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A COMPARISON OF PRECIPITATION CHEMISTRY DATA
AT A CENTRAL ILLINOIS SITE IN 1954 AND IN 1977

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A COMPARISON OF PRECIPITATION CHEMISTRY DATA
AT A CENTRAL ILLINOIS SITE IN 1954 AND IN 1977

Gary J. Stensland

Abstract

In 1954 detailed precipitation chemistry measurements on samples from a manually operated wet-only collector provided data for the concentrations of the major ions for precipitation events. A comparison with data for the same location for 1977, collected with an automatic wet-only collector, showed that the median sulfate and nitrate concentrations were somewhat larger than in 1954 while the median calcium plus magnesium concentration was much lower. The precipitation event median pH was also much lower in 1977. Possible explanations for the present lower calcium plus magnesium concentrations and the correspondingly lower pH values are given.

Introduction

Gases and particles injected into the atmosphere are returned to the earth's surface through wet and dry removal processes. Therefore historical trends of the concentrations of the various trace contaminants in precipitation can serve as an indication of the changes in the levels of these contaminants in the air. Many sulfur budgets have been proposed in the literature and each demonstrates that wet removal of sulfur by precipitation is of major importance compared to dry deposition.[1,2,3]

A precipitation chemistry network has been in operation in Europe since the early 1950's. The data have shown a trend of increasing sulfate and decreasing pH for the network.[4] These acid rains have resulted in significant ecological effects, the most notable being the damage to the fresh water fish populations in Norway.[5]

Research groups at Cornell University have reported more recently that a similar trend of decreasing precipitation pH has resulted in significant damage to the fish populations in the Adirondack Mountains of New York.[6,7] Unfortunately the historical precipitation chemistry data base for the United States is quite limited.

This paper investigates the precipitation chemistry for a rural, central Illinois site for 1954 and 1977. The major question being addressed is whether or not the precipitation has become more acidic at this Midwest site and if so, why? An examination of the atmospheric sulfate data from the U. S. Environmental Protection Agency NASN stations shows that Illinois is in a transition region between the high sulfate areas of the East and the low sulfate areas of the Plains states. Therefore one should not necessarily expect to find the same precipitation

chemistry trends as observed in the East. The 1954 data set, described in detail in the next section, is unique for its time because the sampling technique carefully eliminated any dry deposition and because individual precipitation events were sampled.

Experimental Methods

The earlier data were collected from October 26, 1953 to August 12, 1954, and the recent data from May 15, 1977 to February 6, 1978. For convenience the two sets are referred to as the 1954 data and the 1977 data.

The sampling site in 1954 and in 1977 was at the Champaign-Urbana airport (referred to as CMI in this paper). CMI is located seven kilometers south of Champaign and is surrounded by cultivated fields except for a golf course to the east. CMI is essentially halfway between Chicago and St. Louis.

For the 1977 study an automatic wet/dry collector, of the HASL design, was used. Only the results from the wet side bucket are considered in this paper. The polyethylene bucket was removed within 24 hours of the end of the precipitation event and brought to the laboratory where pH and conductivity were measured followed by sample filtration with a 0.45 micron pore size membrane filter. Since the filtration procedure has been shown to satisfactorily stabilize the ion concentrations, the filtered samples were stored at room temperature.[8] The ions $SO_4^=$, NO_3^-, Cl^-, NH_4^+, Ca^{++}, Mg^{++}, K^+, and Na^+ were determined by standard methods on AutoAnalyzer and atomic absorption units.[8]

The ion levels for the 1954 precipitation events were reported by Larson and Hettick in a 1956 paper.[9] This paper should be consulted for details concerning the sample handling and chemical analysis procedures. The sample pH values were not reported. Private conversations with one of the authors

of the 1956 paper (TEL) indicated that the usual procedure was for all the ions to be measured as soon as four samples were available. Only 16 out of the total of 64 samples were filtered due to the fact that the filters were found to introduce small quantities of some of the ions being determined.

A 1.2 meter diameter stainless steel funnel was used to collect the 1954 samples. The funnel was covered tightly between events. When the cover was removed (manually) to sample a precipitation event, the funnel was immediately rinsed with four liters of ammonia-free water to be certain that dry deposition would not be included in the precipitation samples.

Meteorological information for the time period of each sample collection was included as an Appendix to the 1956 paper. From the raingage precipitation amount listed for each event and the funnel diameter, the sample volume was calculated and compared with that reported (the paper does indicate that the reported sample volume was only an approximate value). The main result of this comparison is that samples with a reported volume of 4 liters corresponded on the average with precipitation amounts that should have produced about 10 liters (calculated values actually ranging from about 4 to 20 liters). Since the glass collection vessel had a volume of 4 liters and thus would accommodate a 3.4 mm precipitation event, it could be suggested that only the initial portions of some precipitation events were sampled. However private conversations with several individuals working at the field site in 1954 suggests that a more likely explanation is that the sample bottles overflowed because no one changed them during rain showers. Since a tube ran from the funnel exit into the unstopped collecting bottle, it seems likely that the 4-liter samples often represented an average for a rain shower, and not just a sample of the first 3.4 mm of showers that produced rainfalls of up to 18 mm.

The climatological data for Urbana, seven kilometers from the CMI site, indicates that about 7% of the 1954 samples and 26% of 1977 samples were at least partially composed of snow (i.e., 3 samples in 1954 and 17 samples in 1977 had snow). The total snowfall was 6.7 inches during the 1954 sampling period and 40.5 inches during the 1977 sampling period.

Calculating pH

The 1954 data did not include pH measurements so the following procedure has been used to calculate the pH.[10] In a rain or melted snow solution, a charge balance is maintained. If a term called Net Ions is defined as

$$(\text{Net Ions}) = (SO_4^=)+(NO_3^-)+(Cl^-)-(Ca^{++})-(Mg^{++})-(NH_4^+)-(Na^+)-(K^+) ,\qquad (1)$$

then the charge balance equation, consisting of the major measured ions, is

$$(H^+) - (HCO_3^-) = (\text{Net Ions}) ,\qquad (2)$$

with each concentration in units of microequivalents per liter ($\mu eq/\ell$). Although Eq. 2 is not exactly correct, since some ions have not been included, the relation has been shown to work reasonably well for rain and snow samples. With the appropriate chemical equilibrium constants, it can be shown that $(HCO_3^-) \simeq 490$ (OH^-) and for samples with pH<8, $(CO_3^=)<<(HCO_3^-)$. Thus, the two ions OH^- and $CO_3^=$ need not be considered in the charge balance equation. Falling raindrops are in equilibrium with atmospheric carbon dioxide ($P_{CO_2} = 320 \times 10^{-6}$ atm) and thus the chemical equilibria relationships can be used to give

$$(HCO_3^-) = K_H K_1 P_{CO_2} / (H^+) .\qquad (3)$$

where K_H is the constant in Henry's Law and K_1 is the first dissociation constant of CO_2 in water (for 25°C, $K_H = 0.034 \times 10^{+6}$ µeq/ℓ/atm and $K_1 = 4.5 \times 10^{-1}$ µeq/ℓ). Substituting Eq. 3 into Eq. 2 and solving the quadratic equation for (H^+) gives

$$(H^+) = \{(\text{Net Ions}) \pm [(\text{Net Ions})^2 + (4K_H K_1 P_{CO_2})]^{0.5}\}/2 \qquad (4)$$

In Eq. 4, only the plus sign in front of the bracketed term gives positive and therefore physically realistic solutions. Eq. 4 is rewritten in terms of pH as

$$pH = +6 - \log_{10} \{\{(\text{Net Ions}) + [(\text{Net Ions})^2 + (4K_H K_1 P_{CO_2})]^{0.5}\}/2\} \qquad (5)$$

where the +6 factor results from the fact that the µeq/ℓ concentration unit is required for the terms in Eq. 5. Figure 1 illustrates Eq. 5 for the parameter ranges found in rain and snow samples. To use Figure 1, the measured ions are combined according to Eq. 1 to determine (Net Ions). This value is located on the left hand ordinate of Figure 1 and then curve B is used to read off the predicted pH. For example, if (Net Ions) equals 10 µeq/ℓ, then the predicted pH is 4.97. If it is assumed that the carbon dioxide had been purged from the solution before the pH was measured, then curve C would be used to predict the pH. The three dashed curves indicate the concentrations of HCO_3^-, OH^-, and H^+ for the various solution pH values, the right hand ordinate of Figure 1 being utilized. It is thus seen that for $P_{CO_2} = 320 \times 10^{-6}$ atm and pH values below about 5, (Net Ions) approximately equals (H^+) and for pH above about 6.3, (Net Ions) approximately equals (HCO_3^-). It should be noted that Figure 1 is general in the sense that additional measured ions which would produce a more accurate charge balance can be included in Eq. 1 and this more accurate value for (Net Ions) can then be used with Figure 1 to predict the pH. Figure 1 was used to calculate the pH values for the 1954 precipitation samples. It is in

the region where curve B has a very steep slope that calculated and measured pH can be expected to have the poorest agreement.[10] Furthermore, if the values of (Net Ions) were distributed symmetrically about zero, then this steep slope in curve B would produce a bimodel pH distribution with a minimum where (H^+) = (HCO_3^-) which is a value of pH = 5.65 for P_{CO_2} = 320 x 10^{-6} atm and T = 25°C.

The 1954 data in the Larson and Hettick paper included estimates of the accuracy of the chemical determinations. These estimates were used for a sensitivity test of equation (5) with the results being shown in Figure 2. The upper limits of the error bars in Figure 2 resulted from the subtraction of the respective accuracy estimates from each of the anions contributing to (Net Ions) and the addition of the respective accuracy estimates to each of the cations [cf. Eqs. 1 and 5]. The error bars clearly indicate that the model will produce the most accurate results for high and low pH values (i.e., | Net Ions | >> 1), as was discussed in the preceding paragraph. The dashed lines connecting some of the data points in Figure 2 identify samples taken consecutively during a single precipitation event.

Larson and Henley[11] developed a procedure for determining alkalinity which gave accurate results even at the low levels found in precipitation samples. This improved procedure was applied by Larson and Hettick to the 1954 samples. For precipitation samples it is reasonable to assume that alkalinity is algebraically equal to -(Net Ions)[12] so this measured chemical parameter was used in Eq. 5 to calculate pH. The results are shown in Figure 2. The pH calculated from (Net Ions) and the pH calculated from alkalinity are in good agreement. It is noted on Figure 2 that the calculated pH values are uncorrected, where the correction factor is discussed in the following paragraph and expressed quantitatively in Eqs. 6 and 7.

Granat has analyzed the data from approximately 1500 monthly precipitation samples from the European chemistry network and noted significant deviations between calculated and measured pH values.[13] Stensland analyzed monthly data for about 1300 precipitation samples collected in the continental United States by the U. S. Public Health Service and found a very similar trend.[14] From these data the following empirical correction to bring calculated and measured pH into agreement has been formulated:[10]

$$pH(corrected) = pH(calculated)-C \qquad (6)$$

where $C = 0.70$ for pH (calculated) ≥ 6.0 and $C = 0.15$ for pH (calculated) ≤ 4.8.

$$pH(corrected) = 0.54 \, pH(calculated) + 2.06 \qquad (7)$$

for $4.8 <$ pH (calculated) < 6.0. A firm explanation as to why Eqs. 6 and 7 were needed for the monthly sample data is not yet available. This author suspects that the dissolution phenomenon investigated by Peden and Skowron[8], which was probably important for the monthly samples discussed above, may in large part explain why Eqs. 6 and 7 were found to be necessary. Because the dissolution phenomenon may have been important in the 1954 event data from CMI, Eqs. 6 and 7 were applied to these data. As will be evident later, this was a conservative decision which does not alter the final conclusions of this paper.

If some of the ion concentrations in precipitation samples are changing during the time between the pH measurement and the other ion measurements, then it is also likely that concentrations were changing between the time when the precipitation reached the ground and the first analytical chemistry measurement. The correction with Eqs. 6 and 7 is an estimate of the error due to the former, but not the latter.

Results

Figure 3 depicts the sulfate concentrations in 46 rain events at CMI for summer 1977. The feature to note is that the sulfate concentration is generally higher for small rainfalls. A similar pattern exists for the other ions. The strong sensitivity to rainfall amount suggests that the 1954 and 1977 data sets should probably have been compared by using the precipitation-weighted average concentrations instead of individual event concentrations. However, the detailed precipitation records necessary to treat the 1954 data in such a manner are not available. Thus, the frequency distributions and median values for the ion concentrations for the individual events were examined.

In the following figures, the precipitation chemistry data were categorized in four ways. First, for the 1954 events there were eight cases where from two to five samples were collected consecutively during the event (sequential samples). The reported volume for each sequential sample, which was only an approximate value, was used to compute a volume weighted average for the event for each ion. These average ion values representing the composite sample have been given a special symbol in Figures 4-7.

Second, there were some 1954 samples which were collected after the precipitation had begun to fall. These samples would be expected to be relatively clean since they missed the higher ion concentrations generally found at the beginning of precipitation events. These samples have been explicitly identified on Figures 4-7 as "precipitation at beginning" samples.

Third, the experimental procedures used in 1977 allowed small precipitation events to be sampled and analyzed. These small samples (0.35 mm $\leq$ precipitation <0.70 mm and precipitation <0.35 mm) are indicated with special symbols on Figure 4. The 1954 data on Figure 4 does not include any small precipitation

events (i.e., <0.70 mm where the precipitation amount was inferred from the volume of the chemistry sample). In Figures 5-7 only samples with precipitation $\geq$0.70 mm have been included.

Finally, the 1977 data have been divided into *green* period data and *brown* period data. In central Illinois, in general, and in particular around the CMI site, the land is used almost exclusively for secondary roads, residential/urban areas, and farming ($\sim$92%) and almost all the farm acreage is utilized for growing corn and soybeans. Thus from about May 15 to September 30 the landscape is *green* due to the fields of corn and soybeans. In the fall, after harvest, most of the farmland is plowed leaving a *brown* landscape until spring, except for periods of snow cover. Thus, dustier air due to wind erosion of bare soil surfaces should be more common in the *brown* period, and this may be reflected in the seasonal rain and snow chemistry. In fact, for the *brown* period for the 1977 data set, the ground surface was either generally moist due to frequent rains or it was snow covered and thus blowing dust was greatly reduced. Because of the relatively small number of data points for 1954, these events were not divided into *brown* and *green* periods.

The frequency distributions of the calculated pH for events in 1954 and for the measured pH for 1977 are presented in Figure 4. The 1954 data include the empirical correction of Eqs. 6 and 7.

From Figure 4 it can be seen that the 1977 event median pH does not change significantly when the small samples are included. The small precipitation events are always heavily loaded with all the ions, in the same manner as for sulfate in Figure 3. It is interesting that in Figure 4 the small rains in the *green* period in 1977 had relatively low pH values while those for the *brown* period had relatively high pH values.

From the event data in Figure 4, it is observed that the *brown* period of 1977 had a somewhat greater median pH than the *green* period, although when the small samples are excluded, the two medians differ by only 0.2 pH unit. The 1977 median pH for the *brown* and *green* periods combined, for events ≥ 0.70 mm, is 4.1. This is to be compared with a median pH for 1954 of 5.9. If those 1954 samples with precipitation at the beginning are excluded, the 1954 median pH = 6.05.

The more basic precipitation in 1954 could have resulted from low levels of acidic ions (e.g., sulfate and nitrate) or from high levels of basic ions (e.g., calcium and magnesium). This issue is addressed with Figures 5-7. The sulfate data are presented in Figure 5. For 1977, the median for the *brown* period was 80 µeq/ℓ; for the *green* period the median was 65 µeq/ℓ. The median for 1954 was 50 µeq/ℓ; when samples with precipitation at the beginning are excluded, the 1954 median is 60 µeq/ℓ. For later calculations, the median concentration of 60 µeq/ℓ will be assumed for 1954 while for 1977 a concentration for the combined *green* and *brown* periods of 70 µeq/ℓ will be assumed.

The nitrate data are presented in Figure 6. As with sulfate for 1977, nitrate had a larger median for the *brown* period. The median nitrate concentration for 1977 for the combined *brown* and *green* periods is 30 µeq/ℓ; for the *brown* period alone it is 38 µeq/ℓ, and for the *green* period alone it is 28 µeq/ℓ. For 1954, the median nitrate concentration is 18 µeq/ℓ; when samples with rain at the beginning are excluded, the median for nitrate is 20 µeq/ℓ.

For the 1954 data, hardness was reported and this is equal to $(Ca^{++} + Mg^{++})$. In Figure 7 the data for $(Ca^{++} + Mg^{++})$ is presented. The median $(Ca^{++} + Mg^{++})$ value for the combined *green* and *brown* periods in 1977 is 10 µeq/ℓ; for the *brown* period it is 15 µeq/ℓ, and for the *green* period it is 10 µeq/ℓ. For 1954, the

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median (Ca^{++} + Mg^{++}) value is 65 µeq/ℓ. When samples with rain at the beginning are excluded, the 1954 median is 82 µeq/ℓ. For the nine 1954 events with (Ca^{++} + Mg^{++}) greater than 100 µeq/ℓ, two were in the *green* period and seven in the *brown* period.

Discussion

Results from the last section are summarized in the first two lines of Table I. Even with the previously discussed difficulties in comparing event concentration data, there can be little question that the samples in 1954 were much more basic than the 1977 samples. Although both ($SO_4^=$) and (NO_3^-) were apparently lower in the 1954 samples, it was the high concentrations of soil related species, (Ca^{++} + Mg^{++}), which produced the high pH in 1954. If (Ca^{++} + Mg^{++}) in 1954 had been 10 µeq/ℓ (the 1977 level), then the pH would have been 4.17 instead of 6.05. The median pH = 6.05 for 1954 includes the empirical correction discussed earlier in this paper (Eqs. 6 and 7). Without this correction the 1954 median pH value would have been about 6.75. If once again it is assumed that (Ca^{++} + Mg^{++}) was 10 µeq/ℓ in 1954, then the pH would have been reduced from 6.75 to 4.34 (as compared to 4.1 in 1977).

Also listed in Table I is precipitation chemistry data for Ithaca, New York, for 1973. These data were for weekly samples collected with a simple system consisting of an uncovered funnel, tubing, and a two liter polyethylene reservoir. (Ca^{++} + Mg^{++}) for Ithaca is higher than observed in 1977 at CMI, but this may have been due to dry deposition effects with the uncovered funnel collector. Of more interest is the fact that ($SO_4^=$) and ($NO_3^=$) for Ithaca were higher than those for CMI, consistent with the higher atmospheric sulfate concentrations reported for the eastern United States.

With respect to the CMI data, several reasons for higher (Ca^{++} + Mg^{++}) in 1954 compared to 1977 can be suggested. The reasons are related to either changes in sample handling procedures or to changes in the concentrations of calcium and magnesium in the air. The recent work by Peden and Skowron has shown that for bulk rain samples which are not filtered soon after collection, (Ca^{++}) and (Mg^{++}) can rise by as much as an order of magnitude over several days, presumably due to the slow dissolution of particles in the samples.[8] This research is being continued in order to assess the importance of the phenomenon for precipitation samples where dry deposition effects are carefully excluded but where filtering is not carried out, analogous to the 1954 samples. (Ca^{++} + Mg^{++}) for the 16 filtered samples from 1954 were compared with the 48 unfiltered samples, and no significant difference was observed. However, it is not known by this author if the 16 samples were filtered immediately after collection or later when the samples were being analyzed.

In the 1954 data set there were eight cases where consecutive samples were collected during a rain event. In one case the values of (Ca^{++} + Mg^{++}), in the order of occurrence, were 214, 86, 36, and 4 μeq/ℓ. Since four samples were obtained, they were probably analyzed immediately, and thus the dissolution effect would have been minimized. From Figure 7 it can be seen that the value of 214 μeq/ℓ is greater than any observed in 1977.

If the pH of a precipitation sample is measured soon after it reaches the laboratory and then the concentrations of Ca^{++} and Mg^{++} increase and raise the pH before these ions are measured, then the calculated pH will be higher than the original sample pH. This trend would be consistent with the empirical corrections in Eqs. 6 and 7. Applying this reasoning to the 1954 data, the implied percentage change in (Ca^{++} + Mg^{++}) can be calculated. The calculated pH of 6.75 corresponds to (Net Ions) equal to -26 μeq/ℓ; the corrected pH of

6.05 to (Net Ions) equal to -4 μeq/ℓ. This difference in (Net Ions) of 22 μeq/ℓ would imply that the (Ca^{++} + Mg^{++}) value of 82 μeq/ℓ evolved from the original average sample concentration of 60 μeq/ℓ. The final result is that the empirically corrected pH for 1954 would be consistent with a 37% rise in (Ca^{++} + Mg^{++}).

Assuming that the reported (Ca^{++} + Mg^{++}) value of 82 μeq/ℓ accurately represented the precipitation falling in 1954, one must then conclude that more calcium and magnesium were present in the air in 1954 than in 1977. The discussion in the previous paragraph produced a 1954 value of 60 μeq/ℓ which is still much greater than the 1977 value of 10 μeq/ℓ. A possible source for the higher concentrations in the air could have been the dust from rural gravel roads. However, a scientist living in the area since 1954 has expressed to this author the feeling that most of the rural roads in the area had an asphalt type surface in 1954, just as they do today, such that roads would probably not have been a larger dust source in 1954.

The size of the machinery used to cultivate the fields has changed in the CMI area since 1954. This could have modified the local dust levels to some extent.

The final suggestion offered for the elevated (Ca^{++} + Mg^{++}) values in the air is that the years 1952-1954 were very dry in many states of the Midwest and the Plains, and thus the land was more susceptible to soil erosion by the wind as compared to 1977. For instance, in 1954 the precipitation was -33% (below normal) in Oklahoma, -25% for Kansas, -14% for Nebraska, -13% for Missouri, +9% for Iowa, and -6% for Illinois. For the Urbana climatological station the precipitation was -17% for the period of the 1954 chemistry study and +29% for the 1977 study period.

Considerable effort could be expended in carefully documenting the 1954 to 1977 time trend of each of the above suggestions for causes of increased calcium and magnesium in the atmosphere, and some of this research is now in progress. In addition we have started research to investigate the role of the soil and road dust sources in determining the current precipitation chemistry at sites in central Illinois.

Conclusions

A comparison of the precipitation chemistry data for wet-only event samples for 1954 and 1977 has been made for an east-central Illinois site. The precipitation samples from 1954 were much more basic than those of 1977, due mainly to the higher concentrations of calcium and magnesium as opposed to the lower concentrations of sulfate and nitrate. There is some concern that the higher concentrations of calcium and magnesium could have in part resulted from a lack of filtering of the 1954 samples soon after they were collected. To at least partially compensate for this possibility an empirical correction was applied to the calculated pH values for 1954. This resulted in a median pH for 1954 of 6.05. Without this empirical correction the median pH for 1954 was 6.75. These values are both much more basic than the 1977 median measured pH value of 4.1.

Although the data are not conclusive, it appears that sample handling was not the major cause of higher concentrations of calcium and magnesium in the 1954 precipitation. The alternative is higher concentrations of these basic substances in the air and consequently in the precipitation. Several suggestions for the cause of elevated concentrations of calcium and magnesium in the air are made. The one most favored by this author is that the severe

droughts occurring in the 1950's resulted in greater concentrations of soil dust over Illinois due to transport from upwind states. If this hypothesis is correct then the acid rain trend at the central Illinois site, suggested by the decrease in pH from 6.05 in 1954 to 4.1 in 1977, is due mainly to the interaction of weather with natural aerosol sources.

The major implication of the results reported in this paper is that calcium and magnesium concentrations must be carefully considered in explaining the acid rain trends for a geographic area. Further research on the effect of different sample handling procedures on the calcium and magnesium values is needed. Also the regional transport of basic aerosols should be evaluated just as the regional transport and transformations of anthropogenic acidic gases and aerosols is currently being evaluated by the atmospheric research community.

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List of Figure Captions

Figure 1. The concentration of Net Ions versus pH for precipitation samples with T = 25°C and P_{CO_2} = 320 x 10^{-6} atm (curve B) or with P_{CO_2} = 0.0 atm (curve C).

Figure 2. Calculated pH for 34 precipitation samples. The sample number identifies the samples as they were reported in Larson and Hettick[9]. The calculated pH values were not corrected via Eqs. 6 and 7.

Figure 3. Sulfate concentration versus rainfall amount for 46 central Illinois rain events in 1977.

Figure 4. Frequency distribution of measured pH for 1977 precipitation events and calculated pH for 1954 precipitation events. The numbers in parentheses indicate the number of data points from which the median was obtained.

Figure 5. Frequency distribution of sulfate for 1954 and 1977 precipitation events. The numbers in parentheses indicate the number of data points from which the median was obtained.

Figure 6. Frequency distribution of nitrate for 1954 and 1977 precipitation events. The numbers in parentheses indicate the number of data points from which the median was obtained.

Figure 7. Frequency distribution of calcium plus magnesium for 1954 and 1977 precipitation events. The numbers in parentheses indicate the number of data points from which the median was obtained.

Table I. Summary of ion concentrations (μeq ℓ^{-1}) and pH for precipitation samples.

	$(SO_4^=)$	(NO_3^-)	$(Ca^{++} + Mg^{++})$	pH
Ill., 1954[a]	60	20	82	6.05[b]
Ill., 1977[a]	70	30	10	4.1
N.Y., 1973[c]	103	46	48	4.05

[a]Median values for CMI event samples.

[b]Includes the empirical correction for calculated pH. Without this correction the value would be about 6.75.

[c]Precipitation-weighted average values for Ithaca, N.Y. from September 1972 to August 1973, listed in Table I of reference 6.
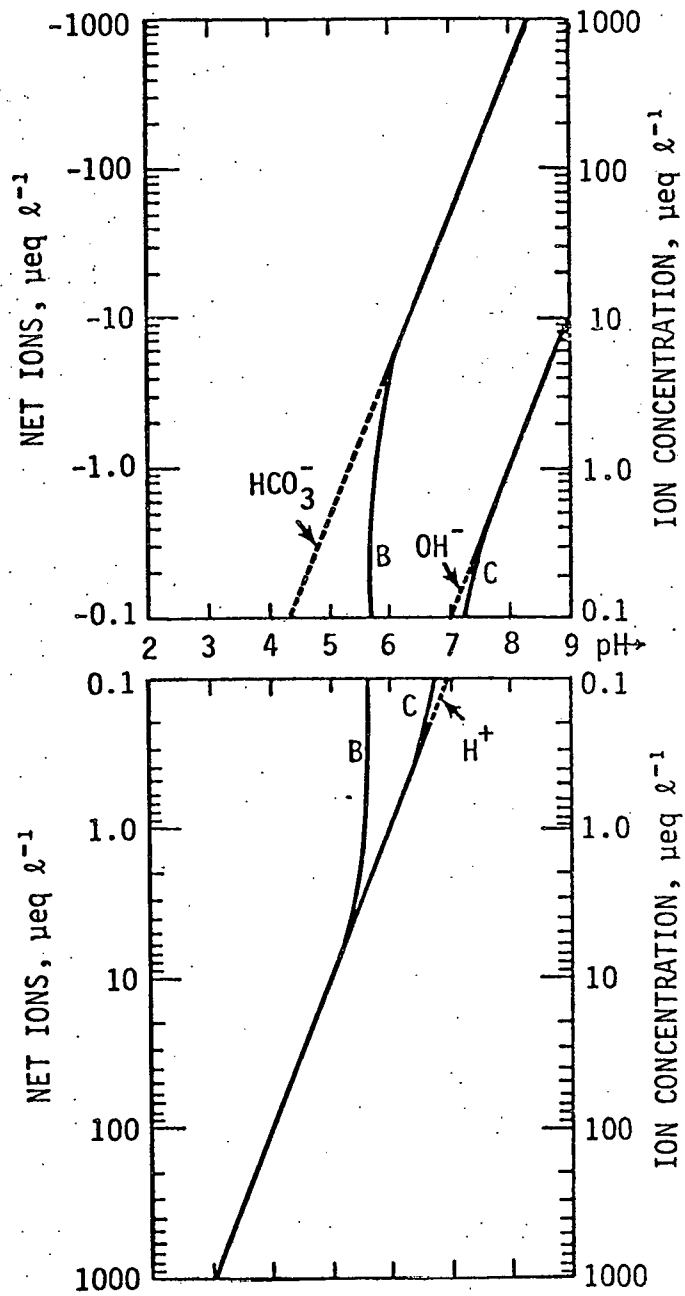
Figure 1. *The concentration of Net Ions versus pH for precipitation samples with $T = 25^O C$ and $P_{CO2} = 320 \times 10^{-6}$ atm (curve B) or with $P_{CO2} = 0.0$ atm (curve C).*
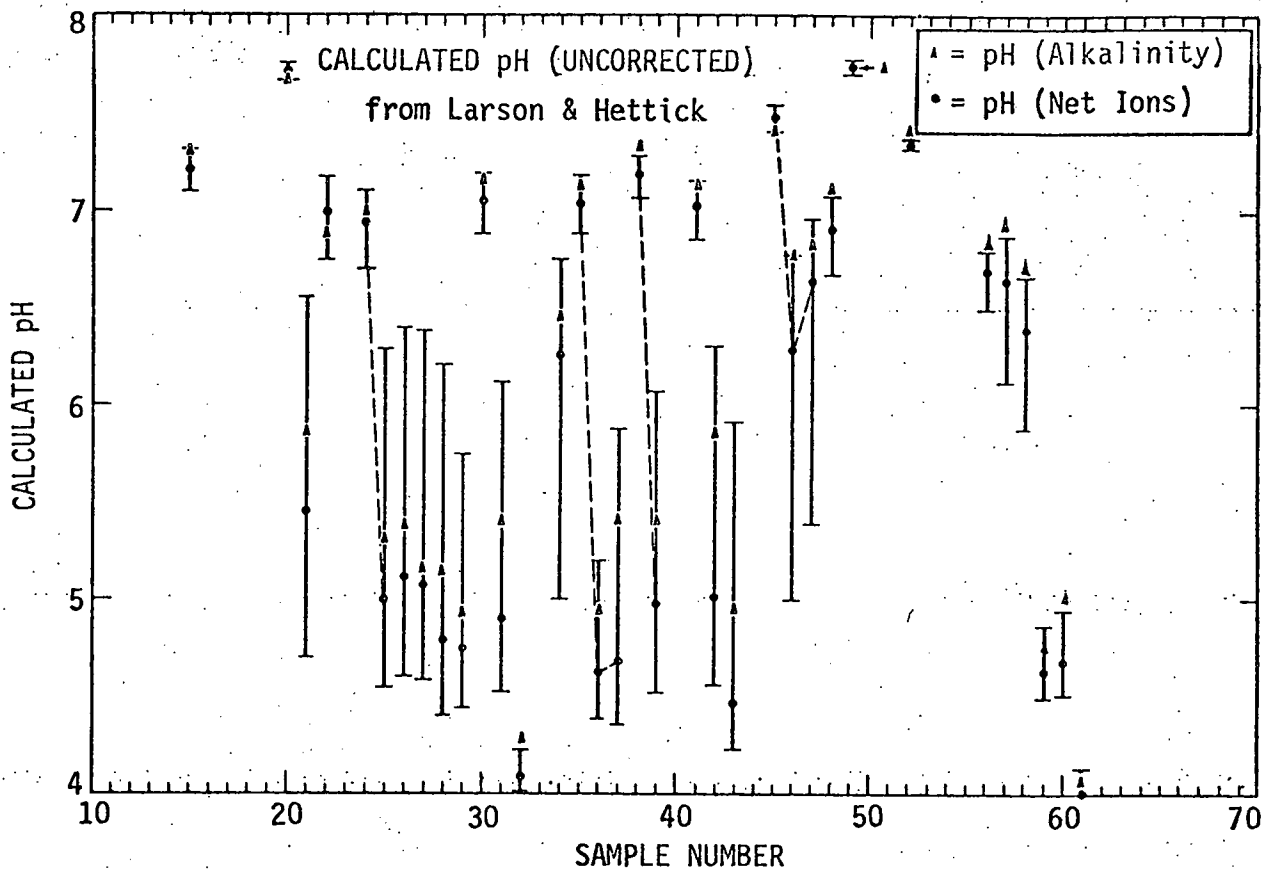
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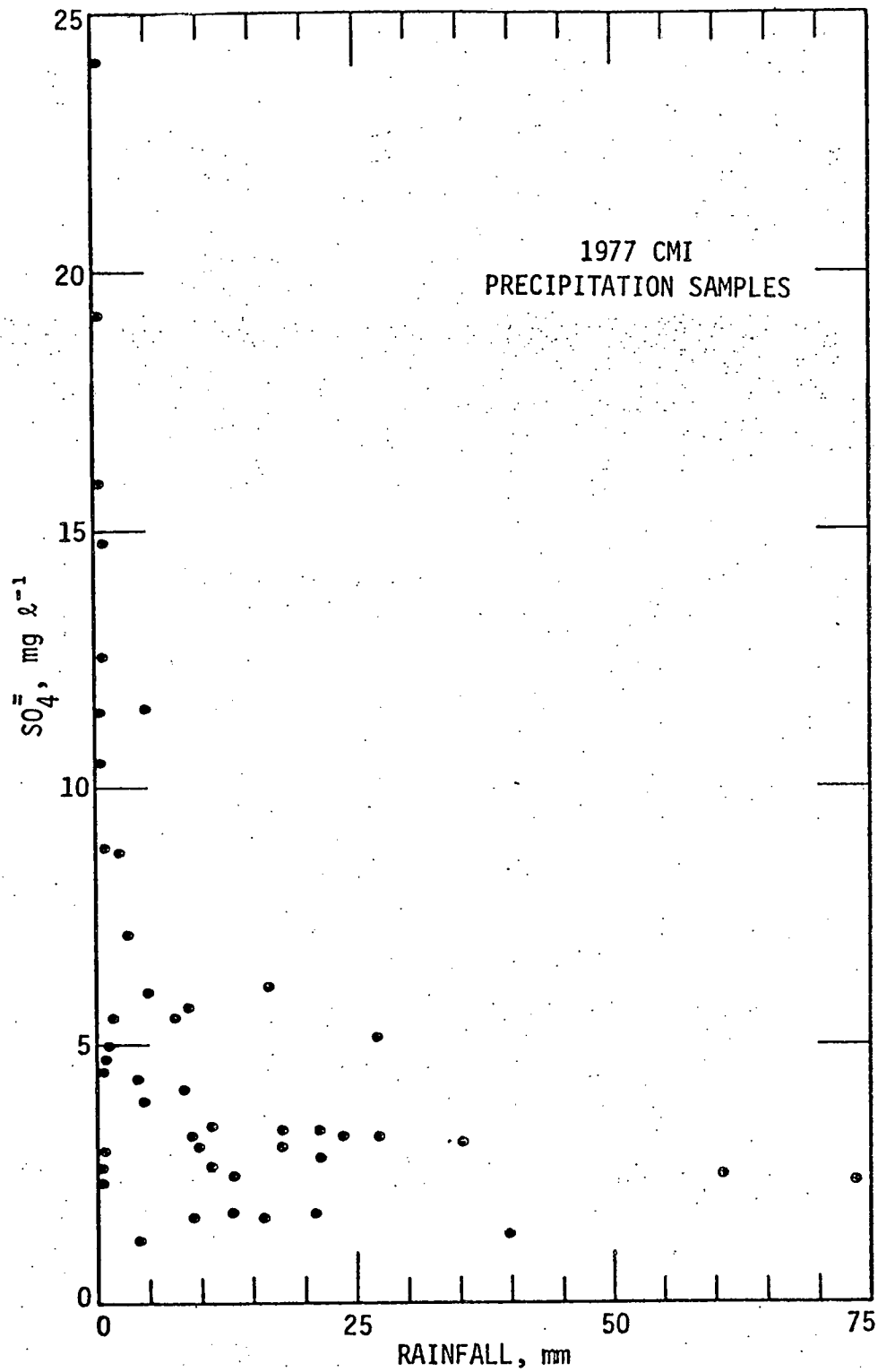The calculated pH values were not corrected via Eqs. 6 and 7.

Figure 3. Sulfate concentration versus rainfall amount for 46
central Illinois rain events in 1977.

CMI PRECIPITATION

M' = Median, all data
M = Median, samples ☐ and ○ excluded
• = Precipitation >0.70 mm
☐ = Precipitation 0.35 mm – 0.70 mm
○ = Precipitation <0.35 mm
▲ = Composite samples, precipitation >0.70 mm
▨ = Precipitation at beginning, and >0.70 mm

M'(40)
(28)M

(a) Oct. 1, 1977 – Feb. 6, 1978
"BROWN" PERIOD

(49)M' M(36)

NUMBER OF EVENTS

(b) May 15, 1977 – Sept. 30, 1977
"GREEN" PERIOD

(c) Oct. 26, 1953 – Aug. 12, 1954

M(38)

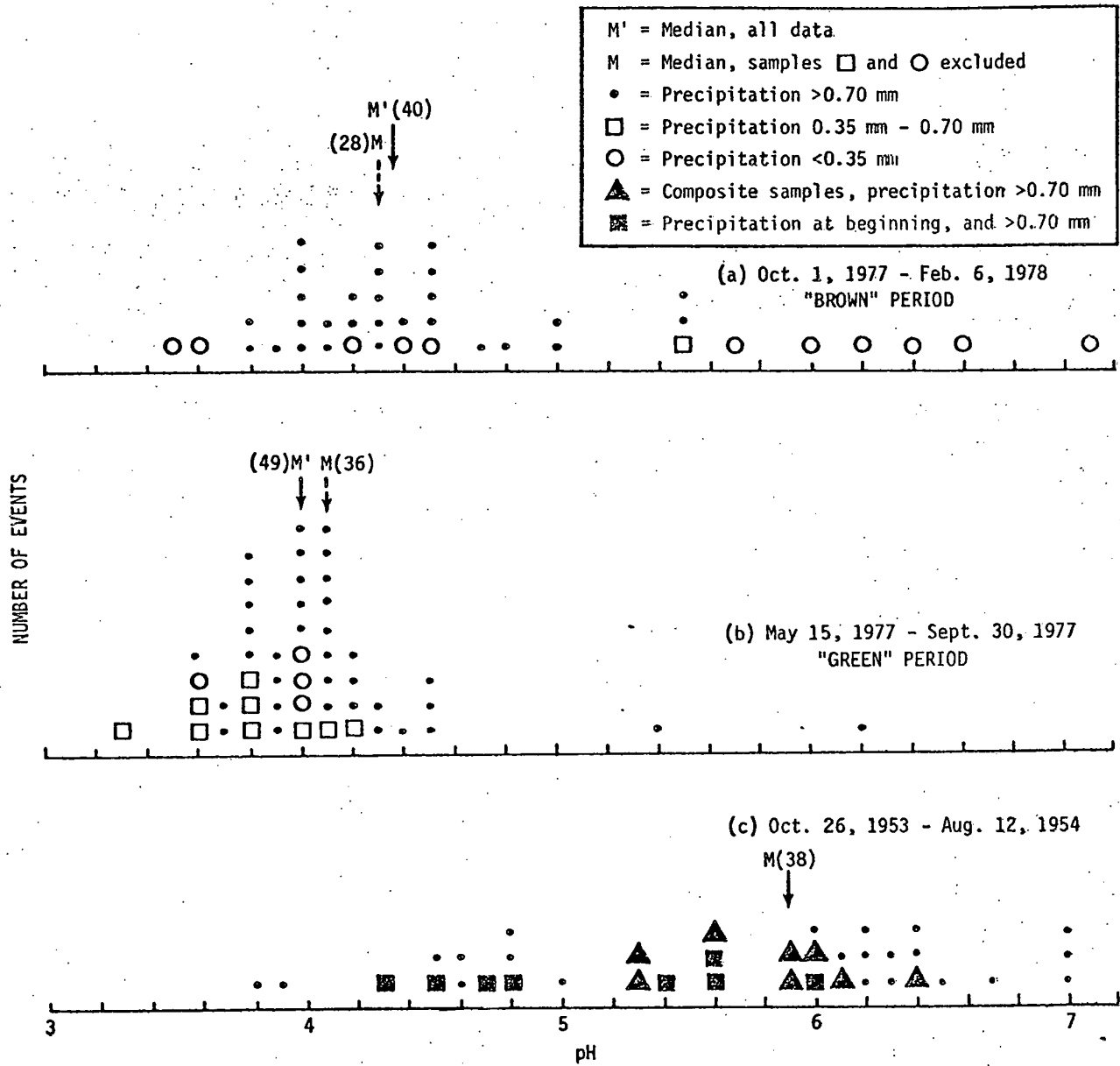3   4   5   6   7
pH

Figure 4.   Frequency distribution of measured pH for 1977 precipitation events
and calculated pH for 1954 precipitation events.   The numbers in
parentheses indicate the number of data points from which the median
was obtained.

CMI PRECIPITATION

M = Median
• = Precipitation >0.70 mm
▣ = Precipitation at beginning
▲ = Composite samples

M(28)

(a) Oct. 1, 1977 - Feb. 6, 1978
"BROWN" PERIOD

M(37)

(b) May 15, 1977 - Sept. 30, 1977
"GREEN" PERIOD

NUMBER OF EVENTS

M(35)

(c) Oct. 26, 1953 - Aug. 12, 1954

0   40   80   120   160   200   240   280   320
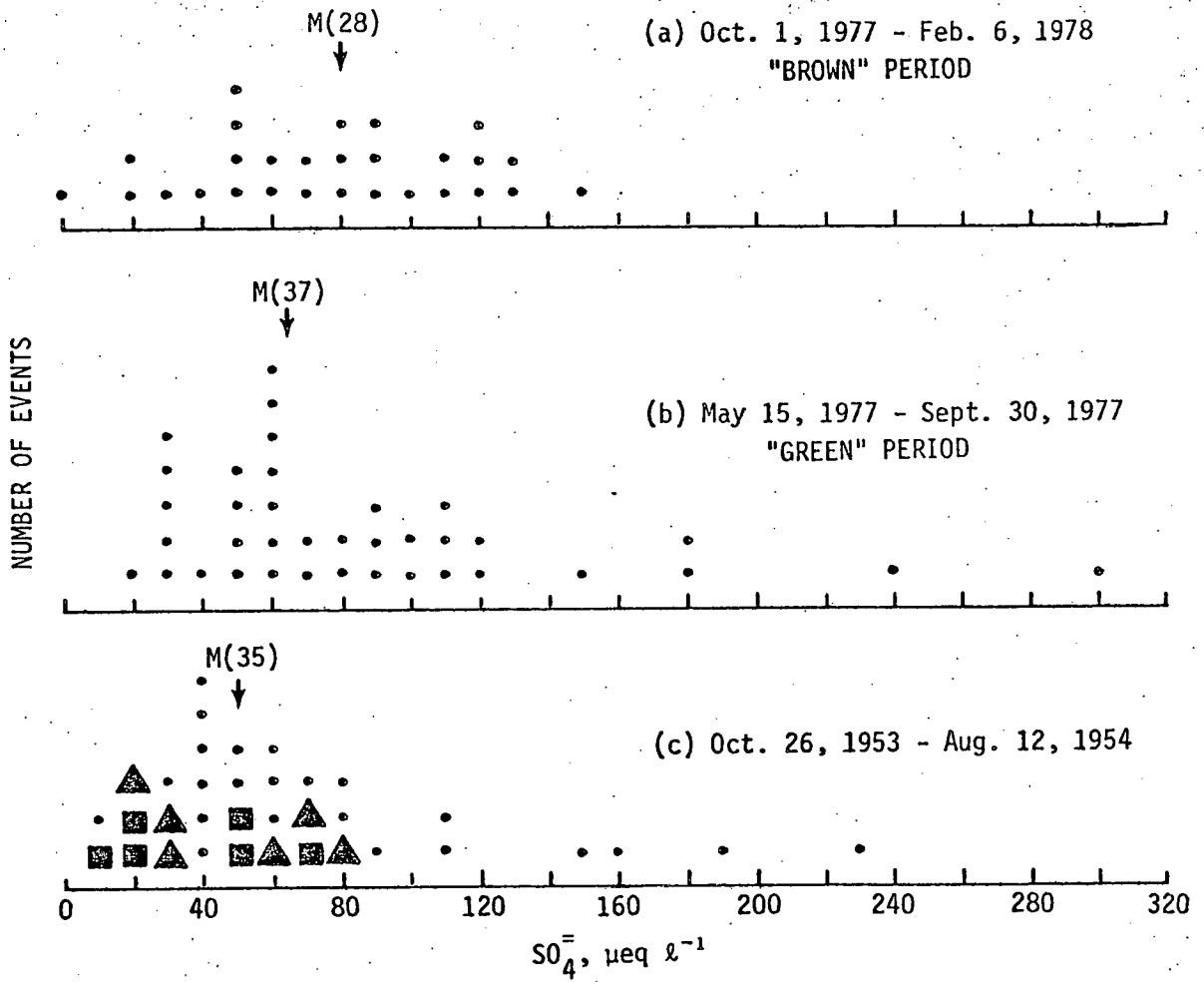
$SO_4^=$, µeq ℓ^{-1}

Figure 5. Frequency distribution of sulfate for 1954 and 1977 precipitation
events. The numbers in parentheses indicate the number of data
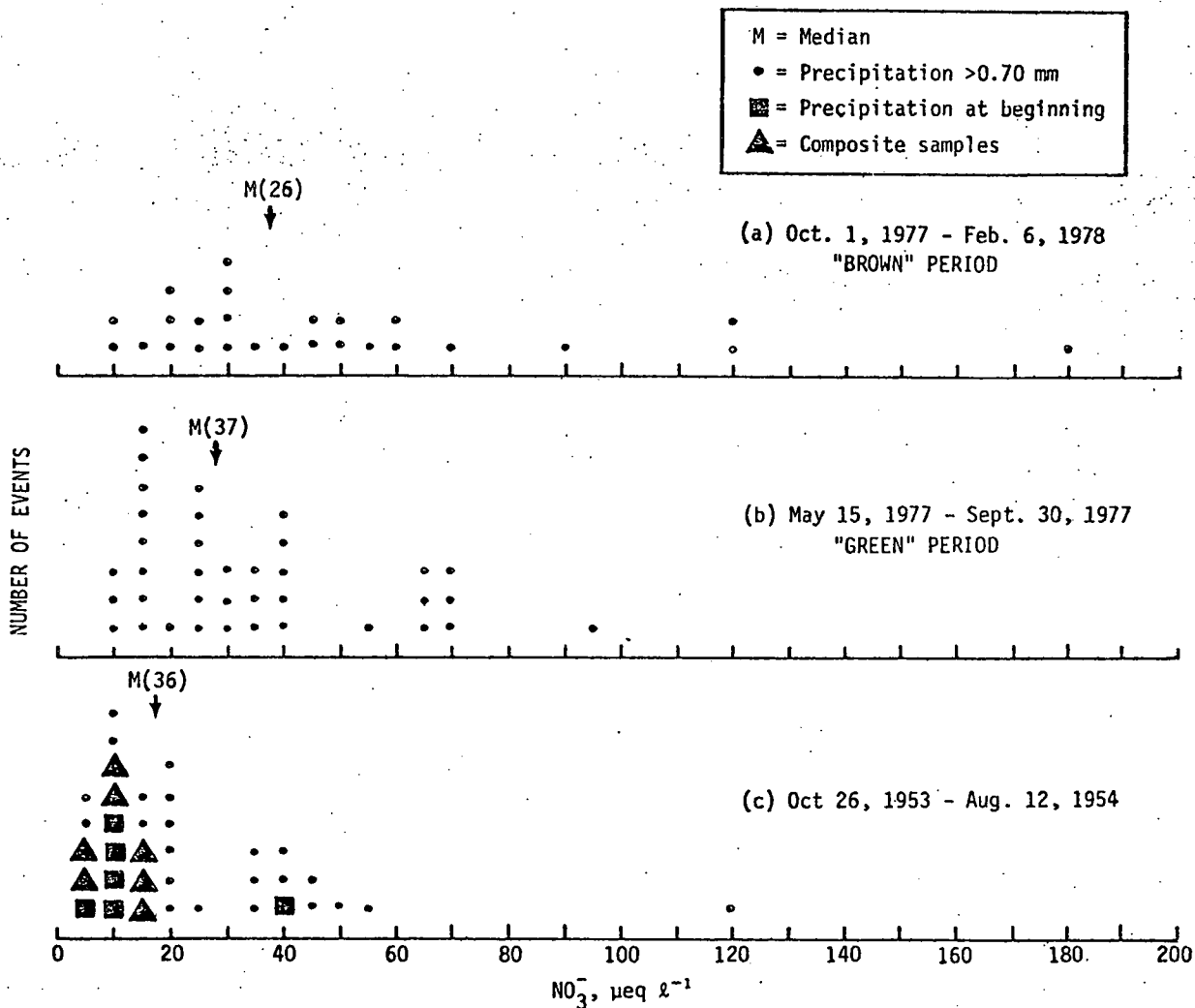points from which the median was obtained.

Figure 6. *Frequency distribution of nitrate for 1954 and 1977 precipitation events. The numbers in parentheses indicate the number of data points from which the median was obtained.*

CMI PRECIPITATION

M = Median
● = Precipitation >0.70 mm
▦ = Precipitation at beginning
▲ = Composite samples

M(26)
↓

(a) Oct. 1, 1977 - Feb. 6, 1978
    "BROWN" PERIOD

NUMBER OF EVENTS

M(37)
↓

(b) May 15, 1977 - Sept. 30, 1977
    "GREEN" PERIOD

M(34)
↓

(c) Oct. 26, 1953 - Aug. 12, 1954

●→(586)
●→(420)
●→(382)

0   20   40   60   80   100   120   140   160   180   200

$Ca^{++} + Mg^{++}$, µeq ℓ^{-1}
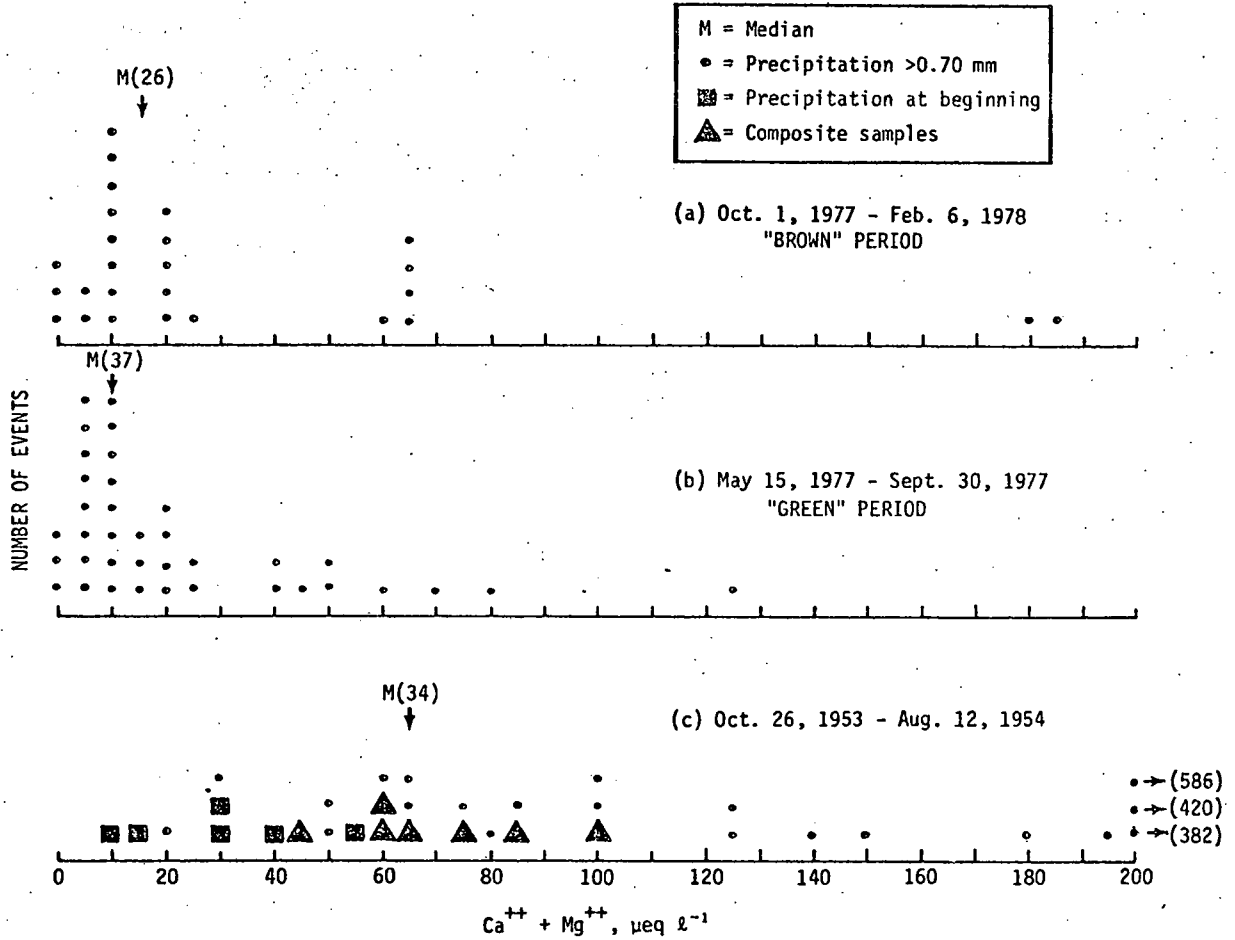
Figure 7.   Frequency distribution of calcium plus magnesium for 1954 and 1977
            precipitation events.   The numbers in parentheses indicate the
            number of data points from which the median was obtained.