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Meteorological and Chemical Relationships from Sequential Precipitation Samples[1,2]

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Abstract

Hourly precipitation samples were collected for chemical analysis with an automatic, sequential sampler. Samples were analyzed for pH, conductivity, sulfate and other constituents. pH is related to sulfate concentration and atmospheric concentration of small particles. Chemical constituents vary seasonally and with precipitation type. Data permit inferences on the relative importance of rainout and washout.

Introduction

Since June, 1976, hourly precipitation samples have been collected at Brookhaven National Laboratory for chemical analyses of their constituents. This project is part of a larger program in which the effects of acid precipitation on vegetation are being studied and which was initiated by concern over the increasing acidity of precipitation in the northeastern United States (1). The purpose of this paper is to describe relationships found to date among certain chemical parameters of precipitation and their relationships to another measure of air pollution and to meteorological variables associated with the precipitation events.

Sampler

The automatic, sequential precipitation sampler used in this study was designed and built at Brookhaven National Laboratory and is described in detail elsewhere (2). The sampler body contains a turntable which holds thirty 1.9-lt polyethylene sampling bottles. A 40.6 cm diameter funnel is mounted on top of the body and protected from dry fallout by a movable cover between precipitation periods. The cover and two precipitation sensors mounted on it are similar in design to those of the HASL Wet/Dry Fallout Collector (3). In normal operation, the first sampling bottle remains under the funnel for one hour from the time precipitation starts and the cover opens. The turntable then steps to the next position each hour until precipitation stops and the cover closes. The funnel is heated during cold weather to melt frozen precipitation. The rain sensors are heated for the same purpose and to evaporate remaining drops after precipitation ceases. Each opening and closing of the cover and each step of the turntable are recorded to the nearest minute.

Samples are removed from the sampler as soon as possible after precipitation ends or once each day if precipitation is prolonged. The funnel and sample bottles are cleaned with distilled water after each use.

Most previous precipitation sampling has been conducted on a weekly or monthly basis and many earlier samplers did not exclude dry fallout. Some sampling in recent years has been conducted on an event basis and shorter period samples have been taken in a few research programs of limited duration. However, no previous program is known in which short period samples excluding dry fallout have been collected in all precipitation events over an extended period of time.

Analyses

The pH of the samples is measured as soon as possible after collection. If other analyses cannot be performed immediately, the samples are transferred to 500 ml covered polyethylene bottles and stored at 4°C until analyzed. In addition to pH, the samples are measured for specific conductivity (μmho/cm) and for concentration (ppm) of nitrate, sulfate, ammonia, sodium and chloride.

Data

From June, 1976 to early February, 1977, 366 hourly samples were taken during 64 precipitation events ranging from brief showers to extended periods of rainfall. In addition to the chemical measurements, date, time and duration of each sample were recorded plus the following meteorological parameters: amount of precipitation, type of precipitation, type of cloud, synoptic situation causing the precipitation, wind direction, wind speed and temperature.

Since the number of variables influencing the results is large and only eight months of data have been collected, the findings presented here are preliminary and conclusions tentative. However, they are presented to show some of the ways in which data with this detail can be analyzed and to demonstrate the range of relationships which must be investigated to properly interpret precipitation chemistry data.

Results

pH is lowest in the summer season (Table 1) when air mass movement is typically slow and air pollution levels in the northeastern United States are often high. Most summer precipitation is shower type so that cleansing of large masses of air by extended periods of precipitation rarely occurs.

However, cleansing of the air during longer periods of precipitation has been documented during other times of year. During a rain on December 7, 1976, pH rose fairly steadily from the first hour while conductivity and concentrations of nitrogen, chlorine, sodium and sulfate all declined, mostly to minimum measureable levels (Figure 1). Ammonia showed an irregular pattern.

During a snow on December 26, 1976, similar effects were seen (Figure 2) although most contaminants were at or soon reached their lower limits of detectability. In several other lengthy periods of precipitation, this cleansing effect did not occur since rainfall rates were too low to effect cleansing or the air was too clean at the beginning of precipitation to show any appreciable change.

Precipitation removes gaseous and particulate contaminants from the atmosphere by several mechanisms. Those occurring during the cloud formation stage or within the cloud are collectively called rainout and those occurring below cloud base are termed washout. Washout takes place largely in the early stages of a precipitation event during which time materials removed by both processes are present in the precipitation. If precipitation continues long enough at a heavy enough rate, contaminants will be largely removed from the below cloud layer and materials still present in the sample can be attributed to rainout. In the two cases presented (Figures 1 and 2) the higher concentrations in the early hours are believed due to both rainout and washout while the nearly steady concentrations in the later hours are of rainout materials only.

pH during thundershowers has averaged much lower than during other types of precipitation (Table 2). This may be partially a seasonal effect since most thundershowers occur in the summer. However, the cumulonimbus clouds which produce thundershowers extend to much higher altitudes in the atmosphere than other rain-producing clouds and have vigorous circulations which pull into their bases large volumes of air from low elevations. They also entrain additional air at higher elevations by turbulent mixing with surrounding air. Thus, large quantities of pollutants may enter a cumulonimbus cloud and subsequently be washed out.

An extended rainfall preceding Hurricane Belle in August, 1976 illustrates both the cleansing with time and the thundershower effects (Figure 3). pH rose rather uniformily with time from the beginning of the rainfall but several thundershowers were embedded in the general rain clouds and each was reflected by a sharp decline in pH except during the early hours before the air was cleansed. This suggests that the thundershowers entrained pollutants from above the altitude washed out by the continuous rain. Thus, the lower pH of thunderstorm rainfall in general may be due to both more polluted air during the summer and to the cloud dynamics which entrain air over a greater range of altitudes.

Previous theoretical and experimental studies have shown that lightning discharges in thunderstorms can form nitrates from atmospheric nitrogen (4). Thus, the nitrate data from June through September, 1976 were examined by precipitation type (Table 3). The higher mean and minimum nitrate concentration in thundershowers could be partially due to this process but may merely reflect higher pollution levels prior to summer thundershowers. Many more cases are needed to resolve this uncertainty.

During the night of August 9-10, 1976, the small hurricane Belle crossed Long Island. Although extensive precipitation preceded the storm, rainfall during the period of peak winds was light and contained a high percentage of wind-driven salt spray from the ocean. Concentrations of sodium and chloride increased steadily as the wind increased (Figure 4) and reached levels about one thousand times normal. Unfortunately, the record was terminated by a power failure after 0200 on August 10.

Relationships among contaminants in the samples have been examined in part. Specific conductivity and pH (Figure 5) show the expected inverse relationship. A slightly better correlation was found between pH and ln conductivity (r= -0.67) than between pH and conductivity (r= -0.62).

Sulfate concentrations were also related to pH (Figure 6). Considerable scatter is evident and the best least squares fit of pH with ln S gives r= -0.39 while the best fit rS gives r= -0.30. These low correlations suggest that other materials also contribute to acidity in precipitation.

Concentrations of small particles in the light scattering region (radius = 0.1-10 μm) are measured continuously by an integrating nephelometer (5) mounted at 128 m above the ground on a meteorology tower about 220 m from the precipitation collector. Particle concentrations in the last hour before precipitation started were related to pH in the sample collected during the first hour of precipitation (Figure 7). Much scatter is evident because the particles measured by the nephelometer are not necessarily those contributing to the acidity in the precipitation and measurements at one height are not necessarily representative of concentrations from the surface to cloud level. However, the trend for lower pH with higher particle concentration is evident and not unexpected since both are indicators of the level of air pollution.

Conclusions

Short period precipitation samples provide information not obtainable from event samples, from samples taken over longer periods or from samples including dry fallout. Concurrent recording of meteorological variables makes it possible to relate precipitation chemistry to causative atmospheric processes. Estimates can be obtained of the relative amounts of material removed from the atmosphere by rainout and washout. The relationships found so far among rainfall constituents and between them and meteorological parameters are consistent with known atmospheric and chemical processes.

Acknowledgements

John McNeil assisted in design of the sampler and collection of the samples. Chemical analyses were performed by Daniel Leahy, Mary Kinsley and other members of the Atmospheric Chemistry Group under the direction of Leonard Newman.

Literature cited

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Table 1

pH by Season

Season	No. Hours	Mean	Standard Deviation
Summer	53	4.26	0.82
Fall	156	5.26	0.83
Winter	107	4.78	0.58

Table 2

pH by Precipitation Type

Precipitation Type	No. Hours	Mean	Standard Deviation
Thundershower	18	3.83	0.48
Thundershower and Rainshower	9	4.89	0.72
Rainshower	45	4.75	0.76
Rain	159	5.20	0.77
Snow	57	4.70	0.42

Table 3

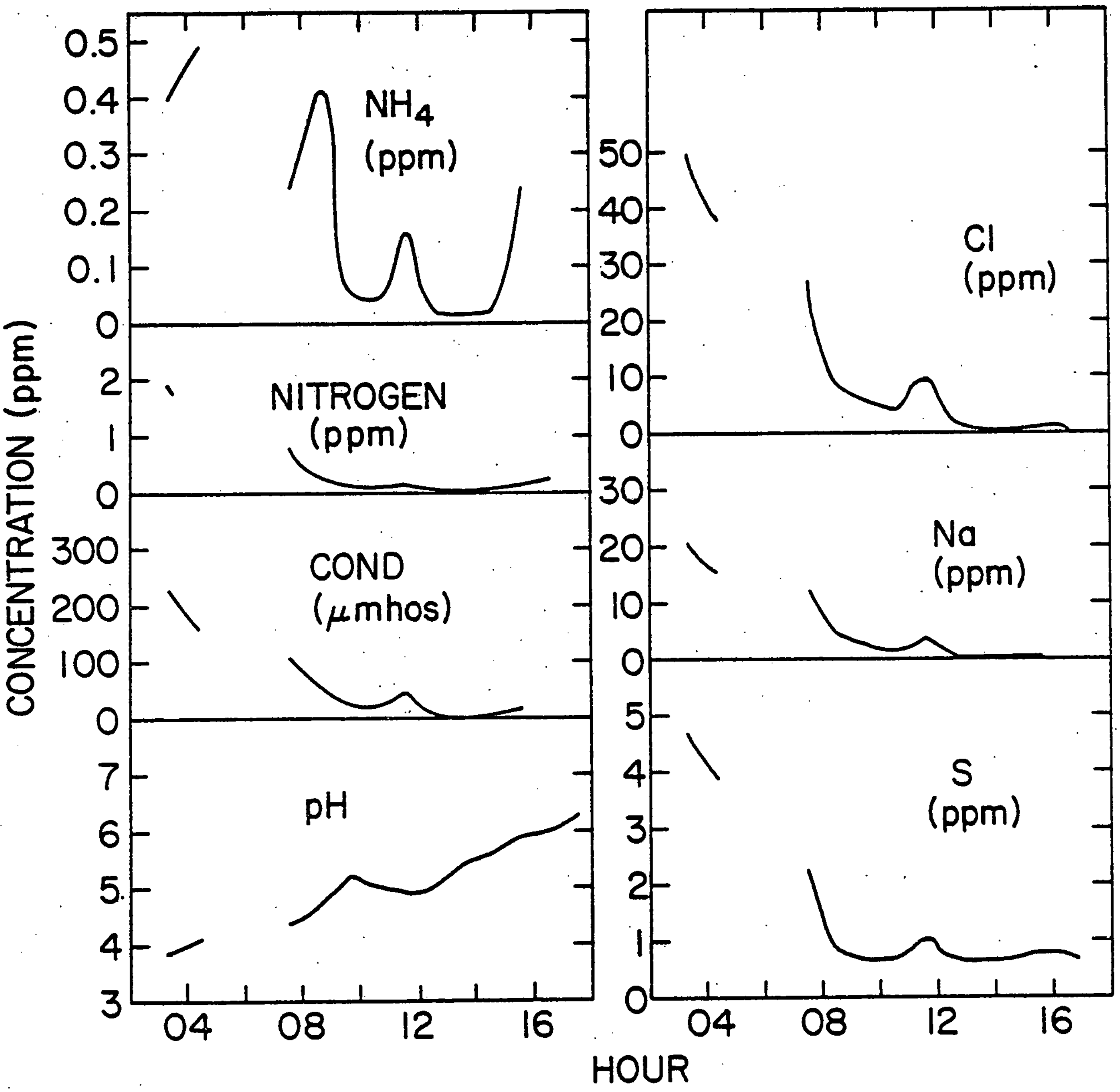
Nitrate Concentration by Precipitation Type

Precipitation Type	No. Hours	Nitrate Concentration (ppm) Minimum	Maximum	Mean
Thundershower	18	0.21	3.28	1.21
Thundershower and Rainshower	9	0.02	2.27	0.37
Rain Shower	23	0.10	2.40	0.81
Rain	46	0.02	4.10	0.60

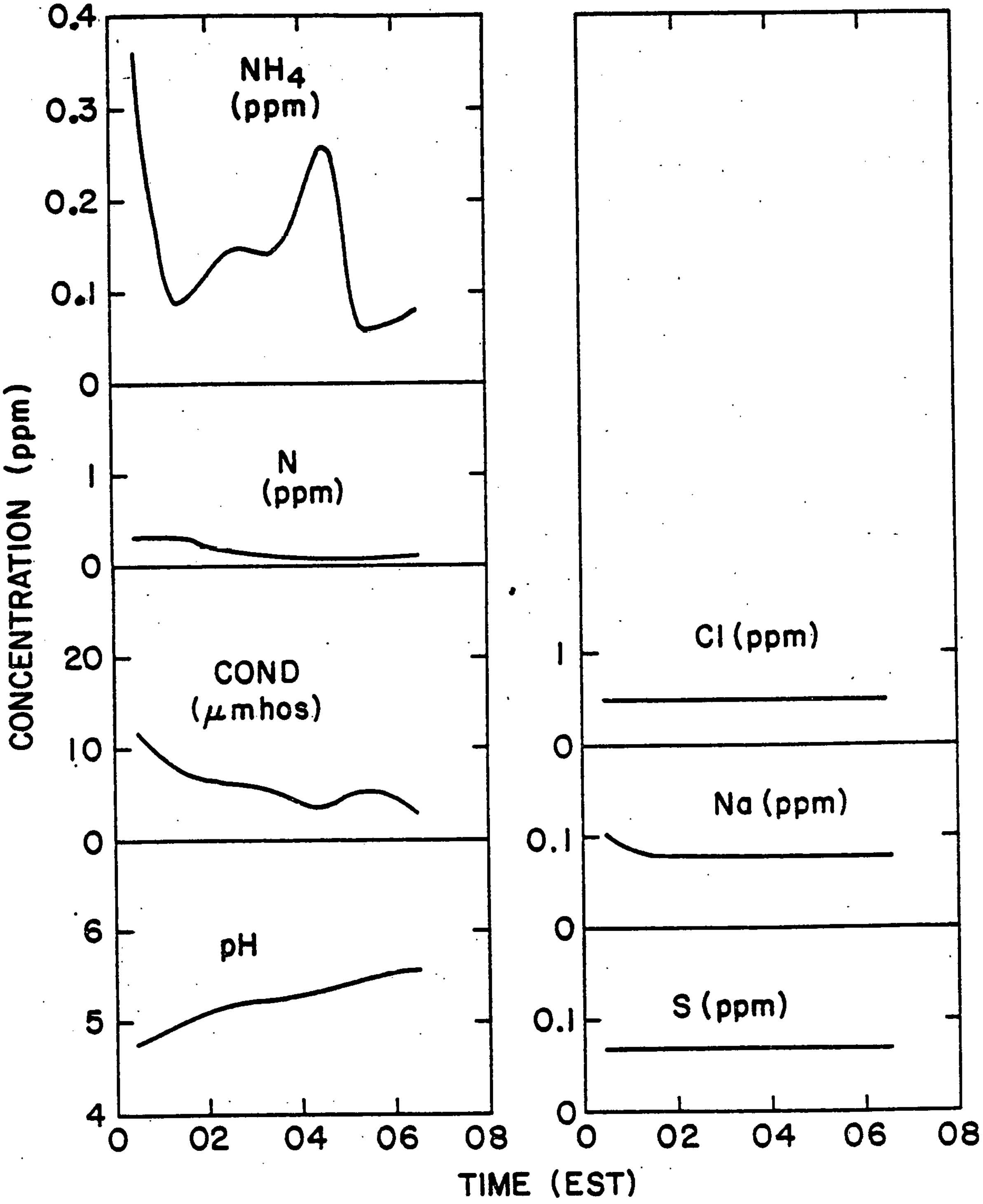
List of Figures

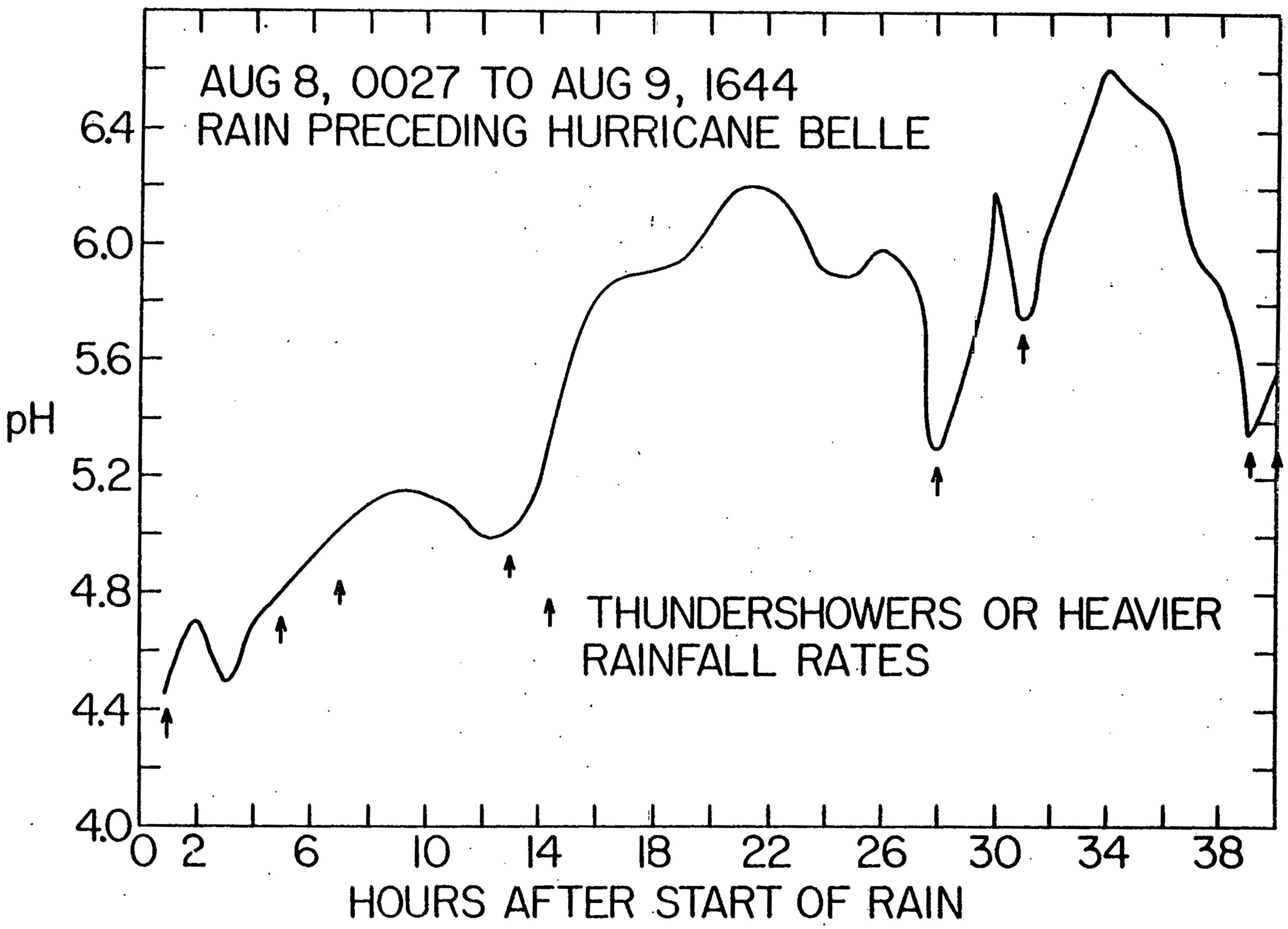
FIG. NO.	NEG. NO.	FIG. NO.	NEG. NO.
1	3-1135-77	6	4-178-77
2	2-347-77	7	4-177-77
3	2-346-77		
4	2-349-77		
5	4-179-77		

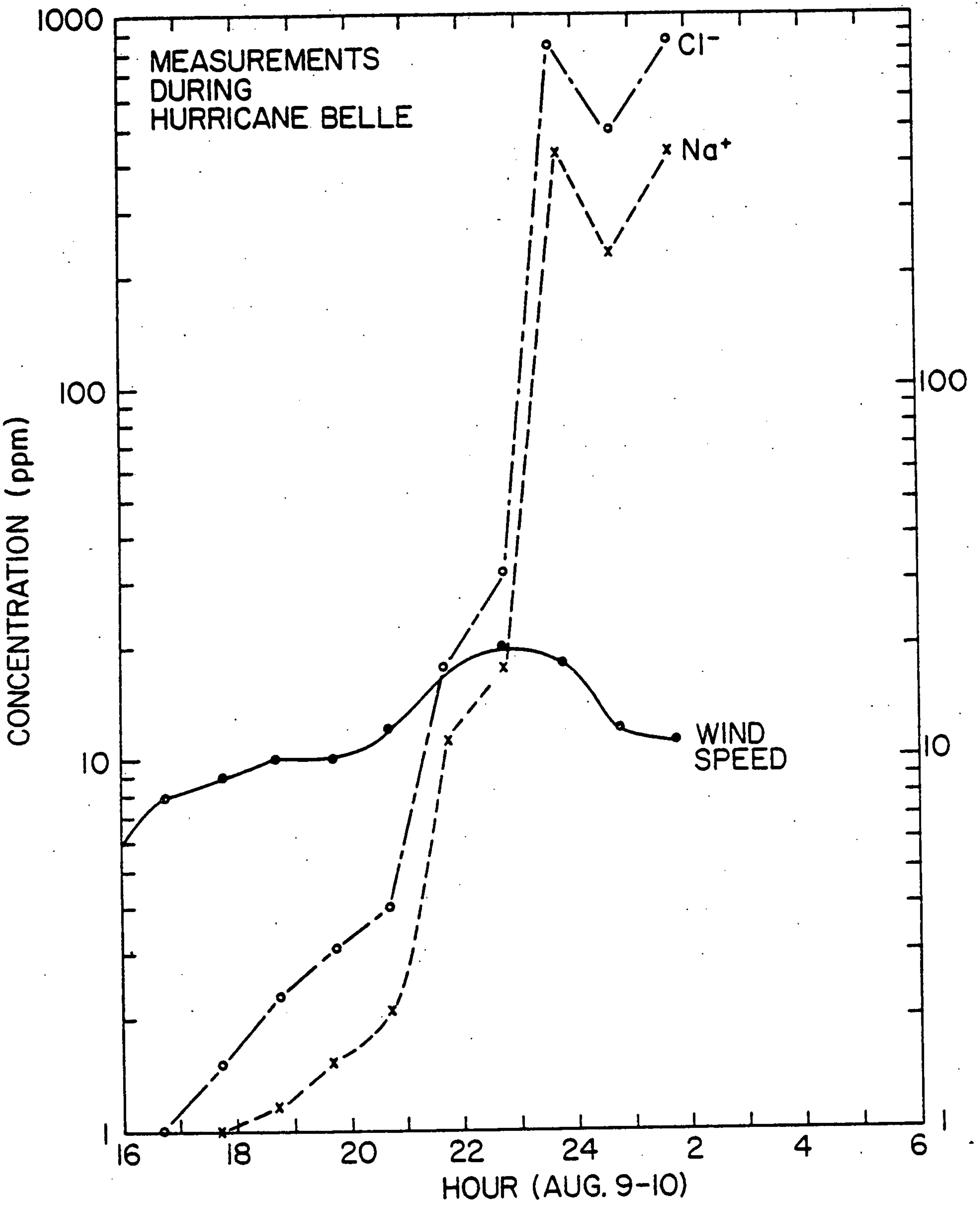
RAIN OF DEC. 7, 1976
0249 - 1815

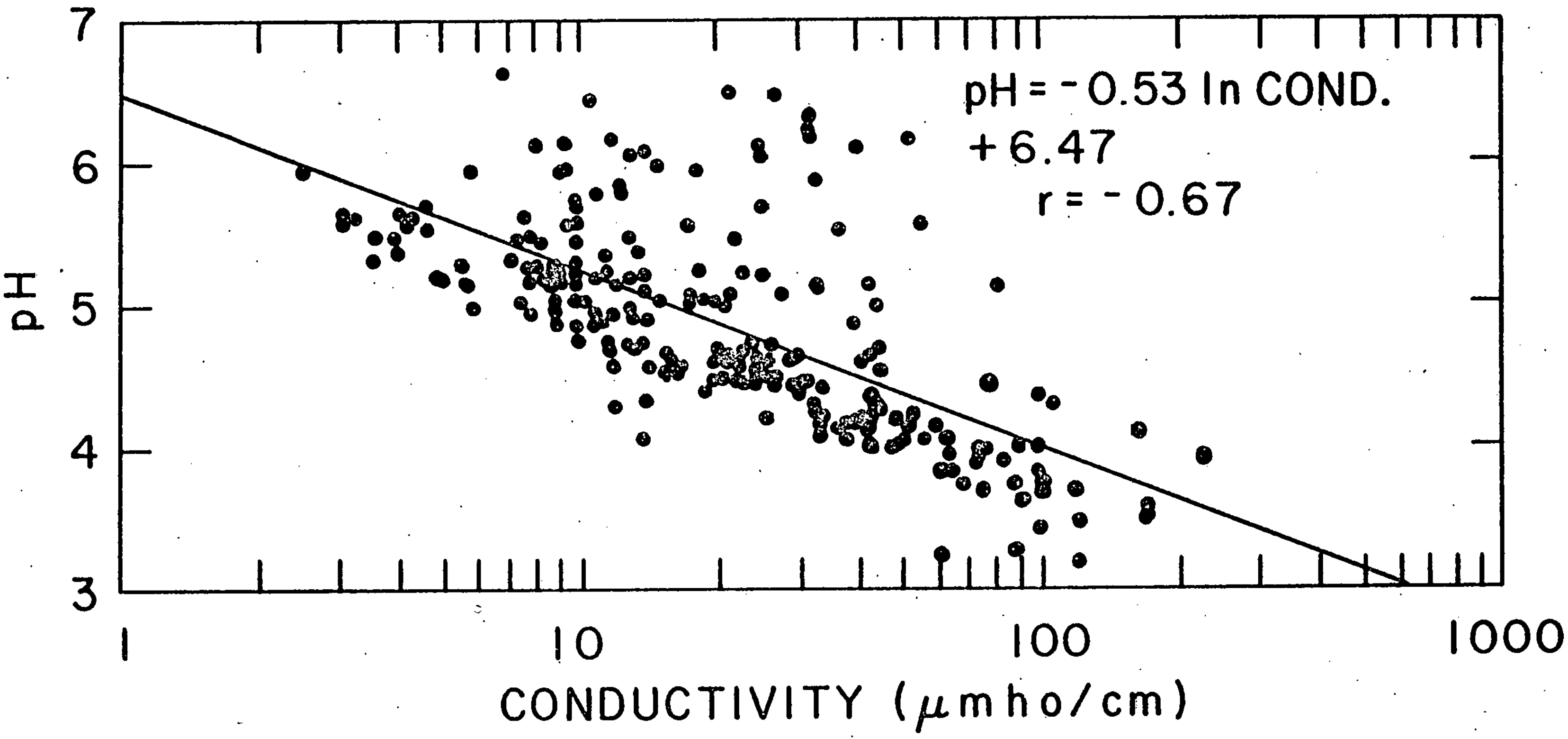


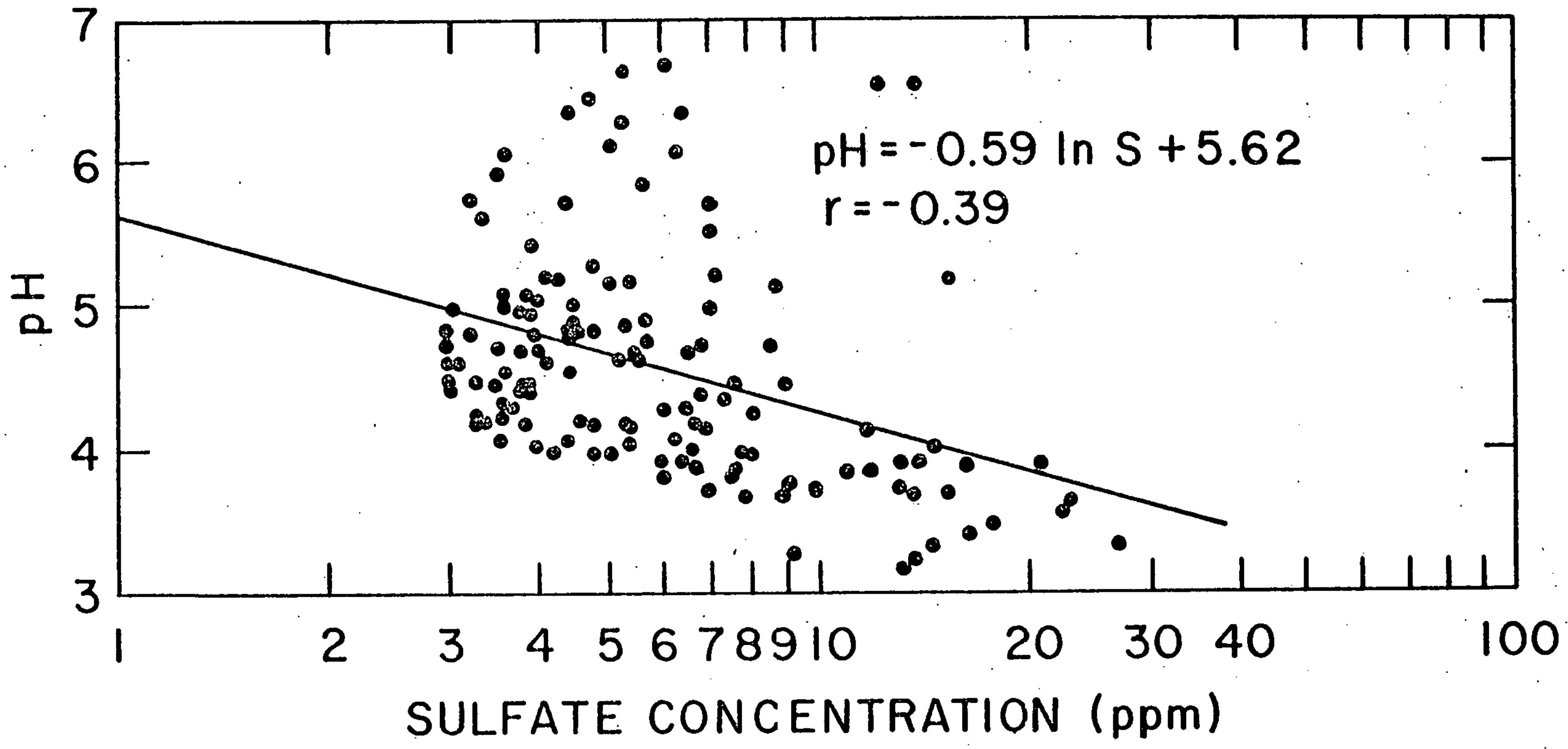
SNOW OF DEC. 26, 1976
0006 - 0807

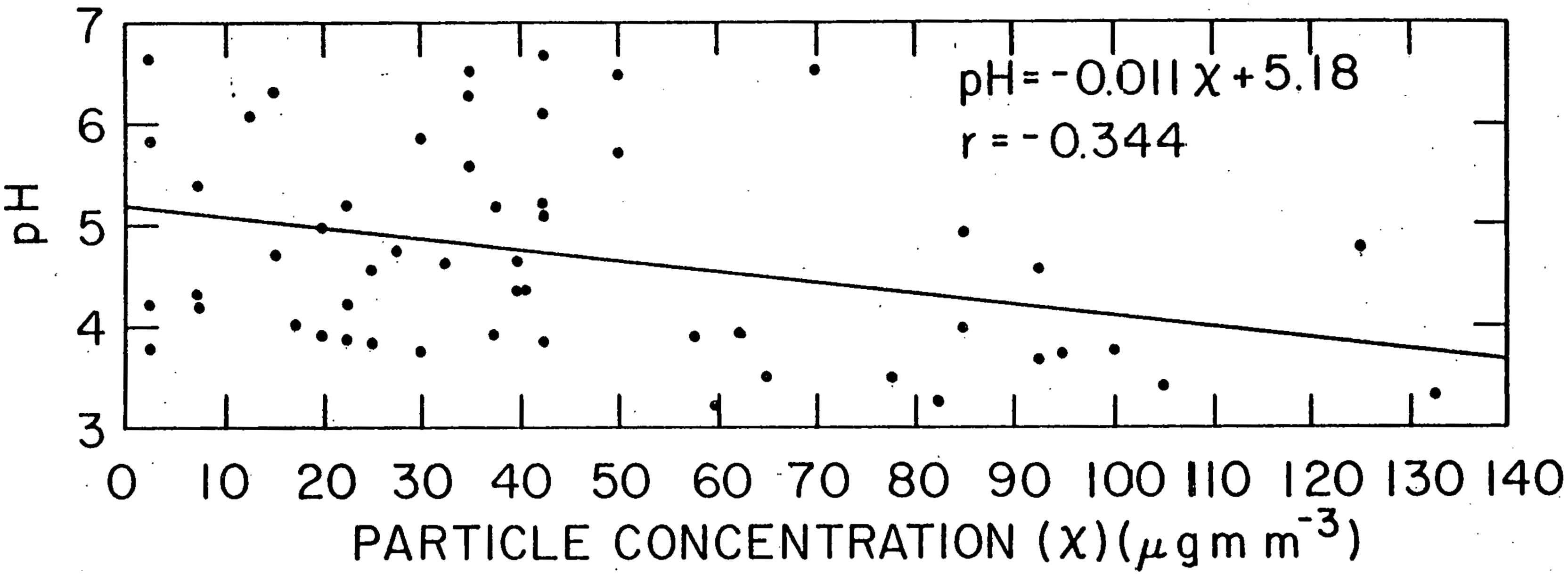



AUG 8, 0027 TO AUG 9, 1644
RAIN PRECEDING HURRICANE BELLE
THUNDERSHOWERS OR HEAVIER RAINFALL RATES
pH
6.4
6.0
5.6
5.2
4.8
4.4
4.0
0
2
6
10
14
18
22
26
30
34
38
HOURS AFTER START OF RAIN


MEASUREMENTS
DURING
HURRICANE BELLE
Cl⁻
Na⁺
WIND
SPEED
CONCENTRATION (ppm)
WIND SPEED (MPS)
1000
100
10
1
100
10
1
16
18
20
22
24
2
4
6
HOUR (AUG. 9-10)


7
6
5
4
3
pH
1
10
100
1000
CONDUCTIVITY (μmho/cm)
pH = - 0.53 ln COND.
+ 6.47
r = - 0.67


pH = -0.59 ln S + 5.62
r = -0.39
pH
7
6
5
4
3
1
2
3
4
5
6
7
8
9
10
20
30
40
100
SULFATE CONCENTRATION (ppm)


pH=-0.011 χ+5.18
r=-0.344
pH
7
6
5
4
3
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
PARTICLE CONCENTRATION (χ)(μg m m^{-3})