A. L. and Houk, R. S. (1992) *Handbook of Inductively Coupled Plasma Mass Spectrometry*, Glasgow, Blackie.

Keene, W. C. et al. (1995) Carboxylic acids in clouds at a high-elevation forested site in central Virginia. *J. geophys. Res.* 100, 9345–9357.

Kowalczyk, G. S., Chouquette, C. E. and Gordon, G. E. (1978) Chemical element balances and identification of air pollution sources in Washington D.C. *Atmospheric Environment* 12, 1143–1153.

Kowalski, A. S. (1996) Occult cloud water deposition to a forest in complex terrains: measurements and interpretation. PhD Thesis, Oregon State University, Corvallis, OR, 213 pp.

Li, S.-M. and Barrie, L. A. (1993) Biogenic sulfur aerosol in the Arctic troposphere: 1. Contributions to total sulfate. *J. geophys. Res.* 98, 20,613–20,622.

Langmuir, I. and Blodgett, K. (1961) Mathematical investigation of water droplet trajectories. In *The Collected Works of Irving Langmuir*, ed. C. G. Suits, Vol. 10. Atmospheric Phenomena, Pergamon, Elmsford.

Leaitch, W. R., Isaac, G. A., Strapp, J. W., Banic, C. M. and Weibe, H. A. (1992) The relationship between cloud droplet number concentrations and anthropogenic pollution: observations and climatic implications. *J. geophys. Res.* 97, 2463–2474.

Lovett, G. M. and Kinsman, J. D. (1990) Atmospheric pollutant deposition to high-elevation ecosystems. *Atmospheric Environment* 24A, 2767–2786.

Merrill, J. T., Bleck, R. and Avila, L. (1985) Modeling atmospheric transport to the Marshall Islands. *J. geophys. Res.* 90, 12,927–12,936.

Mohnen, V. A. and Vong, R. J. (1993) A climatology of cloud chemistry for the eastern United States derived from the mountain cloud chemistry project. *Envir. Rev.* 1, 38–54.

Mohnen, V. A. and Kadlacek, J. A. (1989) *Cloud Chemistry Research at Whiteface Mountain* 41B, 79–91.

Munger, J. W., Collett, J. Jr., Daube, B. Jr. and Hoffmann, M. R. (1989) Chemical composition of coastal stratus clouds: dependence on droplet size and distance from the coast. *Atmospheric Environment* 23, 2305–2320.

Noone, K. J., Charlson, R. J., Covert, D. S., Ogren, J. A. and Heitzenberg, J. (1988) Cloud droplets: solute concentration is size-dependent. *J. geophys. Res.* 93, 9477–9482.

Noone, K. J., Hansson, H.-C. and Mallant, R. K. A. M. (1992) Droplet sampling from crosswinds: an inlet efficiency calibration. *J. Aerosol Sci.* 23, 153–164.

Novakov, T. and Penner, J. E. (1993) Large contribution of organic aerosol to cloud condensation nuclei concentrations: evidence from a marine site. *Nature* 365, 823–826.

Ogren, J. A. *et al.* (1992) Measurements of the size-dependence of the concentration of non-volatile material in fog droplets. *Tellus* **44B**, 570–580.

Ogren, J. A., Heintzenberg, J., Zuber, A., Noone, K. J. and Charlson, R. J. (1989) Measurements of the size-dependence of solute concentrations in cloud droplets. *Tellus* **41B**, 24–31.

Ogren, J. and Rodhe, H. (1986) Measurements of the chemical composition of cloudwater at a clean air site in central Scandanavia. *Tellus* **38B**, 1980–196.

Ogren, J. A. and Charlson, R. J. (1992) Implications for models and measurements of chemical inhomogeneities among cloud droplets. *Tellus* **44B**, 208–225.

Pade, G. P., Larson, T. V. and Covert, D. S. (1987) Design and calibration of a high volume cloudwater collector. *J. atmos. Ocean Technol.* **4**, 340–344.

Pandis, S. N., Seinfeld, J. H. and Pilnius, C. (1990) Chemical composition differences in fog and cloud droplets of different sizes. *Atmospheric Environment* **24A**, 1957–1969.

Pruppacher, H. R. and Klett, J. D. (1978) *Microphysics of Clouds and Precipitation*. D. Reidel, Dordrecht.

Saltzman, E. S., Savoie, D. S., Prospero, J. M. and Zika, R. G. (1986) Methane sulfonic acid and non-seasalt sulfate in Pacific air: regional and seasonal variations. *J. atmos. Chem.* **4**, 227–240.

Savoie, D. L. (1984) Nitrate and non-seasalt sulfate aerosols over major regions of the world ocean. Ph.D. thesis, University of Miami.

Schell, D., Georgii, H.-W., Maser, R., Jaeschke, W., Arends, B. G., Kos, G. P., Winkler, P., Schneider, T., Berner, A. and Kruisz, C. (1992) Intercomparison of fogwater samplers. *Tellus* **44B**, 612–631.

Schememauer, R. S. and Cereceda, P. (1992) The quality of fog water collected for domestic and agricultural use in Chile. *J. appl. Met.* **31**, 275–290.

Schemenauer, R. S., Banic, C. M. and Urquizo, N. (1995) High elevation fog and precipitation chemistry in Southern Quebec, Canada. *Atmospheric Environment* **29**, 2235–2252.

Seinfeld, J. H. (1986) *Atmospheric Chemistry and Physics of Air Pollution*, p. 25 Wiley, New York.

Taylor, S. R. (1964) Abundance of chemical elements in the continental crust: a new table. *Geochim. Cosmochem. Acta* **28**, 1273–1285.

Vincent, J. H. (1989) *Aerosol Sampling Science and Practice*, pp. 86–118. Wiley, New York.

Vong, R. J., Sigmon, J. and Mueller, S. F. (1991) Cloudwater deposition to Applachian Mountain forest. *Envir. Sci. Technol.* **25**, 1014–1021.

Vong, R. J. and Kowalski, A. S. (1995) Eddy correlation measurements of size-dependent cloud droplet turbulent fluxes to complex terrain. *Tellus* **47B**, 331–352.

Vong, R. J., Bailey, B., Markus, M. and Mohnen, V. A. (1990) Factors governing the cloudwater composition in the Applachian Mountains. *Tellus* **42B**, 435–453.

Vong, R. J., Hansson, H.-C., Ross, H. B., Covert, D. S. and Charlson, R. J. (1988a) Northeastern Pacific sub-micrometer aerosol and rainwater composition: a multivariate analysis. *J. geophys. Res.* **93**, 1625–1637.

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

Vong, R. J. (1990) Mid-latitude northern hemisphere background sulfate concentration in rainwater. *Atmospheric Environment* **24A**, 1007–1018.

Vong, R. J. (1993) Atmospheric chemometrics for the identification of trace element sources in precipitation. *Anal. Chim. Acta* **277**, 389–404.

Weathers, K. C. *et al.* (1988) Cloudwater chemistry from ten sites in North America. *Envir. Sci. Technol.* **22**, 1018–1026.

Winkler, P. (1986) Observation of fogwater composition in Hamburg. In *Atmospheric Pollutants in Forest Areas*, ed. H. W. Georgii, pp. 143–151. D. Reidel.