

## A Ten-Winter Record of Cloud-Droplet Physical and Chemical Properties at a Mountaintop Site in Colorado

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### ABSTRACT

Cloud-droplet spectra and coincident cloud water pH measurements have been made for a portion of ten consecutive winters (1983/84–1992/93) from clouds that enveloped Storm Peak Laboratory in northwestern Colorado; cloud water ion measurements were made for eight of the winters. To determine if the physical and chemical properties are related, the data were stratified into three populations:  $\text{pH} \leq 3.6$ ,  $3.6 < \text{pH} < 4.6$ ,  $\text{pH} \geq 4.6$ . It was found that clouds with the smallest pH values (3.4) had the largest droplet concentrations ( $N = 329 \text{ cm}^{-3}$ ), smallest mean droplet diameters ( $D_{\text{bar}} = 6.4 \text{ }\mu\text{m}$ ), and largest ion concentrations (e.g.,  $\text{SO}_4^- = 5.7 \text{ mg L}^{-1}$ ), while clouds with the largest pH values (5.1) had the smallest  $N$  values ( $189 \text{ cm}^{-3}$ ), largest  $D_{\text{bar}}$  values ( $8.0 \text{ }\mu\text{m}$ ), and smallest ion concentrations ( $\text{SO}_4^- = 3.9 \text{ mg L}^{-1}$ ). Nevertheless, all three populations had similar liquid water contents ( $\text{LWC} \cong 0.070 \text{ g m}^{-3}$ ). The equation  $\text{LWC} = \pi/6 D_{\text{bar}}^3 N \rho$ , where  $\rho$  is the density of water, closely describes the relationship between LWC,  $D_{\text{bar}}$ , and  $N$ . The range in pH values could not be completely explained by entrainment, or variations in cloud-base height or in LWC; differences in cloud condensation nucleus composition appear to be a major factor. No significant trends in average winter  $N$ ,  $D_{\text{bar}}$ , and pH values were found in the ten-winter record.

### 1. Introduction

A major scientific problem is determining the impact of anthropogenic cloud condensation nuclei (CCN) on clouds that form away from anthropogenic CCN sources. Clouds that form in the vicinity of most sources usually contain elevated droplet concentrations and reduced droplet sizes (e.g., Fitzgerald and Spyers-Duran 1973; Hobbs et al. 1980). If concentrations of CCN increase away from anthropogenic sources, it is expected that clouds that form in these regions will have characteristics similar to clouds that form in the vicinity of the sources. For example, Leitch et al. (1992) measured clouds over eastern North America and found that high concentrations of small droplets occur when the cloud water contains elevated sulfate concentrations; this they attribute to anthropogenic CCN. They calculated that the change in cloud albedo resulting from the anthropogenic sulfate could change the radiation balance by  $2\text{--}3 \text{ W m}^{-2}$  for eastern North America. Furthermore, Liou and Ou (1989) calculate that, on a global scale, slight changes in mean cloud droplet diameters will affect the production of precip-

itation and, hence, affect the cloud radiative balance. Therefore, it is important to determine, through measurements, if cloud-droplet concentrations and cloud water ionic concentrations are increasing and mean droplet diameters are decreasing away from anthropogenic CCN sources.

To identify trends in these values, long-term measurements of cloud-droplet physical and chemical properties are required. To the author's knowledge, no systematic measurements of these properties have been obtained at one location as in the  $\text{CO}_2$  measurements of Keeling et al. (1976); the measurements that initiated the global warming predictions.

As a first step in obtaining long-term measurements, we have measured cloud-droplet spectra and cloud water chemical compositions for a portion of every winter from the winter of 1983/84 through the winter of 1992/93 in clouds that enveloped 3220-m Storm Peak Laboratory (SPL). SPL is located on the crest of the Park Range in northwestern Colorado. Because of its high-elevation, midcontinent location, the site is affected by long-range transport over a variety of pathways as demonstrated by Borys et al. (1986). The purpose of this paper is to report the results from cloud-droplet physical and chemical measurements obtained for the ten winters and identify and attempt to explain significant trends in values of cloud-droplet concentrations

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$N$ , mean droplet diameters  $D_{\text{bar}}$ , liquid water contents LWC, and chemical constituents.

## 2. Measurements

Clouds envelop SPL most often during the winter months; during the months of December and January SPL is enveloped in cloud approximately 25% of the hours according to Hindman (1986). The clouds form when stably stratified air from the Pacific Ocean is forced over the north-south-oriented Park Range as described by Lee (1984) and Rauber et al. (1986). The clouds that envelop SPL are composed of supercooled cloud droplets and snow crystals; approximately 80% of the clouds contain droplets and snow crystals and 20% of the clouds contain only droplets. The average duration of a cloud event at SPL is about 4 h but events have persisted 48 and 72 h. Droplet measurements have been made primarily during the months of December and January and the number of cloud events has varied from winter to winter. For example, during a 2-week period in January 1991 SPL was in clear air for only 24 h, the remainder of the period SPL was in cloud. In contrast, during a 2-week period in January 1992, SPL was enveloped by cloud for only 24 h; the lab was in clear air the remainder of the period. The variable duration and occurrence of the cloud events caused the cloud-droplet sample size to unavoidably vary from winter to winter.

Cloud-droplet spectra were obtained with a "cloud gun" (a direct-impaction device) described by Hindman (1987a); accurate droplet spectra were produced with the instrument because all of the operational variables were measured. Droplets as small as 2- $\mu\text{m}$  diameter and as large as about 70  $\mu\text{m}$  could be measured; larger drops shatter upon impact. The largest droplets impacted were less than 40  $\mu\text{m}$ . One to two droplet spectra were obtained during a cloud event as frequently as every half hour to augment the cloud chemistry investigations described by Borys et al. (1988) and Carter and Borys (1992). More commonly, spectra were obtained every 2–4 h. Since the winter of 1990/91, three droplet spectra were obtained every 6 h at 0000, 0600, 1200, and 1800 UTC to coincide with the 0000 and 1200 UTC National Weather Service upper-air soundings to facilitate back-trajectory calculations. The 2D trajectories were calculated by hand on the 700-mb surface (SPL is located near the 700-mb level) using the method of successive approximations developed by Petterssen (1956). For each cloud-droplet spectra, the  $N$ ,  $D_{\text{bar}}$ , and LWC values were determined:  $N$  values were determined by summing the droplet concentrations in all size intervals,  $D_{\text{bar}}$  values were determined from the arithmetic mean of the spectra, and LWC values were determined by summing the LWC of the droplets in all size intervals.

Cloud water samples were collected at the same time as the cloud-droplet spectra. Both passive (Borys et al.

1988; Hindman et al. 1992a) and active (Rogers et al. 1983) collectors were used. The cloud droplets were always collected at temperatures below 0°C and, hence, the droplets were supercooled. The smallest droplets collected with 50% efficiency were about 4  $\mu\text{m}$  in diameter for both types of collectors. The droplets impacted and froze on the collectors. The resulting ice deposits were removed from the collectors for chemical analyses. A portion of each ice deposit was melted, and immediately its pH and conductivity were measured to avoid possible contamination due to absorbed gases and particles (it is assumed the pH of the subcooled droplets did not change when the droplets impacted and froze on the collectors). The pH was determined using a micro-pH probe that could analyze samples as small as 0.1 mL to an accuracy of  $\pm 0.1$  pH unit. The conductivity, corrected to 25°C, was determined using a conductivity bridge and probe; reported values have an uncertainty of  $\pm 5\%$ . The remainder of each ice deposit was kept frozen for ionic and trace-element analyses as described by Borys et al. (1988). The latter analyses were performed on select winter samples for the studies of Borys et al. (1988) and Carter and Borys (1993). Therefore, not all winters had ionic or trace-element measurements. Beginning with the winter of 1991/92, a majority of the cloud water samples had ionic composition measurements.

The winter of 1987/88 did not have pH measurements, but had ionic composition measurements ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ). Consequently, pH values were calculated from the ionic composition measurements assuming the  $\text{H}^+$  were associated with sulfuric, nitric, and hydrochloric acids. To test the calculation procedure, calculated pH values from ionic composition measurements from 17 cloud water samples were compared with corresponding pH measurements. The calculated pH values were found to be systematically high; apparently not all the important acid species were measured. Nevertheless, the resulting linear regression between the measured and calculated pH values was

$$\text{pH}_{\text{meas}} = 0.55\text{pH}_{\text{calc}} - 1.945, \quad (1)$$

with a correlation of 0.43 and  $P$  value of 0.009. Equation (1) is valid for  $\text{pH}_{\text{calc}}$  values between 3.6 and 4.7. Equation (1) was applied to  $\text{pH}_{\text{calc}}$  values resulting from ionic composition measurements to produce expected  $\text{pH}_{\text{meas}}$  values.

Five hundred and thirty-two cloud-droplet spectra were obtained at SPL for the winters of 1983/84–1992/93. Three hundred sixty-three of the spectra had corresponding cloud water pH measurements and 22 had corresponding  $\text{pH}_{\text{meas}}$  values from (1) for a total of 385 spectra. Of these 385 spectra, 199 had corresponding ionic composition measurements and 152 had corresponding ionic composition and conductivity measurements.

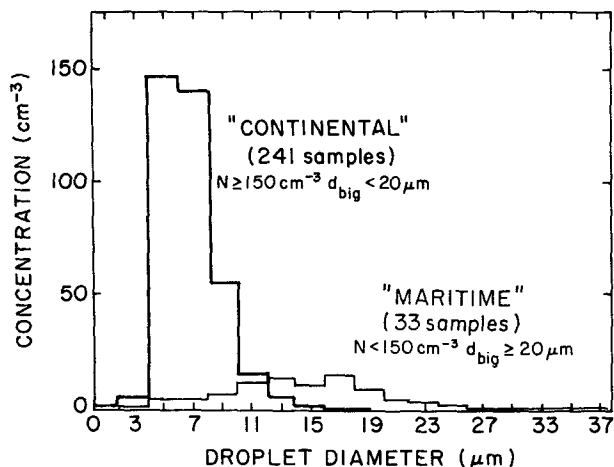


FIG. 1. Average continental and maritime cloud-droplet spectra at SPL for the winters of 1983/84–1990/91 (from Hindman et al. 1992b). Continental spectra were those with concentrations  $N$  greater than or equal to  $150 \text{ cm}^{-3}$  and the largest droplet less than  $20 \mu\text{m}$  ( $d_{\text{big}}$ ) and vice versa for maritime spectra.

**3. Results**

Rauber and Grant (1986) measured droplet spectra from aircraft in wintertime clouds that formed over SPL and it is useful to compare their results with our surface measurements. Summarizing data in their Table 1, the six spectra with large  $N$  values ( $\sim 200 \text{ cm}^{-3}$ ) typically had small  $D_{\text{bar}}$  values ( $\sim 9 \mu\text{m}$ ) and the 22

spectra with small  $N$  values ( $\sim 70 \text{ cm}^{-3}$ ) typically had large  $D_{\text{bar}}$  values ( $\sim 14 \mu\text{m}$ ); the spectra, on average, contained about the same LWC ( $\sim 0.12 \text{ g m}^{-3}$ ). Their airborne measurements were obtained at the upper levels of the clouds due to terrain-avoiding flight restrictions.

Similar droplet spectra occur near the base of the clouds at SPL. The 368 cloud-droplet spectra obtained for the winters of 1983/84–1990/91 were stratified by Hindman et al. (1992a) into “continental” and “maritime” spectra and the results are given in Fig. 1. As can be seen, a majority of the spectra (241) had continental characteristics: large  $N$  values ( $350 \text{ cm}^{-3}$ ), small  $D_{\text{bar}}$  values ( $7 \mu\text{m}$ ), and small LWC values ( $0.090 \text{ g m}^{-3}$ ); 33 spectra had maritime characteristics: small  $N$  values ( $126 \text{ cm}^{-3}$ ), large  $D_{\text{bar}}$  values ( $16 \mu\text{m}$ ), and large LWC values ( $0.27 \text{ g m}^{-3}$ ). The remaining 94 spectra had mixed continental and maritime characteristics.

Isobaric trajectories of air parcels arriving at SPL at the time of the continental and maritime droplet spectra are given in Fig. 2. As can be seen, there is no obvious difference between the trajectories of the air parcels in which the two droplet populations formed (it is interesting to note that all the maritime trajectories had anticyclonic curvature). Also, Hindman et al. (1992b) reported there was no significant difference in the wind speeds or directions occurring at the time of the “continental” and “maritime” droplet spectra: respectively, wind speed  $6.0 \pm 0.54 \text{ m s}^{-1}$  versus  $6.8$

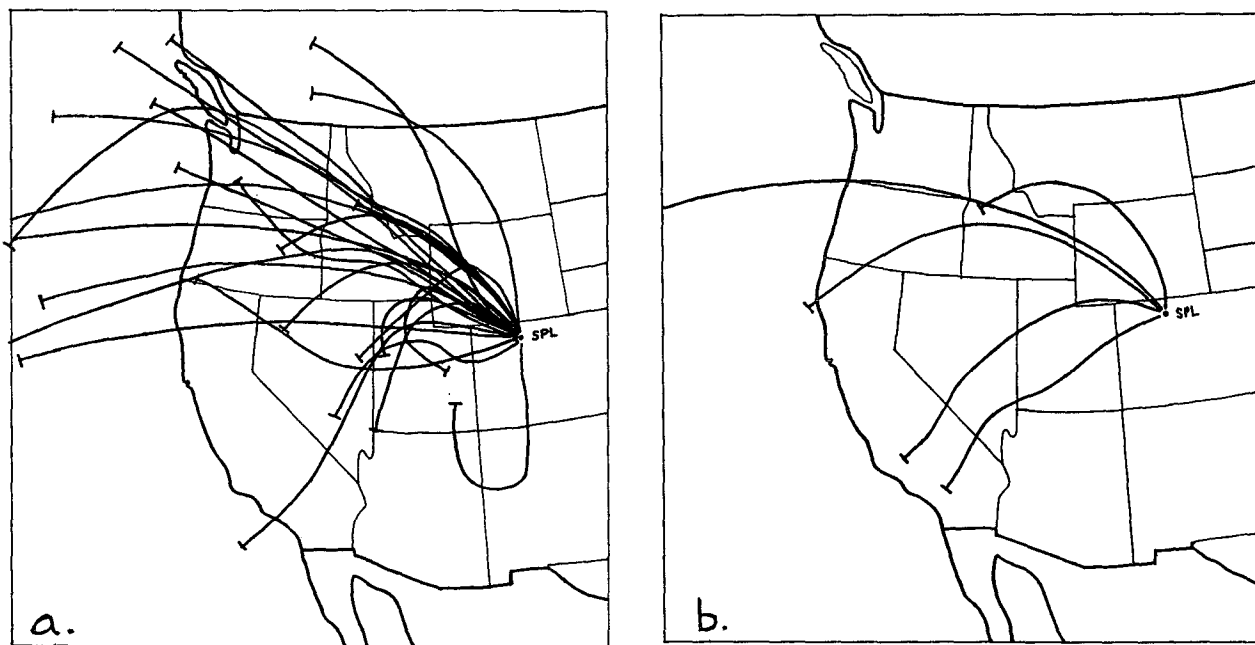


FIG. 2. Forty-eight-hour, 700-mb back trajectories originating at SPL for the winters of 1983/84–1990/91: (a) air parcels in which continental droplet spectra formed, (b) air parcels in which maritime droplet spectra formed. The trajectories were computed for spectra taken within  $\pm 2 \text{ h}$  of either 0000 or 1200 UTC (from Hindman et al. 1992b).

$\pm 0.80 \text{ m s}^{-1}$  and wind direction  $275^\circ \pm 9.5^\circ\text{T}$  versus  $290^\circ \pm 7.4^\circ\text{T}$ . But, they reported that the continental spectra formed in significantly colder clouds than did the maritime spectra ( $-9.1^\circ \pm 0.6^\circ\text{C}$  versus  $-5.8^\circ \pm 0.7^\circ\text{C}$ ).

Given the potential importance of cloud-droplet size in climate-change issues such as optical properties (Leitch et al. 1992) and ice-crystal riming rates (Borys et al. 1988), we investigated the relationship between  $D_{\text{bar}}$  and  $N$  for droplet spectra with similar values of LWC. To determine the most frequent LWC values at SPL, the 385 droplet spectra with corresponding pH measurements were stratified into  $0.02 \text{ g m}^{-3}$  LWC intervals and the results are presented in Fig. 3. As can be seen, the most frequent LWC values range from  $0.020$  to  $0.040 \text{ g m}^{-3}$  with a sample size of 90. The  $D_{\text{bar}}$  and corresponding  $N$  values for droplet spectra with these LWC values are plotted in Fig. 4. As can be seen, for similar LWC values, increasing values of  $D_{\text{bar}}$  results in decreasing values of  $N$ . This result is a truism for monomodal spectra; a majority of SPL droplet spectra are monomodal (Fig. 1). Further, the result is consistent with a similar analysis of additional LWC data from SPL by Hindman (1987b). Combining the analyses of Hindman (1987b) with the analysis shown in Fig. 3 results in the following relationship between LWC ( $\text{g m}^{-3}$ ),  $D_{\text{bar}}$  (m), and  $N$  ( $\text{m}^{-3}$ ) for wintertime clouds at SPL,

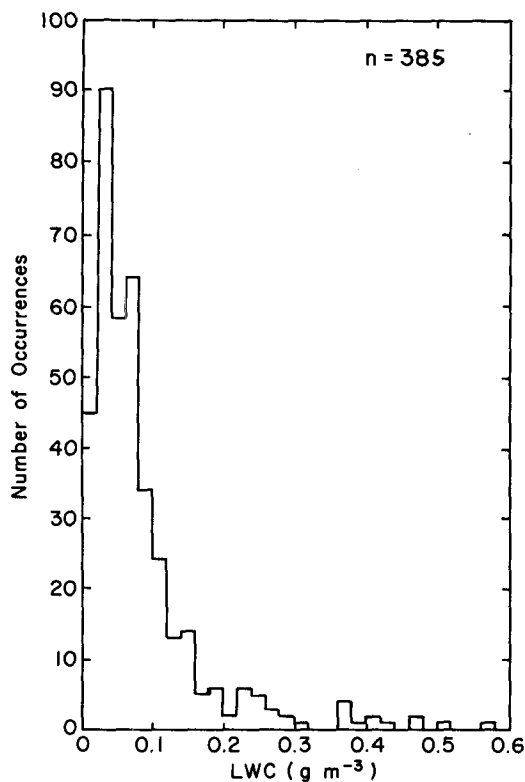


FIG. 3. Number of occurrences of liquid water content values for the 385 cloud-droplet samples with corresponding pH values collected at SPL for the winters of 1983/84–1992/93.

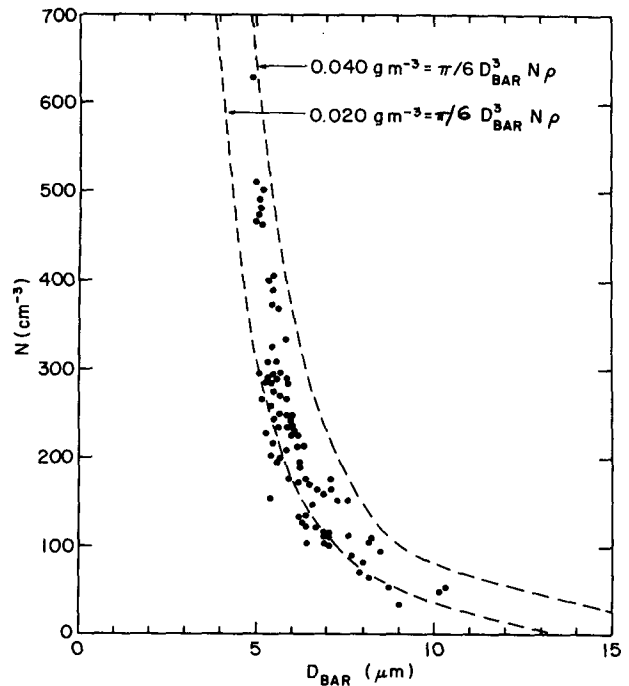


FIG. 4. Correlation of total droplet concentrations  $N$  and average droplet sizes  $D_{\text{bar}}$  for the 90 droplet samples in Fig. 3 with liquid water contents between  $0.020$  and  $0.040 \text{ g m}^{-3}$ . The results of solving Eq. (2) for liquid water contents of  $0.020$  and  $0.040 \text{ g m}^{-3}$  are indicated.

$$\text{LWC} = \frac{\pi}{6 D_{\text{bar}}^3 N \rho} \quad (2)$$

where  $\rho$  is the density of water ( $\text{g m}^{-3}$ ). Assuming the average cloud liquid water contents do not change in the future at SPL and if the average  $D_{\text{bar}}$  value ( $8 \mu\text{m}$ , Table 3) decreased about  $1 \mu\text{m}$ , according to (2) the average  $N$  value would increase about  $100 \text{ cm}^{-3}$ . Leitch et al. (1992) calculate such a change in  $D_{\text{bar}}$  and  $N$  would affect cloud albedos.

We have shown with (2) that, for droplet spectra with the same LWC values, spectra with large  $N$  values will have small  $D_{\text{bar}}$  values and vice versa. Because each cloud droplet formed on an aerosol particle containing soluble material, the droplet spectra with large  $N$  values activated the most CCN. Further, the same amount of water vapor condensed onto all the droplet spectra because the spectra were chosen to have similar LWC values. Assuming the soluble component of the CCN is the same for all droplet spectra, more ions would go into solution from the spectra with large  $N$  values. Consequently, cloud water samples from droplet spectra with large  $N$  values would be expected to be more chemically concentrated than samples with smaller  $N$  values, keeping LWC constant.

To test this idea, values of  $N$  are correlated with corresponding values of pH in Fig. 5 for the 90 cloud droplet spectra with LWC values between  $0.020$  and

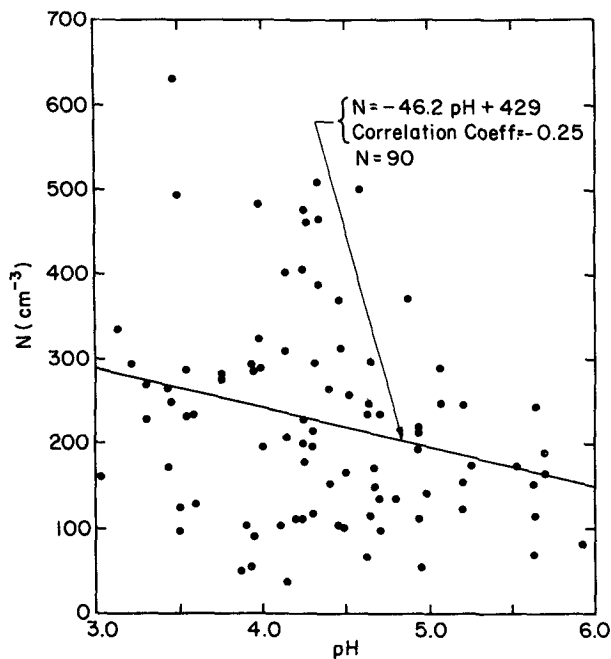


FIG. 5. Correlation of total droplet concentrations  $N$  and pH values for the 90 droplet samples in Fig. 3 with liquid water content values between  $0.020$  and  $0.040 \text{ g m}^{-3}$ . The least-squares, linear regression, and correlation coefficient for these data are indicated.

$0.040 \text{ g m}^{-3}$ . As can be seen, there is almost no correlation between  $N$  and pH. For example, droplet spectra with small  $N$  values (e.g.,  $200 \text{ cm}^{-3}$ ) had pH values that varied between 3.3 and 5.5. A droplet spectra with an  $N$  value of 200 formed on 200 CCN. Therefore, the 200 CCN must have been quite acidic to produce the cloud water sample with the pH of 3.3. Conversely, the 200 CCN must have been less acidic to produce the sample with the pH of 5.5. So, the chemical composition of CCN at SPL appears to vary for similar number concentrations and size distributions. Thus, a portion the scatter in pH values in Fig. 5 can be explained by variations in CCN chemical composition.

Walcek and Brankov (1993) calculate that pH values of cloud water can vary due to entrainment of dry air into a cloud keeping CCN constant. The effect of entrainment on pH is estimated as follows. Consider a droplet spectrum measured at SPL with an  $N$  value of  $200 \text{ cm}^{-3}$ , a  $D_{\text{bar}}$  value of  $5 \mu\text{m}$ , and an LWC value of  $0.02 \text{ g m}^{-3}$ , and a pH value of 3.5. Let us assume the spectrum had experienced entrainment of dry air and all the droplets that were measured had partially evaporated from the original spectrum that formed upwind of SPL. When the spectrum was newly formed, the values of  $N$ ,  $D_{\text{bar}}$ , and LWC were, respectively,  $200 \text{ cm}^{-3}$ ,  $10 \mu\text{m}$ , and  $0.1 \text{ g m}^{-3}$ ; these values were derived from (2). The  $[\text{H}^+]$  of the measured spectrum (pH = 3.5) was 0.000316. The mass of water decreased by a factor of 5 from the original spectrum to the spec-

trum measured at SPL. Therefore, the original  $[\text{H}^+]$  was  $0.00316/5$  or  $0.000632$ , which corresponds to a pH of 4.19. In this case, the pH was estimated to change from 4.19 to 3.5 due to entrainment. Thus, about half the scatter in pH values in Fig. 5 can be explained by entrainment.

To further investigate the relationship between droplet spectra and pH values, the 385 cloud-droplet spectra with coincident pH measurements were sorted into samples with the smallest and the largest pH values:  $\text{pH} \leq 3.60$  (53 samples) and  $\text{pH} \geq 4.60$  (128 samples); 204 samples had pH values between 3.60 and 4.60. The average  $N$ ,  $D_{\text{bar}}$ , LWC, and pH values of the three populations are listed in Table 1. As can be seen, the population with the smallest pH values contained the largest droplet concentrations and the smallest mean diameters while the population with the largest pH values contained the smallest droplet concentrations and the largest mean diameters. The differences between the two populations are statistically significant at less than the 1% level using the Student's  $t$ -test. It can be seen that the population with the intermediate pH values contained intermediate  $N$ ,  $D_{\text{bar}}$  values. The LWC values of the three populations were essentially the same.

To investigate the relationship between droplet spectra and ion concentrations, the 199 cloud droplet spectra with coincident pH and ionic measurements were sorted into those with  $\text{pH} \leq 3.60$  (38 samples) and  $\text{pH} \geq 4.60$  (69 samples); 92 samples had pH values between 3.60 and 4.60. The average physical and chemical properties of the three populations are listed in Table 2. As can be seen, the average LWC values of the three populations were nearly the same. The population with the smallest pH values contained the largest droplet concentrations, the smallest average droplet sizes, and the largest ion concentrations while the population with the largest pH values contained the smallest droplet concentrations, the largest average droplet sizes, and the smallest ion concentrations. It can be seen that the population with the intermediate pH values contained intermediate  $N$ ,  $D_{\text{bar}}$ , and ion values. The ion concentrations and conductivity values are consistent with the pH values: large ion concentrations and conductivity values occur with small pH values and vice versa.

TABLE 1. Average characteristics of cloud-droplet spectra from ten winters (1983/84–1992/93) of coincident droplet and pH measurements (385 samples). The plus/minus values represent standard errors,  $\sigma/(n - 1)^{1/2}$ .

	pH $\leq$ 3.6 (53 samples)	3.6 < pH < 4.6 (204 samples)	pH $\geq$ 4.6 (128 samples)
$N$ ( $\text{cm}^{-3}$ )	$360 \pm 24$	$282 \pm 12$	$190 \pm 13$
$D_{\text{bar}}$ ( $\mu\text{m}$ )	$6.4 \pm 0.18$	$8.2 \pm 0.21$	$8.4 \pm 0.32$
LWC ( $\text{g m}^{-3}$ )	$0.070 \pm 0.014$	$0.098 \pm 0.0075$	$0.079 \pm 0.0080$
pH	$3.38 \pm 0.022$	$4.15 \pm 0.019$	$5.08 \pm 0.034$

TABLE 2. Average characteristics of cloud-droplet spectra from ten winters (1983/84–1992/93) of coincident droplet, pH, and anion measurements (199 samples). The plus/minus values represent standard errors,  $\sigma/\sqrt{n}$  ( $n = 1$ ).

	pH $\leq$ 3.6 (38 samples)	3.6 < pH < 4.6 (92 samples)	pH $\geq$ 4.6 (69 samples)
$N$ ( $\text{cm}^{-3}$ )	329 $\pm$ 30	298 $\pm$ 16	189 $\pm$ 14
$D_{\text{bar}}$ ( $\mu\text{m}$ )	6.4 $\pm$ 0.23	7.6 $\pm$ 0.21	8.0 $\pm$ 0.33
LWC ( $\text{g m}^{-3}$ )	0.069 $\pm$ 0.019	0.078 $\pm$ 0.0065	0.056 $\pm$ 0.0052
pH	3.39 $\pm$ 0.024	4.12 $\pm$ 0.027	5.10 $\pm$ 0.051
$\text{SO}_4^-$ ( $\text{mg L}^{-1}$ )	5.72 $\pm$ 0.59	3.28 $\pm$ 0.28	3.86 $\pm$ 0.39
$\text{NO}_3^-$ ( $\text{mg L}^{-1}$ )	3.43 $\pm$ 0.36	2.72 $\pm$ 0.30	2.49 $\pm$ 0.31
$\text{Cl}^-$ ( $\text{mg L}^{-1}$ )	1.13 $\pm$ 0.24	0.91 $\pm$ 0.13	0.58 $\pm$ 0.058
Conductivity ( $\mu\text{mho cm}^{-1}$ at 25°C)*	47.8 $\pm$ 6.7 (19 samples)	34.2 $\pm$ 2.8 (66 samples)	28.9 $\pm$ 3.3 (67 samples)

\* The conductivity values are from 152 samples with coincident droplet, pH, anion, and conductivity measurements.

The results in Tables 1 and 2 indicate a relationship between droplet physical and chemical properties for similar LWC values. The results in Fig. 5 show no strong correlation between  $N$  and pH values, however. The results in Tables 1 and 2 are averages of samples and the results in Fig. 5 are for individual samples.

Averaging the results from individual measurements appeared to have reduced the fluctuations due to the effects of different CCN compositions and entrainment, which were evident in Fig. 5. An example of fluctuations in values of  $N$ ,  $D_{\text{bar}}$ , LWC, and pH during a 72-h cloud event at SPL is given in Fig. 6. As can be seen, in general, large droplet concentrations coincided with small mean droplet diameters and small liquid water contents; the smallest pH value occurred with the largest droplet concentration and smallest mean diameter.

Combining the results of Tables 1 and 2, the average physical and chemical properties of the cloud-droplet populations at SPL are related: clouds with large  $N$  and small  $D_{\text{bar}}$  values have small pH and large ion concentrations and clouds with small  $N$  and large  $D_{\text{bar}}$  values have larger pH and smaller ion concentrations; these results are independent of LWC values.

To determine if trends are evident in the ten-winter cloud-droplet record, the measurements from each winter were averaged and the results are shown in Fig. 7; the results also are listed in Table 3. The measurements are considered random samples from a population of cloud events because of the variable occurrence and duration of the cloud events each winter. As

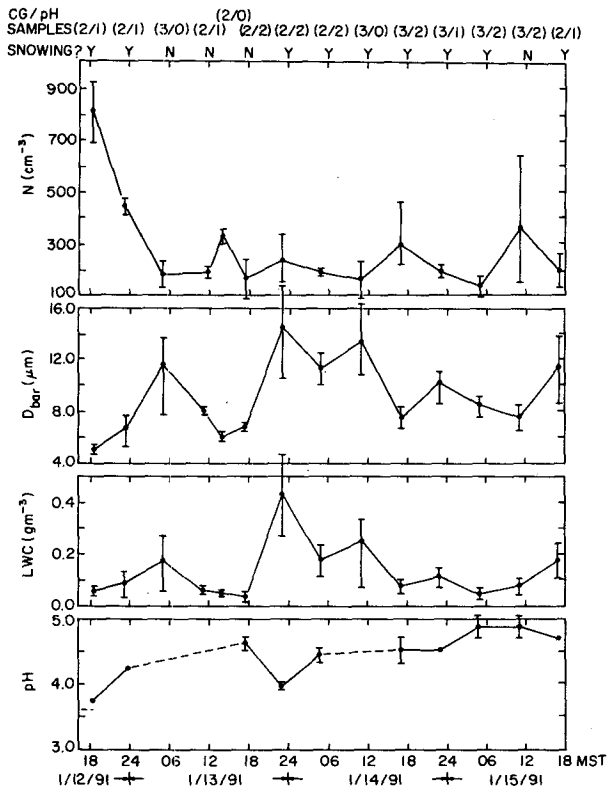


FIG. 6. Average cloud-droplet concentrations  $N$ , mean diameters  $D_{\text{bar}}$ , liquid water contents LWC, and pH values measured during a 72-h cloud event at SPL between 12 and 15 January 1991. The error bars represent the range in values; the cloud gun (CG) and pH sample sizes are indicated. A polluted cloud event occurred between 1800 and 2400 UTC 12 January 1991.

TABLE 3. Average wintertime values and standard errors of  $N$  ( $\text{cm}^{-3}$ ),  $D_{\text{bar}}$  ( $\mu\text{m}$ ), LWC ( $\text{g m}^{-3}$ ), and pH;  $n$  is the sample size.

Winter	$n$	$N$	$D_{\text{bar}}$	LWC	pH
1983/84	8	312 $\pm$ 71	8.2 $\pm$ 1.3	0.086 $\pm$ 0.026	4.10 $\pm$ 0.18
1984/85	103	247 $\pm$ 15	8.2 $\pm$ 0.30	0.088 $\pm$ 0.0084	4.23 $\pm$ 0.060
1985/86	29	491 $\pm$ 29	7.2 $\pm$ 0.33	0.14 $\pm$ 0.026	3.84 $\pm$ 0.074
1986/87	11	336 $\pm$ 30	7.3 $\pm$ 0.16	0.081 $\pm$ 0.010	3.77 $\pm$ 0.16
1987/88	14	221 $\pm$ 53	8.8 $\pm$ 0.72	0.073 $\pm$ 0.015	3.69 $\pm$ 0.13
1988/89	9	263 $\pm$ 59	6.0 $\pm$ 0.27	0.036 $\pm$ 0.0092	3.58 $\pm$ 0.070
1989/90	28	199 $\pm$ 38	12.8 $\pm$ 1.0	0.23 $\pm$ 0.037	4.24 $\pm$ 0.12
1990/91	45	312 $\pm$ 28	7.9 $\pm$ 0.39	0.097 $\pm$ 0.017	4.32 $\pm$ 0.070
1991/92	37	225 $\pm$ 30	6.2 $\pm$ 0.30	0.031 $\pm$ 0.0050	4.33 $\pm$ 0.070
1992/93	101	211 $\pm$ 13	7.5 $\pm$ 0.25	0.053 $\pm$ 0.0040	4.92 $\pm$ 0.053
Averages	385	282 $\pm$ 37	8.0 $\pm$ 0.52	0.092 $\pm$ 0.016	4.10 $\pm$ 0.10

can be seen from the figure, the  $N$ , LWC, and pH values oscillate with no systematic trends evident.

There are two significant peaks in Fig. 7; the large  $N$  value in the 1985/86 data and the large  $D_{\text{bar}}$  value in the 1989/90 data. The large  $N$  value ( $500 \text{ cm}^{-3}$ ) is most likely due to higher CCN concentrations. CCN measurements were not made in 1985/86 but CN measurements were (in-cloud CN measurements represent the total particle concentration entering the cloud because the cloud droplets are also drawn into the CN counter and subsequently evaporate, leaving behind their nucleus). The average of the CN measurements made at the times of the 1985/86 droplet measurements could have been as high as  $7000 \pm 1555 \text{ cm}^{-3}$ . In comparison, during the next winter with simultaneous CN and droplet measurements (1991/92), the average of the CN measurements was  $1100 \pm 300 \text{ cm}^{-3}$  and the droplet concentrations were  $230 \text{ cm}^{-3}$ .<sup>1</sup> Thus, the total particle concentrations entering the clouds were larger in 1985/86 than in 1991/92. The CCN concentrations also were likely larger in 1985/86 than in 1991/92 explaining the significantly larger 1985/86 droplet concentrations.

The large  $D_{\text{bar}}$  value in the 1989/90 data in Fig. 7 is due to the fact that the samples were obtained in early April from warm clouds ( $-2^\circ\text{C}$ ) with unusually large LWC values and small  $N$  values; a majority of the other winter samples illustrated in Fig. 7 were obtained during December and January. This conclusion is based on the trend of decreasing  $N$  values and increasing  $D_{\text{bar}}$  value between 30 December 1992 and 10 April 1993 at SPL shown in Fig. 8.

#### 4. Discussion

As can be seen in Tables 1 and 2, cloud water pH values and ionic concentrations at SPL, on average, appear to be independent of cloud LWC values but depend on  $N$  and  $D_{\text{bar}}$  values. Further, for clouds with similar water contents,  $N$  and  $D_{\text{bar}}$  are related by (2). Therefore, on average, clouds at SPL with large  $N$  values have small  $D_{\text{bar}}$  values, small pH values, and large ion concentrations; clouds with small  $N$  values have larger  $D_{\text{bar}}$  values, larger pH values, and smaller ion concentrations, and clouds with intermediate  $N$  values have intermediate  $D_{\text{bar}}$ , pH, and ion concentrations.

Pueschel et al. (1986) and Leitch et al. (1992) have reported a similar finding from, respectively, summertime clouds that enveloped Whiteface Mountain, New

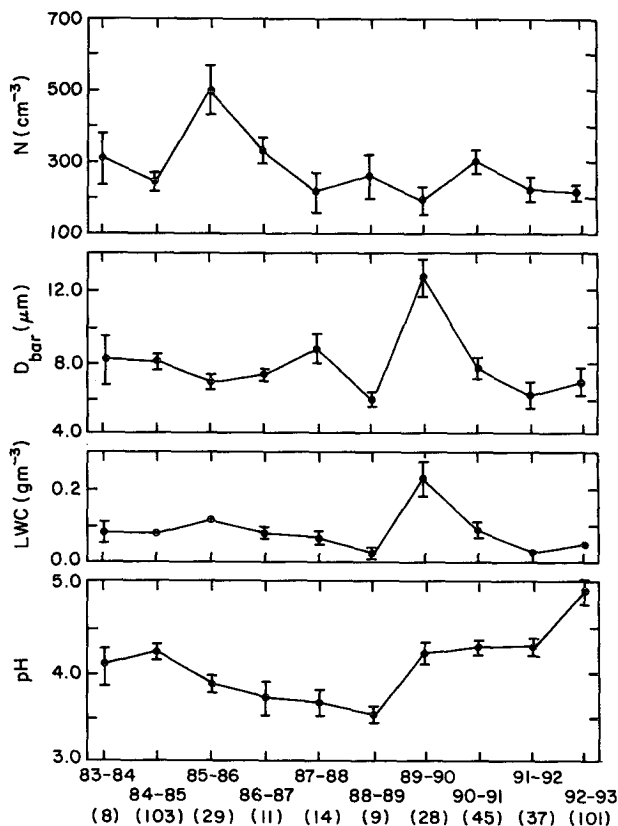


FIG. 7. Average cloud-droplet concentrations  $N$ , mean diameters  $D_{\text{bar}}$ , liquid water contents LWC, and pH values for measurements obtained each winter at SPL. The sample size for each winter is indicated as the number in parentheses. The error bars represent the standard error [ $\sigma/(n-1)^{1/2}$ ]; points without bars mean the error is less than the size of the point.

York, and airborne measurements from clouds over eastern North America. Pueschel et al. reported significant differences between cloud-droplet physical and chemical properties: polluted continental clouds had the largest  $N$  ( $750 \text{ cm}^{-3}$ ), LWC ( $0.51 \text{ g m}^{-3}$ ), and  $\text{SO}_4^-$  ( $474 \mu\text{e L}^{-1}$ ) values and the smallest pH values (3.27); the background continental clouds had intermediate  $N$  ( $127 \text{ cm}^{-3}$ ), LWC ( $0.0061 \text{ g m}^{-3}$ ),  $\text{SO}_4^-$  ( $42 \mu\text{e L}^{-1}$ ), and pH (3.93) values; the well-aged maritime clouds had the smallest  $N$  ( $64 \text{ cm}^{-3}$ ), LWC ( $0.030 \text{ g m}^{-3}$ ), and  $\text{SO}_4^-$  ( $13 \mu\text{e L}^{-1}$ ) values, and largest pH (4.15) values. Their results are for individual clouds in June 1981 and 1982 and show a much broader range in physical and chemical properties than the average SPL values. They attribute the dramatic differences in physical and chemical properties to pollution episodes.

Similar pollution episodes appear to occur at SPL. For example, the onset of the cloud event shown in Fig. 6 reveals unusually large  $N$ , small  $D_{\text{bar}}$ , and small pH values. The values rapidly diminish indicating, perhaps, a removal of the pollutants by cloud and precipitation formation. Another pollution episode was

<sup>1</sup> CN measurements were made in 1985/86 with a manual Gardner counter (Liu and Pui 1974) and in 1991/92 with an automatic Thermo Systems Inc. Model 8020 PortaCount Plus [principle described by Agarwal and Sem (1979)]. Phillips (1993, personal communication) compared the two instruments and found the Gardner to systematically produce the lowest CN values. The TSI instrument is considered the most accurate and, thus, the following correction was applied to the 1985/86 Gardner data:  $\text{CN}_{\text{Gardner}} = 5.4 \text{ CN}_{\text{TSI}}^{0.65}$  ( $100 \text{ cm}^{-3} \leq \text{CN}_{\text{TSI}} < 6000 \text{ cm}^{-3}$ ).

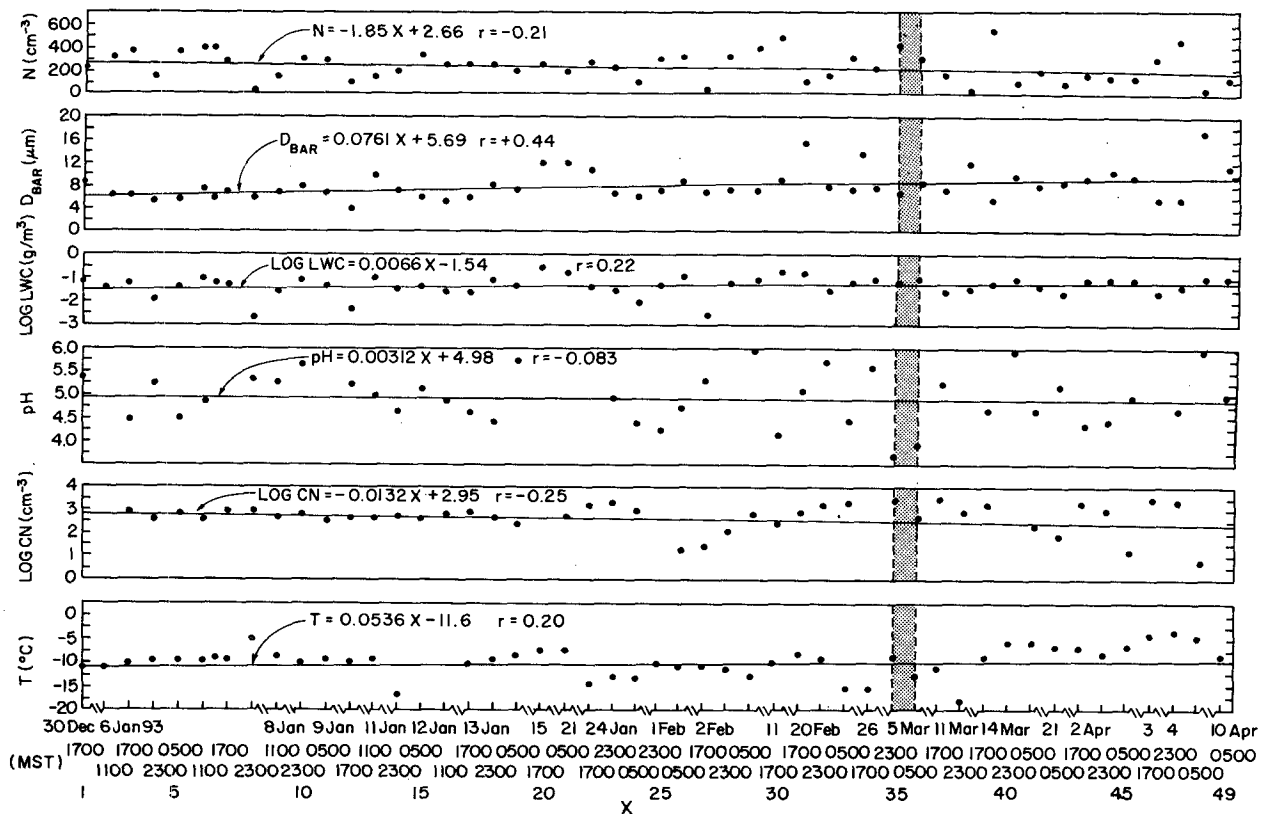


FIG. 8. Individual  $N$ ,  $D_{\text{bar}}$ , LWC, pH, CN, and  $T$  measurements at SPL between 30 December 1992 and 10 April 1993. The straight lines are least-squares fits to the data; correlation coefficients are indicated. The shaded region is a pollution event.

detected on 5 March 1993 as shown in Fig. 8. Not all cloud events were measured during the winter of 1992/93, however; thus, pollution episodes may have been missed. The measurement interval at SPL, therefore, should be decreased from 6 to 3 h to increase the chance of detecting pollution episodes.

Droplet spectra at SPL depend on the meteorological conditions: the warmer the cloud the larger the LWC values and more "maritime" the droplet spectra, the colder the cloud the smaller the LWC values and more "continental" the droplet spectra as determined by Hindman et al. (1992b). However, the reported factor of 2 difference in the LWC values between the warmer ( $-5.8^{\circ}\text{C}$ ) "maritime" clouds and colder ( $-9.1^{\circ}\text{C}$ ) "continental" clouds could not be due to differences in temperatures of the clouds for the following reasons. Cloud base occurs at about 2800 m (typically 710 mb) on the windward slopes of the Park Range; SPL is typically at 680 mb on the crest of the range (3220 m). An air parcel with an initial temperature of  $-5.8^{\circ}\text{C}$  rising adiabatically between cloud base and SPL will produce only a factor of 1.2 more liquid water than a  $-9.1^{\circ}\text{C}$  parcel. If, however, cloud base occurred at 2500 m (730 mb) in the warmer storms instead of 2800 m, the factor of 2 difference in LWC can be explained. Larger LWC values occur at SPL with lower

cloud bases and vice versa. For example, in Fig. 6, cloud base on 13 January 1991 between 1315 and 1420 MST was at 3000 m (700 mb) and the LWC was  $0.05 \text{ g m}^{-3}$ , while on 14 January 1991 between 1055 and 1255 MST the cloud base was at 2300 m (740 mb) and the LWC value was  $0.24 \text{ g m}^{-3}$ . Thus, LWC values at SPL depend primarily on cloud-base height and secondarily on temperature.

Hindman et al. (1992b) also found no significant difference in wind speeds, wind directions, and 48-h back trajectories at SPL between the warmer, maritime and colder, continental clouds (see Fig. 2). Wind speeds decrease with decreasing elevation on the slope upwind of SPL; wind speed averaged  $3.6 \text{ m s}^{-1}$  at SPL and  $1.5 \text{ m s}^{-1}$  at Thunderhead Lodge (2774 m) during the storm reported in Fig. 6, a difference of a factor of 2.4. The increase in measured wind speeds with elevation is assumed to be reflected in vertical velocities. Therefore, the vertical velocities that occur at the low cloud bases are expected to be smaller than the vertical velocities that occur at the higher cloud bases by approximately a factor of 2.4.

Could the factor of 2.4 variation in updraft cause the difference in  $N$  values of 360 and  $190 \text{ cm}^{-3}$  in Table 1? Rogers and Yau (1989) presented the following re-



relationship between cloud-droplet concentration  $N$  and updraft  $U$ :

$$N \cong 0.88 C^{2/(k+2)} (0.07 U^{3/2})^{k/(k+2)}, \quad (3)$$

assuming a CCN spectrum of the form  $N = CS^k$  where  $C$  is the concentration parameter,  $k$  is the slope parameter, and  $N$  is the concentration of CCN active at supersaturation  $S$ . A typical continental  $C$  value of  $600 \text{ cm}^{-3}$  and a  $k$  value of 0.5 from Twomey and Wojciechowski (1969) were used in (3). The vertical velocity difference using  $N$  values of 360 and  $190 \text{ cm}^{-3}$  in (3) is a factor of 9.4; 1.5 versus  $0.16 \text{ m s}^{-1}$ . Also, what change in  $C$  will produce the difference between the  $N$  values in Table 1? A constant vertical velocity of  $1 \text{ m s}^{-1}$  was used in (3) and  $C$  values of, respectively, 622 and  $316 \text{ cm}^{-3}$  resulted. Thus, a change in  $C$  by a factor of 2.0 would cause the difference between the  $N$  values. Hindman and Phillip (1990) reported a factor of 1.5 between the concentrations of CCN [ $360 \pm 104 \text{ cm}^{-3}$  versus  $543 \pm 210 \text{ cm}^{-3}$  ( $S_{crit} = 0.8\%$ )] occurring with the continental and maritime droplet spectra, respectively. The required variation in vertical velocity of a factor of 9.4 is much larger than the measured factor of 2.4 while the required variation in CCN concentrations of a factor of 2.0 is much closer to the measured variation of a factor of 1.5. It appears variations in CCN concentration exert a greater influence on droplet concentration than do variations in vertical velocities.

As shown in Tables 1 and 2, small pH values correspond to large  $N$  values and large pH values correspond to the small  $N$  values, LWC values remaining constant. The range in pH values must be due, in part, to the amount of water condensed on the CCN. The amount of water condensed on CCN is a function of distance above cloud base. Therefore, pH values are expected to be a function of distance above cloud base; this phenomena has been reported by DeFelice and Saxena (1990) and Mohnen (1992). Using the DeFelice and Saxena model results that had a pH near cloud base of 2.35 and applying their results to SPL as a first approximation, we could expect the pH to vary at SPL from 3.35 to 3.15 for cloud bases of, respectively, 2500 m (warm cloud) to 2800 m (cold cloud). This pH range is much smaller than our measured range reported in Tables 1 and 2. So, the range in pH at SPL must be due primarily to other factors; for instance, differences in chemical compositions of the CCN. Carter and Borys (1993) report clouds at SPL that contain maritime and continental droplet spectra have corresponding maritime and continental cloud water compositions that they attribute to differences in CCN chemical compositions.

The droplet physical and chemical properties at SPL appear to depend primarily on CCN concentrations and compositions and to a lesser extent on the meteorological conditions. The CCN are expected to vary from storm to storm and the number of storms vary

from winter to winter. Nevertheless, the limited samples comprising each winter's population are considered representative. Therefore, the samples from each winter were averaged. The resulting ten-winter time series of the average winter values of  $N$ ,  $D_{bar}$ , LWC, and pH plotted in Fig. 7 show no significant trends. Also, for the same period no significant trends are evident in annual emissions of  $NO_x$ ,  $SO_x$ , and total particulate matter in the western states upwind of SPL as reported by Pechen (1992). Further, Hofmann (1993) reports that there is evidence for a decreasing trend of 1.6%–1.8% per year in the optically active tropospheric aerosol component over the past 20 years at Laramie, Wyoming (which is 80 km north of SPL), and the decreasing trend may be related to similar reduction in sulfur emissions in the United States over this period.

The relatively constant anthropogenic emissions and aerosol particle concentrations in the western United States suggest relatively constant CCN concentrations, which is consistent with the relatively even droplet concentrations measured at SPL (except the spike in 1985/86 values that was attributed to unusually large CCN concentrations). On the other hand, it can be argued the natural CCN concentrations may have remained constant and anthropogenic emissions may have contributed little to the CCN at SPL. This statement is based on Twomey and Wojciechowski (1969), who concluded from global CCN measurements that a widespread and relatively uniform source of CCN appears to exist over the oceans and over the land and the sources of nuclei are not largely dependent on anthropogenic emissions. Further, Politovich and Vali (1983) report the following cloud droplet spectra characteristics measured from orographic clouds at Elk Mountain Observatory (EMO) located near Laramie, for the winters of 1975/76–1978/79:  $N$  of  $255 \text{ cm}^{-3}$ ,  $D_{bar}$  of  $8.9 \mu\text{m}$ , and LWC of  $0.15 \text{ g m}^{-3}$ . These values are quite close to the SPL values in Table 3. Thus, relative uniform average droplet spectra appeared to have occurred for the winters of 1975/76–1992/93 in the region of EMO and SPL.

If the concentrations of CCN increased at SPL during the ten-winter period, assuming the CCN compositions remained constant and LWC values did not change, it is expected that  $N$  values would have increased,  $D_{bar}$  values would have decreased, and pH values would have decreased. It can be seen in Fig. 7 that the average LWC values did not remain constant for the ten-winter period. Therefore, it is not possible to determine a trend in CCN concentrations from Fig. 7. Nevertheless, winters with small pH values are assumed to be affected by more polluted storms and less clean storms; winters with large pH values are assumed to be affected by less polluted storms and more clean storms. As can be seen from Fig. 7, there is no obvious correlation between polluted winters and large  $N$  and small  $D_{bar}$  values. Likewise, there is no obvious correlation between clean winters and small  $N$  and large  $D_{bar}$  values. In fact, the

most polluted winter (1988/89) did have the required small  $D_{\text{bar}}$  values but did not have the large  $N$  values. A relationship must be established between clean clouds and lack of anthropogenic CCN and polluted clouds and a source of anthropogenic CCN before conclusions can be made about the frequency and magnitude of the effects of anthropogenic CCN on cloud-droplet spectra at SPL.

## 5. Conclusions

Wintertime cloud-droplet spectra and cloud water pH and ion measurements have been made from clouds that enveloped Storm Peak Laboratory (SPL) in the northern Colorado Rockies over a ten-winter period (1983/84–1992/93). To determine if the droplet spectra and chemical constituents were related, the measurements were sorted into samples with the smallest, intermediate, and largest pH values,  $\text{pH} \leq 3.6$ ,  $3.6 < \text{pH} < 4.6$ ,  $\text{pH} \geq 4.6$ , and averaged. It was found that clouds with the smallest pH values (3.4) had the largest droplet concentrations ( $N = 329 \text{ cm}^{-3}$ ), smallest mean droplet diameters ( $D_{\text{bar}} = 6.4 \mu\text{m}$ ), and largest  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$  values (5.7, 3.4, 1.1  $\text{mg L}^{-1}$ ), while clouds with the largest pH values (4.7) had the smallest droplet concentrations ( $189 \text{ cm}^{-3}$ ), largest mean droplet diameters (8.0  $\mu\text{m}$ ), and smallest  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{Cl}^-$  values (3.9, 2.5, 0.58  $\text{mg L}^{-1}$ ), and clouds with intermediate pH values (4.1) had intermediate droplet concentrations (298  $\text{cm}^{-3}$ ), mean droplet diameters (7.6  $\mu\text{m}$ ), and  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$  values (3.3, 2.7, 1.0  $\text{mg L}^{-1}$ ); the three groups had similar liquid water contents ( $\text{LWC} \cong 0.07 \text{ g m}^{-3}$ ). Cloud water chemical compositions at SPL, on average, appear to be independent of LWC but dependent on  $N$ . The equation

$$\text{LWC} = \frac{\pi}{6D_{\text{bar}}^3 N \rho},$$

where  $\rho$  is the density of water, closely describes the relationship between LWC,  $D_{\text{bar}}$ , and  $N$  for the droplet spectra at SPL. Thus, for clouds with similar LWC values, clouds with large  $N$  values have small  $D_{\text{bar}}$  values and vice versa.

It was found that LWC at SPL varies inversely with cloud-base height, and cloud-base updrafts vary directly with cloud-base height. Using a relationship between updraft,  $N$ , and cloud condensation nucleus (CCN) concentrations, variations in CCN concentrations appear to exert a greater influence on  $N$  values than variations in updraft. The large range in pH values measured at SPL could not be explained by entrainment or variations in cloud-base height or in LWC values; differences in CCN composition appear to be a major factor. The chemical composition of CCN at SPL may vary for CCN with similar number concentrations and size distributions; that is, for two similar aerosol particle spectra the chemical composition of particles of similar

sizes may be acidic in one spectrum and basic in the other spectrum.

No significant trends in  $N$ ,  $D_{\text{bar}}$ , LWC, and pH values were found in the ten-winter record. Likewise no significant trends in annual anthropogenic emissions of  $\text{SO}_x$  and  $\text{NO}_x$  or concentrations of optically active aerosol particles occurred in the western United States during the period. Also, it may be that anthropogenic emissions make a small contribution to the CCN at SPL.

The results of this study suggest that long-term measurements of cloud-droplet physical and chemical properties at remote mountaintop sites may be used to infer trends in CCN concentrations and compositions. CCN physical and chemical properties need to be measured at SPL to provide input to cloud formation models that include chemical processes (e.g., Seidl 1989). Modeling studies (e.g., Chen 1992) are required to quantitatively explain the measured variations in droplet physical and chemical properties at SPL. Data suitable for these calculations exist: CCN supersaturation spectra and aerosol particle compositions as a function of size were obtained at SPL, respectively, by J. Hudson (1988, personal communication) and Borys et al. (1988).

Snowfall occurred at SPL during a majority of the cloud events. The effect of crystal riming in changing droplet spectra by removing large droplets has been demonstrated by Borys et al. (1988) but has not been quantified. The magnitude of the effect of crystal riming on  $N$  and  $D_{\text{bar}}$  values needs to be determined to establish the robustness of the results presented here.

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