ON THE DISTRIBUTION OF ACIDITY WITHIN CLOUDS AS A FUNCTION OF DROPLET SIZE

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ABSTRACT

Previous work has indicated that the acidity within a cloud is concentrated in the smaller droplets. On Mount Washington in New Hampshire, a rotating multicylinder was exposed to supercooled clouds and used to measure the acidity of graduated portions of cloud droplet spectra. This study confirms the expected relationship between acidity and droplet size, and indicates that a weak relation exists between acidity and volume median droplet diameter.

INTRODUCTION

The summit of Mount Washington, at 1914 m, is enveloped by clouds approximately 60% of the time. If the clouds in contact with the mountain contain acidic elements, what can be said about the direct deposition of those elements onto alpine surfaces? This question was addressed by Houghton as early as 1955, when he sampled pH, chloride, and sulfate on the summit of Mount Washington. Others (Weathers et. al. 1986) have investigated the acidity of cloud droplets at various locations and elevations more recently.

Studies conducted by Falconer and Falconer (1980) and Falconer and Kadlecek (1981) at Whiteface Mountain, and an analysis of samples from a rotating mulitiicylinder by Borys and Hindman (1985) on the summit of Mount Washington indicate that in almost all cases cloud water is more acidic than precipitation and that the smaller the cloud water droplet, the more acidic it will be.

Studies of rime accumulations at the Storm Peak Laboratory in Colorado (Hindman et al., 1982) indicate that the fraction of water mass deposited to the mountain due to direct mountain-surface riming was between 4% and 11% of the total water mass deposited. Combining the effect of direct rime deposits with rime encased snowflakes and ice crystals can account for more than 60% of the total water in the snowpack. Consequently, the acidity of cloud droplets and the mechanisms of their collection and deposition can be very significant inputs to the overall acidity of the snowpack.

A limited program of measuring the acidity of the rime being deposited on Mount Washington, with an emphasis on drop-size dependency, was begun in the fall of 1984.

EXPERIMENTAL METHOD

One method for gathering rime samples consists of exposing a metal frame strung with thin wires, as described by a group at Whiteface Mountain (Camarota et. al. 1983). Exposure of the device when warm allowed a thin ice coating to develop over the wires to create a compatible surface for subsequent riming. Sample removal was accomplished by scraping the wires with a template bored to the dimension of the iced wire. In this way, the rime sample would be protected from contamination that might result from direct contact with the metal. Eventually, the wires were replaced with teflon strings of various sizes to furthur reduce the potential for contamination. Vibrations introduced in these filament collectors by wind made them unsatisfactory for sampling most Mount Washington icing episodes. Interlacing the teflon strings diminished the vibration problem somewhat by making the collector more rigid, but at the expense of a clear relationship between filament diameters and the droplet spectrum of a collection due to the creation of collector nodes at the filament junctures. This method of sampling was abandoned for the above and other reasons. It was found for example that the loss of accumulation through vibration was frequently substantial. Also, the collection efficiency of the sampler taken as a whole was unknown. As an example, although efficiencies for each strand could be calculated for given wind speeds, and different portions of the droplet spectra sampled by choosing different size strands, there was concern that a variable accumulation of rime on the whole collector might well bias the data by interfering with the overall air flow through the collector.

The use of a rotating multicylinder to sample rime, along with other cloud physics parameters, became a plausible alternative to sampling with flexible strands. Multicylinder theory is reasonably well understood and, although the actual drop size distribution cannot always be determined with confidence, the approximate breadth of the distribution can be deduced, as well as the volume median drop diameter (Dd) and the liquid-water content (LWC) of the cloud sampled. Unlike filament collectors, the multicylinders are not subject to excessive vibrations. Familiarity with the multicylinder led us to use this device for the gathering of the rime samples for the remainder of the investigation.

Tests were conducted on the Observatory's brass rotating multicylinder to determine the effect of the metal on pH readings. Deionized water used to rinse the brass cylinders showed an increase of a few percent in pH over uncontaminated deionized water. Completing the same tests after coating the brass cylinders with a thin layer of DuRont Molycote silicone resin indicated that the coated cylinders yielded results not significantly different from the original rinse water. Therefore, only coated cylinders were used in the study.

Exposures were made on the railing of the Observatory tower, and the samples were weighed and measured to obtain cloud physics data by standard methods. The individual cylinders were then suspended in polyethylene bags at room temperature until the rime accumulation had melted and collected at the bottom of the bag. pH measurements were made with an Amber Science model 4503A Solution Analyzer and a Microelectrodes model MI-410 pH probe. This probe requires a very small sample volume as its tip is only 1.2 mm in diameter. In some exposures, the larger of the multicylinders collected a very small amount of rime, if any at all, resulting in just a few drops of sample being available for examination. The MI-410 probe is suited for the measurement of sample volumes on the order of 5 microliters.

Standard procedures were developed for calibrating the pH meter and probe both before and after the measurements. The samples were usually small in volume, so they were evaluated as quickly as possible to reduce the possibility of contamination of the sample by ambient air (Cragin 1984).

RESULTS AND DISCUSSION

The pH readings obtained during the course of our investigation are used comparatively and are not assumed to be absolute. Although the buffer solutions used to calibrate the sensor are accurate to +/- 0.02 pH units, no intercomparison with other laboratories was done.

The data set comprises 59 multicylinder exposures with pH analyses taken over two winter seasons. Additional multicylinder data taken over the same two winter periods, but without pH evaluation, indicate that the particular exposures used for pH analyses are representative of the distributions, liquid-water contents, and volume median droplet diameters observed over the remainder of the respective seasons. During the multicylinder data reduction process any significant variations from expected values may be determined, and the run discarded. For example, an exposure which does not result in a reasonable LWC may be assumed to be in error and would not be used. The overall average of the pH of each cylinder for each of the two seasons appears in Table 1.

	Cylinder No.					
	1	2	3	4	5	6
1985-1986	4.95	5.38	5.66	5.77	5.96	6.14
1986-1987	4.81	5.05	5.17	5.72	5.87	6.35

Table 1: pH values for each of the six cylinders, averaged for the whole of the indicated season.

The data in Table 1 show that the smaller cylinders (1,2) which tend to collect almost all of the droplets present in a specified volume of cloud show lower pH (higher acidity) than those cylinders (5,6) which collect only the largest droplets.

The multicylinder method is insensitive to the details of the droplet size distribution. Rather, distributions are described as being very narrow (type A) through very broad (type J), centered around the volume median droplet diameter. Further discussion of the specific determination of these distribution types may be found in Howe (1960). A summary of the distribution data is found in Table 2.

	Distribution Type								
	A	B	C	D	E	F	G	H	J
1985-1986	40	17	17	7	7	7	3	0	3
1986-1987	31	7	17	7	3	10	7	14	3

Table 2: Percentage of the total number of distributions observed in each of the standard type categories for each of the two seasons.

As presented in Table 2, the 1985-1986 season was typified by slightly more narrow droplet size distributions than was the 1986-1987 season, with about a 10% increase in the number of broader distributions in 1986-1987 than the previous year. Also, the 1985-1986 season exhibited slightly higher Dd values over that of the 1986-1987 season, as depicted in Figure 1. If an increase in the acidity of the sample is associated with the presence of increasingly smaller droplets, then this should be reflected in a downward shift of the pH values for the smaller cylinders for 1986-1987 season. This shift is observed in Table 1.

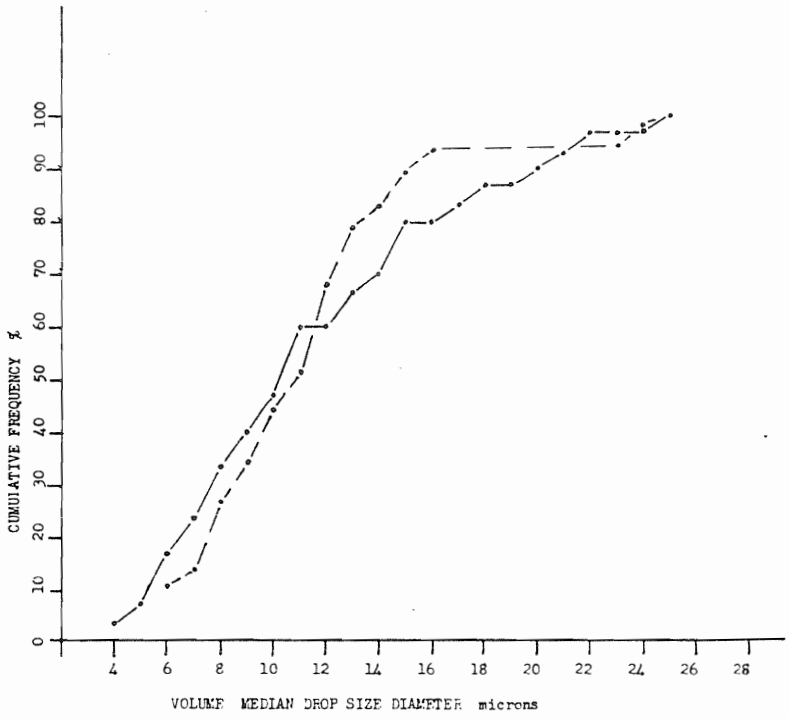

Figure 1. Cumulative frequency distribution of volume median droplet diameter for both experimental seasons.
Key: Solid line= 1985-1986, Dashed line= 1986-1987.

Analysis of multicylinder cloud physics data allows a further breakdown of the data when we examine the pH values of a sample (in this case, from the smallest cylinder) relative to the LWC, Dd, or the type of droplet size distribution of the cloud yielding it. In each of the cases examined, no strong relationship between these parameters was found. See Figures 2 and 3. For example, the LWC of the cloud showed no totally consistent relationship to the pH of the sample for either of the two years studied, although there is a slight indication of more neutral samples associated with higher LWC values in Figure 3. This is, however, consistent with results found elsewhere (Borys 1985). The data in Figures 2 and 3 are separated only for convenience and clarity, and should be taken as a whole.

When the data points on Figures 2 and 3 are annotated with their respective values of Dd and distribution types, some tendencies become apparent. In both Figures 2 and 3, for example, the Dd values of the samples tended to increase as the pH of the first cylinder increased and the LWC increased, although a scatter plot of Dd versus pH of the smallest cylinder did not yield any obvious relationship.

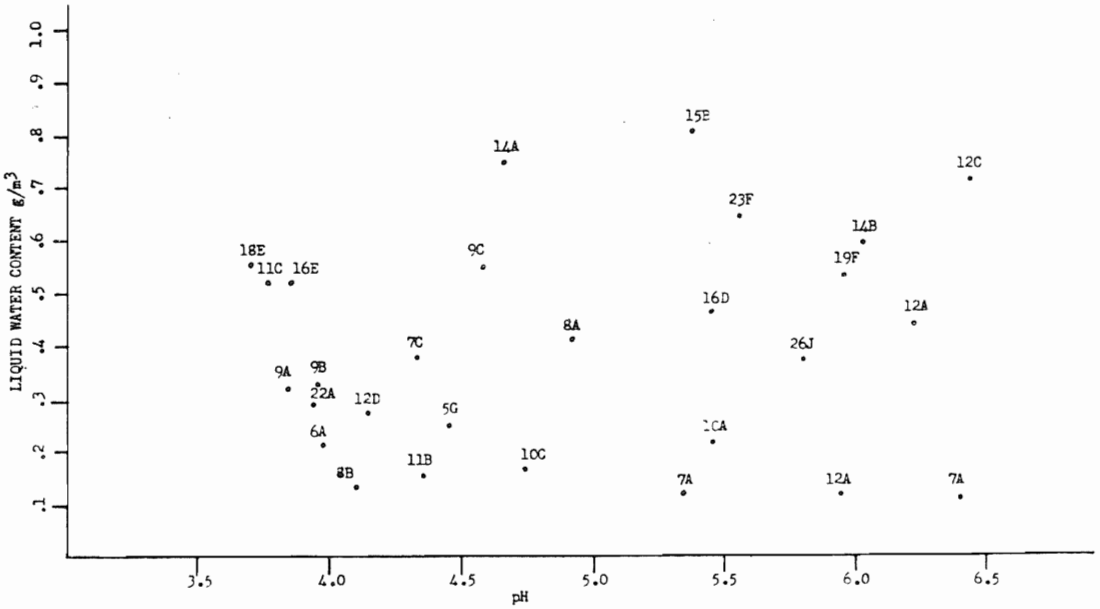

Figure 2. Scatter diagram of liquid water content versus pH of smallest cylinder with volume median drop diameter in micrometers (numbers) and droplet distribution type (letters) annotated for the 1985-1986 season.

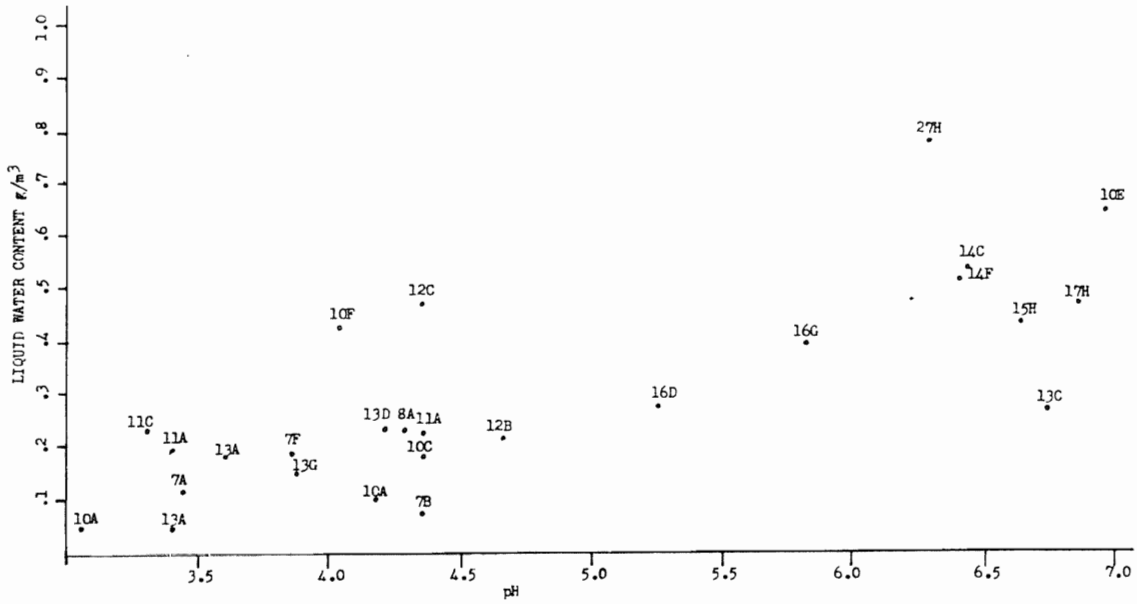

Figure 3. Scatter diagram of liquid water content versus pH of smallest cylinder with volume median drop diameter in micrometers (numbers) and droplet distribution type (letters) annotated for the 1986-1987 season.

Referring again to Figures 2 and 3, and considering the droplet size distribution type, it is apparent that the narrower distributions (nearer to type A) were most frequently associated with lower pH (higher acidity) and lower liquid-water contents, while the broader distributions (nearer to type J) were most frequently associated with higher pH (lower acidity) and higher liquid-water content values.

In the two previous examples, data values tend for the most part to be grouped in general regions of the figure, although not exclusively. In Figure 2, for example, three of the four broadest distributions occurred below 5.5 on the pH scale, while the narrower distribution types showed up almost evenly across the same scale. In Figure 3, the broader distributions were grouped in two rather separate portions of the scale, with three values clustered around pH 4.0 and five more clustered between pH 5.8 and 7.0. Other authors (Moody et. al., 1985) have grouped their data by other, objective, means and have found a reasonable separation of events within clusters typified by a specific range of meteorological conditions. With the limited number of samples in the present study this type of analysis was not done.

CONCLUSIONS

It is interesting that more significant differences were not found between individual samples with widely varying cloud physics parameters. This may be expected when one considers the meteorological variations that are possible. For example, even though samples may exhibit the same liquid-water content, they may be taken from entirely different types of cloud. In as much as this study was concerned with only cold-season events, the types of clouds examined may be limited. Others (Topol. et. al. 1986) analyzed chemical deposition constituents as a function of storm type and season and found very small differences between cold season precipitation samples for some of the major ions. Specifically, significant statistical differences between cold and warm season precipitation pH was not found in their study, indicating very small differences between storm types during the cold season. Likewise, a sample taken from an orographic-type cap cloud might have some similar characteristics to that of a non mountain-related stratus cloud, but would not necessarily exhibit the same distribution of acidity within its droplet spectrum.

In addition to the above, the data were not gathered or documented with respect to the lifetime of the cloud, and there is, therefore, no way of determining what portion of the cloud's lifetime was sampled. Future analyses should include this information.

It would appear that there may be relationships between liquid-water content, pH, volume median droplet diameters and droplet size distributions that could be determined more accurately with the use of some type of cluster analysis, combined with the inclusion of additional meteorological parameters. Furthur analysis of past data, and the additional analysis of future samples, will proceed in this direction.

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