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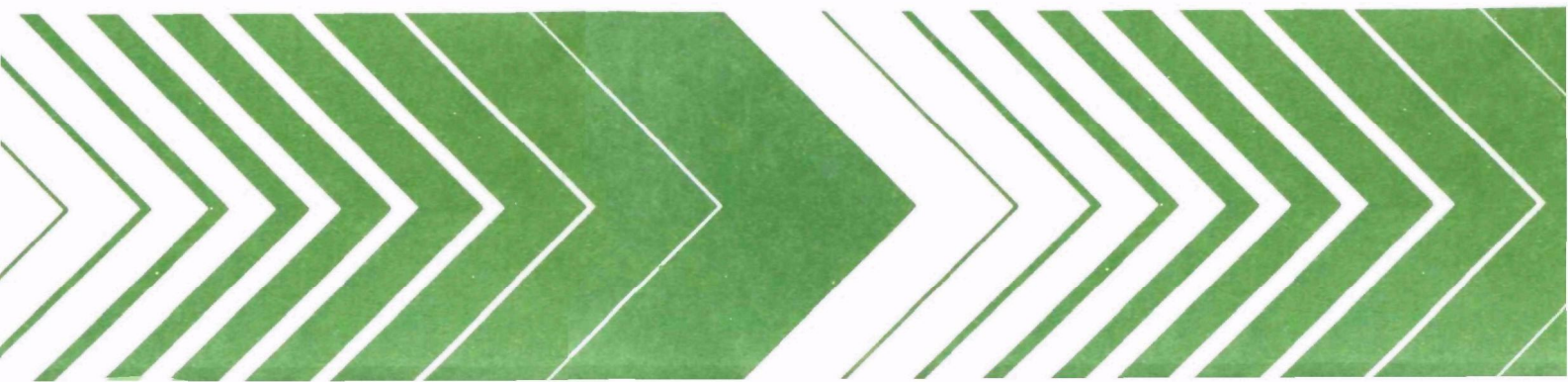
Environmental Sciences Research
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Research Triangle Park NC 27711

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Research and Development



Chemistry of Precipitation from Sequentially Sampled Storms



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CHEMISTRY OF PRECIPITATION FROM SEQUENTIALLY SAMPLED STORMS

by

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ABSTRACT

Sequential sampling techniques and applications to collect precipitation are reviewed. Chemical data for samples collected by an intensity-weighted sequential sampling device in operation at the U.S. Military Academy, West Point, New York from October 1976 to April 1978 are presented and discussed. The problem of dry deposition is explored. A newly designed intensity-weighted sequential sampler that excludes dry deposition is presented.

The experiments have shown that intensity-weighted sequential sampling is a viable technique for monitoring the rapid changes in precipitation chemistry within a storm. Complete chemical data are needed from individual storms to evaluate intensity related scavenging.

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SECTION 1

INTRODUCTION

Considerable attention has been focused recently on the increasing acidity of precipitation in the northeastern and north central United States.^{1,2}

As a result of this concern, increased monitoring of precipitation chemistry on a regional basis has been proposed.^{3,4,5} This proposed network and others currently in operation (CANSAP, MAP3S, and NADP)⁺ collect precipitation samples on a weekly or monthly basis. This frequency of collection provides an indication of how much material has been deposited on the earth's surface by precipitation but fails to explore the instantaneous acidity extremes and underlying ion chemistries within a storm that may be potentially more damaging to the environment than the averages reported.

The purpose of the research reported here was to examine the changes in precipitation chemistry within individual storm events. This research is part of a program of research designed to investigate below cloud scavenging by precipitation. In this portion of research, an attempt was made to test a number of hypotheses using data collected by sequentially sampling precipitation. These hypotheses are enumerated below:

1. The concentration of dissolved constituents in precipitation is inversely proportional to the intensity of precipitation within the study pH range.

- - - - -
⁺Canadian Network for Sampling Precipitation (CANSAP)
Atmospheric Environment Service, Ontario, Canada.

Multistate Atmospheric Power Production Pollution
Study (MAP3S) Precipitation Chemistry Network
sponsored by the Department of Energy.

National Atmospheric Deposition Program (NADP)
sponsored by the North Central Regional Association
of Directors of the Agricultural Experimental Research
Stations.

2. The concentration of dissolved constituents in precipitation decreases as the storm passes over the collector.
3. The relationships in 1 and 2 apply to both frontal storms and convective storms.
4. A seasonal variation in the weighted-average pH of storms exists.
5. The chemistry of precipitation within a storm is a result of the source area from which the storm originated.
6. Values of pH above 5.6 are due to disequilibrium between rain drops and the air pollutants rather than the presence of basic ions.

Each of these hypotheses will be discussed more fully in Section 7 along with the data collected during the program.

SECTION 2

CONCLUSIONS

1. Intensity-weighted sequential sampling is a viable technique for monitoring the rapid changes in precipitation chemistry within a storm.
2. Dry deposition in the West Point area is very acidic in nature. Collection vessels left open to the atmosphere prior to a storm, or after a storm become quickly contaminated by dry deposition. During periods of light precipitation, dry deposition is large and may exceed wet deposition as the dominant process. Any precipitation chemistry data for storm events in the West Point area in which dry deposition was not specifically excluded must be viewed as being possibly contaminated by dry deposition or be considered as a bulk precipitation sample (wet and dry precipitation combined).
3. Complete chemical data are needed from individual storms to evaluate intensity related scavenging.
4. During periods of high intensity precipitation scavenging causes pH to increase and the amount of dissolved constituents to fall to low levels.

SECTION 3
RECOMMENDATIONS

1. Sequential sampling of storms be continued with the following restrictions:
 - a. dry deposition be excluded from collection by use of an automated closure device, and
 - b. concurrent collection of meteorological parameters be made.
2. Every sequential sample within a storm should be analyzed for Na^+ , NH_4^+ , K^+ , Ca^{+2} , Mg^{+2} , Cl^- , PO_4^{-3} , NO_3^- , SO_4^{-2} , pH, and conductivity.
3. Selected storms or the initial and intense portions of all storms should be analyzed for:
 - a. heavy metals
 - b. organic acids
4. The ambient air should be sampled continuously before, during, and after the sequential sampling of precipitation to monitor gaseous and particulate pollutants to attempt to evaluate scavenging of below cloud pollutants from the air mass.

SECTION 4

SEQUENTIAL SAMPLING

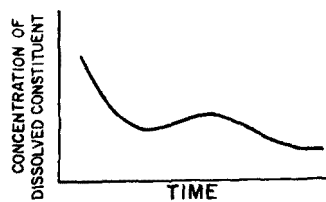
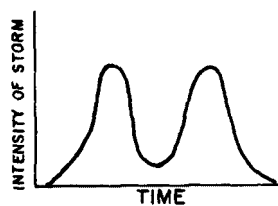
DEFINITIONS

The chemistry of precipitation has been monitored for many years. Each researcher's objectives influence the choice of sampling methods and observation frequency. Those interested in atmospheric loading to the environment sample on a monthly, weekly, or perhaps single storm basis. Those interested in cloud processes and scavenging have used a sequential sampling method.

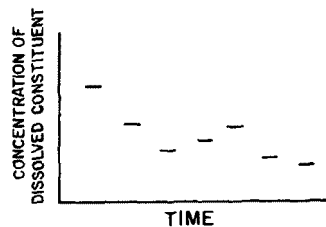
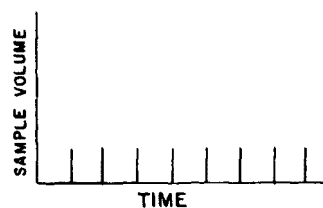
Sequential sampling produces a number of samples through the course of a storm, each sample representing the portion of the storm from which it was collected. A number of sequential sampling strategies have been used. An analysis of these methods shows the five basic approaches outlined below:

1. Grab Sampling: Samples are taken without respect to time or volume, but usually to provide at least a minimal amount for analysis. Generally samples are collected proportional to intensity.
2. Time related grab sampling (Figure 1b): Samples of equal volume are collected at fixed time intervals. Once the set volume is collected the excess is allowed to spill until the next time interval starts. An incomplete sample of the storm will be collected.
3. Time weighted sequential sampling (Figure 1c): Samples of unequal volume are collected consecutively for a predetermined time interval. The volume of each sample varies depending on the intensity of precipitation during its collection interval. The container volume is set large enough to collect the volume from the most intense storm period expected. Samples are collected without time break for the whole storm period.
4. Intensity weighted sequential sampling (Figure 1d): Samples of equal volume, collected at unequal time intervals. Sampling frequency is proportional to the

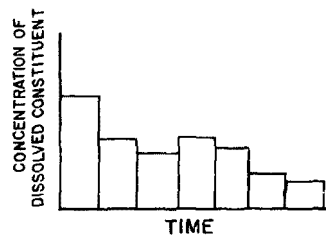
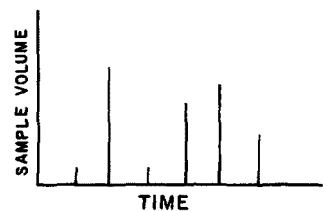
A. HYPOTHETICAL STORM INTENSITY AND CHEMISTRY



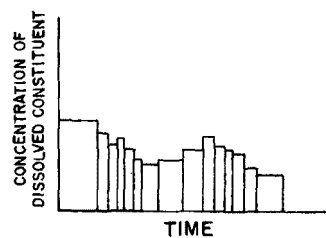
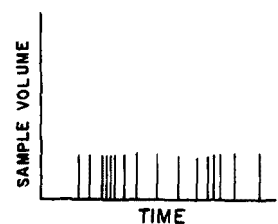
B. TIME RELATED GRAB SAMPLING



C. TIME WEIGHTED SEQUENTIAL SAMPLING



D. INTENSITY WEIGHTED SEQUENTIAL SAMPLING



E. CONTINUOUS MONITORING

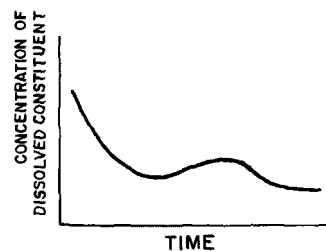
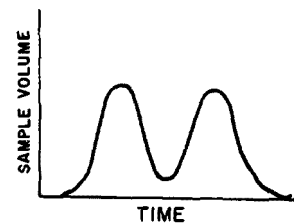


FIGURE 1. COMPARISON OF SAMPLING STRATEGIES.
See definitions in text.

intensity of the storm or volume of precipitation. Samples are collected consecutively without time break for the whole storm period.

5. Continuous monitoring (Figure 1e). Precipitation is routed through a sensor or sensors as it is collected. A continuous record of the instantaneous response from the sensor is recorded.

FACTORS LEADING TO THE CHOICE OF METHOD USED

The objective of any of the above sampling methods is to describe the chemistry of the storm as accurately as possible. From this standpoint continuous monitoring gives the best results, but the unavailability of adequate sensors for all but a few ions of interest and the problems of interference have limited its use. Both intensity weighted sampling and time weighted sequential sampling provide an average concentration value for the period of collection of each individual sample. By shortening the time between collections a closer approximation to the storm chemistry is achieved. This presents a problem in time weighted sampling since enough sample to perform all analytical tests of interest may not be collected.

Intensity-weighted sequential sampling is used in this study because it provides the following advantages:

1. Sample size is determined by the amount needed to perform all analytical tests. This provides for easier sampler design.
2. The volume of sample collected is related to the amount of precipitation by the surface area of the collector. Thus, as sample volume requirements change, adjustments are relatively easy to accomplish by changing the siphon volume and the volume of the collection vessel. Each sample reported herein represented 0.015 to 0.025 inches of precipitation. Although the amount of precipitation collected per sample varied from storm to storm, the amount was constant within a storm.
3. More samples were collected the harder it rained. Thus, samples for low intensity periods give an average concentration value for the period of collection, but during intense periods the time intervals were shortened to fractions of minutes and give a good indication of changing chemistry within the storm.

REVIEW OF SEQUENTIAL SAMPLING

In the following paragraphs the sequential sampling methods used by others and the application of the various techniques are reviewed and categorized.

Sequential samplers fit into four basic categories:

- a. manually segmented samples.
- b. linked collection vessels.
- c. automatically segmented samples.
- d. continuous monitors.

Each has its advantages and disadvantages which make it better suited for the particular research program or for the analytic technique employed.

Manual methods are the least expensive in terms of equipment costs, but all require a researcher to change the collection vessel at the appropriate time. Manual methods can be employed on a time-weighted, intensity-weighted, or grab sample basis. The simplest application is a funnel and bottle or an open wide mouthed container. Gatz and Dingle⁶ used a 2.5 m² funnel for 2 to 8 liter samples. Dana et al.^{7,8} used a 1 m² funnel mounted on the roof of an automobile for following convective storms. Warburton and colleagues^{9,10,11} have used sheets of plastic stacked in a frame and withdrawn one after another to sample snow and hail. Perkins et al.¹² used a large plastic sheet over a roof to direct rain water to an ion exchange column which trapped the radionuclides of interest. In this case the ion exchange column was changed manually. Time of collection must be maintained manually for all the manual methods.

Linked collection vessel samplers have been employed by three research groups. They all consist of a series of bottles linked together by tubing. When one bottle is full, the rainwater flows into the next in line (Figure 2). Bottle filling time is proportional to intensity. The groups differ in the precautions taken to prevent mixing of incoming rain with that already in a bottle. Cooper et al.¹³ have the simplest device (Figure 2a) which relies on the narrow tubing leading to the bottle to prevent mixing. Kennedy et al.¹⁴ use air vents on the bottles as shown in Figure 2b to prevent siphoning between bottles. The most sophisticated is that used by Liljestr nd and Morgan (Personal communication, Figure 2c) in which air vents and a floating stopper are used to prevent mixing. All three methods will segment a storm unattended. If collection times are desired they must be monitored by a researcher or calculated from intensity data and funnel area. The automated methods can be divided into timer actuated, volume actuated, or actuated by a related parameter to segment the storm. The most widely used sampler is a tipping bucket (weight)

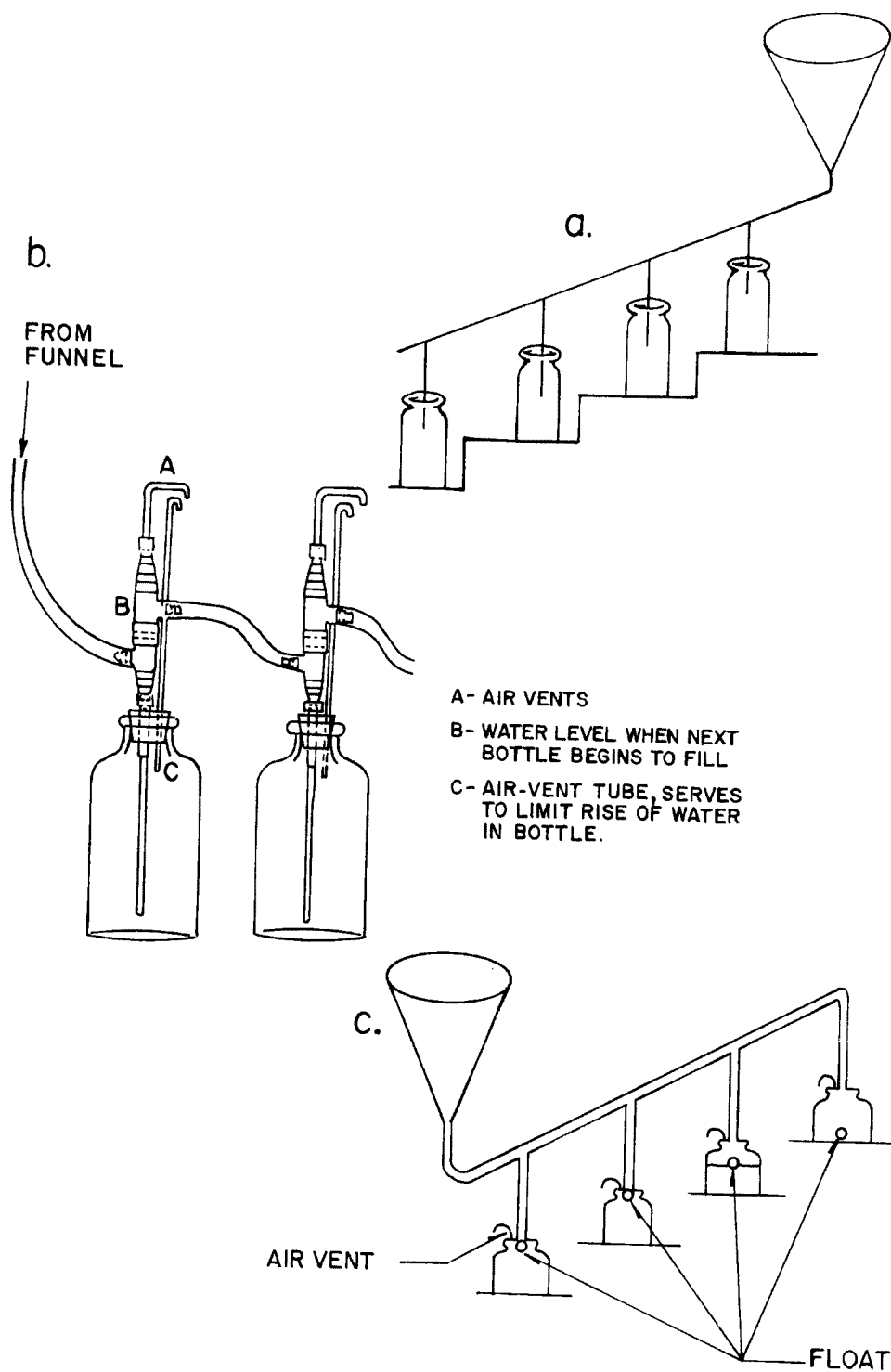


FIGURE 2. COMPARISON OF LINKED BOTTLE SAMPLERS.
a. Cooper et al., 1976; b. Kennedy et al., 1976;
c. Liljestrand and Morgan, personal communication

actuated device developed at Argonne National Laboratory by Gatz et al.¹⁵ and used by Dingle¹⁶ and Adam et al.¹⁷ in conjunction with the Metromax study in St. Louis, Missouri. Raynor and McNeil¹⁸ have designed a timer actuated device at Brookhaven National Laboratory. Time periods are preset but, adjustable between runs. Results reported by Raynor and Hayes¹⁹ are for one hour collection periods. Krupa (personal communication) at the University of Minnesota has designed a sampler which senses that a bottle is full by means of a conductivity detector in the overflow port. The University of Minnesota sampler is the only automated sampler which seals the bottle off from the atmosphere to prevent exchange of gases after collection. The others utilize open bottles in a rack which remain open after collection. A sampler based on Krupa's design is now commercially available.²⁰ Stensland²¹ and Pickerell et al.²² have used a siphon to measure fixed volumes of sample.

The automated methods vary in complexity. Some require manual starting, but most now are sensor actuated. All have chart recorders to record sampling time and cover position. Gatz (personal communication), now at the Illinois Water Survey, has a new version of the tipping bucket sampler which operates in either timer actuated or weight actuated mode. Semonin (personal communication) reports that the device will operate in intensity (weight) mode, but can be preset so that if an extended time passes without a sample being taken a new collection vessel is moved into place (and presumably the tipping bucket first emptied).

Few cases of continuous monitoring have been reported. Stensland²¹ illustrates a continuous pH monitor, but presents no data. Falconer (personal communication) is currently using a device similar to Stensland's. Most continuous monitoring has been confined to looking at nuclei in air samples during rain and snow storms. Radke et al.²³ have used an integrating nephelometer for this purpose. Gradel and Franey²⁴ have used a cloud nuclei counter and optical particle counter for the same purpose.

Table 1 summarizes the applications to which sequential samplers have been applied. Most deal with attempts at discerning cloud processes or below cloud processes.

TABLE 1. APPLICATION OF SEQUENTIAL PRECIPITATION SAMPLING

APPLICATION	AUTHOR	COLLECTION DEVICE		SAMPLING STRATEGY	REMARKS
		Opening Method	Segmenting Method		
Rainfall-Runoff of a Watershed	Kennedy <u>et al.</u> ¹⁴	Manual	Linked Bottles	Intensity-Weighted	Mattole River Basin California
Convective Storm Processes	Adam <u>et al.</u> ¹⁷	Manual	Tipping Bucket	Intensity-Weighted	Metromax Study - Scavenging
	Dana <u>et al.</u> ⁸	Always Open	N/S	N/S	Metromax Study - Modeling
	Dingle ¹⁶	Manual	Tipping Bucket	Intensity-Weighted	
	Linkletter & Warburton ¹³	Manual	Plastic Sheets	Grab	Hail Suppression
Scavenging	Warburton ⁹	Manual	Plastic Sheets	Grab	Hail Storms
	Dana <u>et al.</u> ⁷	Always Open	Manual	Grab	Power Plant Plumes
	Gatz & Dingle ⁶	Manual	Funnel & Bottles	Grab	
	Gatz <u>et al.</u> ¹⁵	Manual	Tipping Bucket	Intensity-Weighted	
	Perkins <u>et al.</u> ¹²	Always Open	Ion-Exchange Column	Grab	Cosmogenic Radionuclides
	Warburton & Owens ¹⁰	Manual	Plastic Sheets	Grab	Lake Effect Storms-Tracer
	West Point ²²	Manual Automated	Siphon Siphon	Intensity-Weighted Intensity-Weighted	In Service Oct 76 to May 78 In Service after Nov 78 Heated for Snow & Ice
Acid Rain	Cooper <u>et al.</u> ¹³	N/S	Linked Bottles	Intensity-Weighted	Austin, Texas
	Falconer*	N/S	Continuous	Continuous	Cloud Water pH
	Krupa*	Automated	Overflow Sensor	Intensity-Weighted	Minneapolis, Minn.
	Liljestrang & Morgan*	N/S	Linked Bottles	Intensity-Weighted	Pasadena, California
	Raynor & Hayes ¹⁹	Automated	Timer	Time-Weighted	Upton, N.Y.;
	Stensland ²¹	Always Open	Siphon	Intensity-Weighted	Heated for Snow & Ice Lake George, N.Y.;
					Concurrent Continuous pH

N/S = not stated or not determinable from figures and text presented.

* = personal communication

SECTION 5

THE WEST POINT SAMPLER

DESIGN CRITERIA

Galloway's²⁵ study of precipitation samplers provided a basis for design and selection of construction materials for the West Point sampler. Unattended automatic operation was one of the requirements. On sensing precipitation, the sampler was to be activated (funnel opened, first collection vessel positioned, and a record of the time made). Dry deposition was to be excluded prior to the storm, during interludes in the storm, and after the storm. Since year round operation was desired, the sampler had to be able to detect and collect rain and snow. The time of collection of each sample was to be recorded as well as the funnel cover position (open or closed).

Intensity-weighted sequential sampling was chosen as the basis of design (see Section 4). In this method of collection a fixed sample volume, primarily determined by the amount of sample needed to perform all analytical tests of interest, is the governing design feature. Initial interest was in determining pH, and the concentration of the common ions in solution (Na^+ , K^+ , NH_4^+ , Ca^{+2} , Mg^{+2} , Cl^- , F^- , NO_3^- , SO_4^{-2} , PO_4^{-3}). At a later time, tests for conductivity and the concentrations of trace metals and organics may be useful. Ion chromatography was chosen for the ion analyses and an automated ion selective electrode for pH. These selections allowed a design volume of 14 ml (5 ml for pH and 3 ml for each of three runs on the ion chromatograph) to be chosen. Any additional tests could be accommodated from the same 14 ml sample by combining an automated flow-through conductivity meter in series with the pH electrode (conductivity ahead of pH) and by using an autoinjector to reduce the volume of the sample needed for ion chromatography to 2 ml total. The remaining 7 ml could be analyzed for metals by carbon-rod atomic absorption spectrophotometry and for low molecular weight organic acids by ion exclusion chromatography.

The sample volume (14 ml) had to be equivalent to a convenient multiple of the amount of rain falling over the area of the funnel. One-one hundredth of an inch of rain (0.254 mm) was selected, but this required a funnel diameter of 9.43 inches (264.10 mm). At the time of construction the only funnel avail-

able was 7.5 inches in diameter. At 100% efficiency of collection, each 14 ml of sample would represent 0.0193 inches (0.491 mm) of precipitation with the 7.5 inch funnel.

THE SAMPLER

The current design of the sampler is shown schematically in Figure 3. The funnel (c in Figure 3) is polyethylene and 7.5 inches in diameter. It is covered by a closure mechanism (Figure 4; b in Figure 3) activated by a Weathermeasure model 566 precipitation sensor (a in Figure 3). The precipitation sensor (h in Figure 3) is heated to:

1. melt snow and sleet in winter allowing all weather activation of the closure mechanism.
2. dry the sensor so that upon cessation of precipitation the mechanism covers the funnel thus excluding dry deposition.

The closure mechanism is powered by a reversible motor with limiting switches restricting its range of travel. The roof of the cover is canted in the open position (Figure 4b) to reduce splashing from the cover into the funnel and to allow snow and ice to slide off (the roof will be heated if necessary to aid in snow removal).

The precipitation sensor activates a double throw-triple pole relay which performs four tasks:

1. provides power and directional control to the motor;
2. provides power to the fraction collector;
3. provides event marking for sensing of funnel cover position;
4. changes recorder speed from 2.2 cm/hr to 11 cm/hr.

A schematic wiring circuit is provided in Figure 5. The funnel is connected to the fractionator by a Tygon tube leading to the Pyrex glass siphon (d in Figure 3; Figure 6) portion of the fractionator. The siphon is attached by a rubber tube to a switch operated by the air trapped in the siphon. This switch activates a relay within the fractionator (f in Figure 3) which advances a rack of disposable 16 x 150 mm polyethylene culture tubes below the siphon and at the same time places a mark on the chart recorder (g in Figure 3). The fractionator is a commercially available Buchler Fractomettte 200 which will operate in volume, time, or drop mode. The fractionator (Figure 7) has 20 racks of 10 culture tubes which move around the tray in race track fashion. Dust is prevented from falling into the open tubes by a plastic baffle. A magnet placed in the 200th culture tube activates a shutoff mechanism in the fractionator which prevents culture tubes from passing under the siphon more than once.

The chart recorder is a Linear model 255 single pen chart recorder with event pen. It is operated at a chart speed of 11 cm per

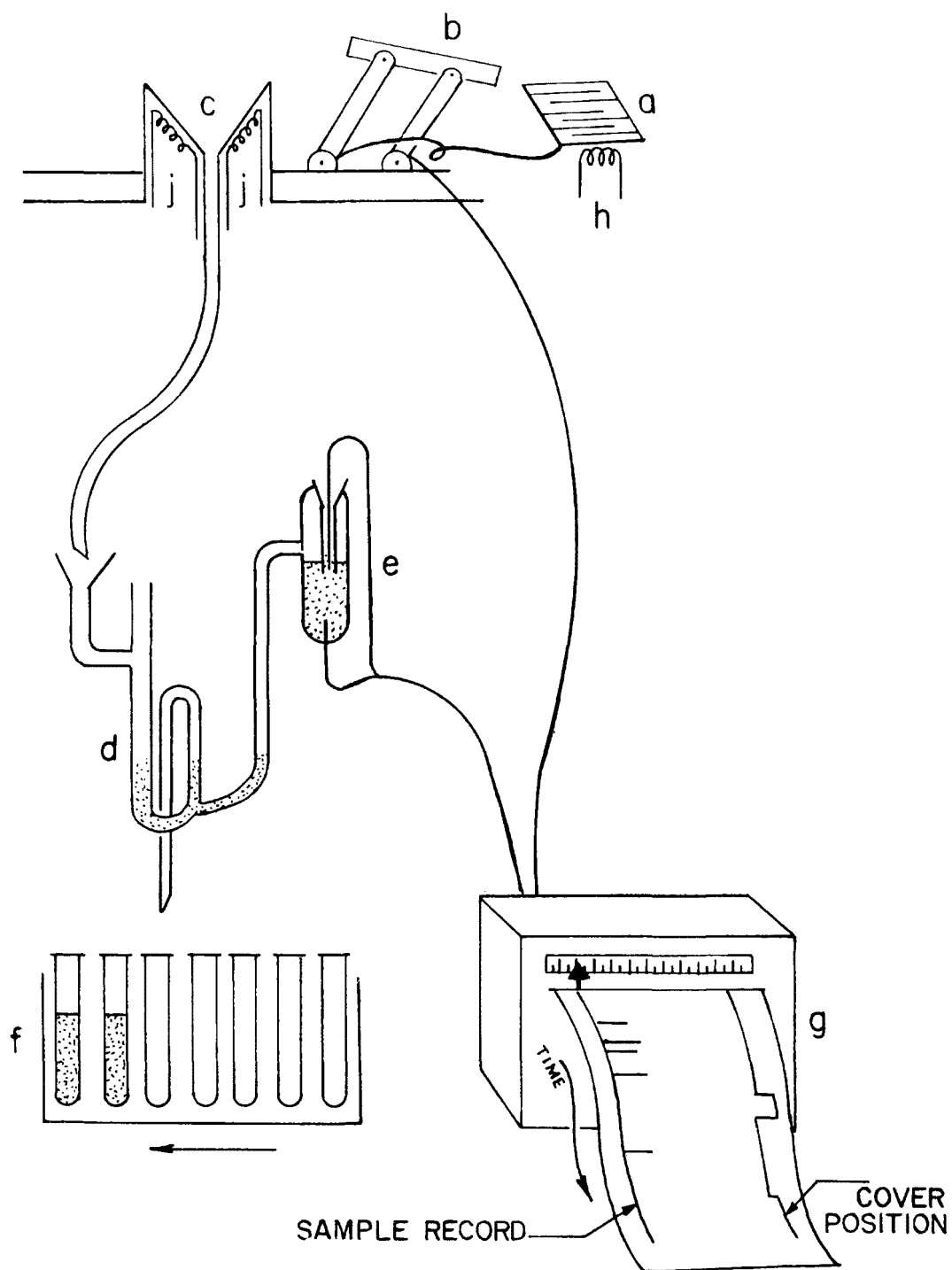


FIGURE 3. SCHEMATIC DIAGRAM OF THE WEST POINT SAMPLER.

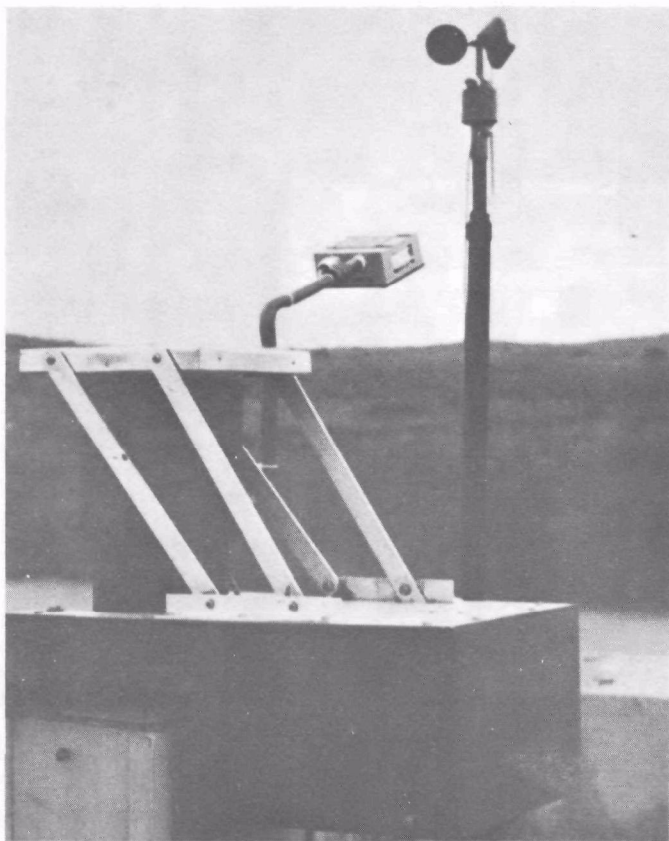


Fig 4a. The closure mechanism for the West Point Sampler, closed position. The precipitation sensor is on the surface of the small box.

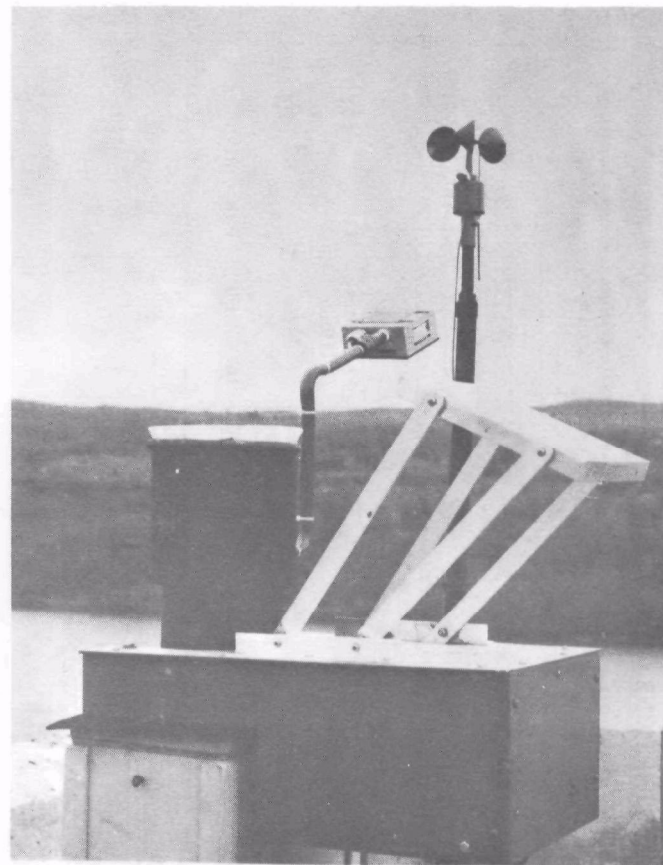


Fig 4b. West Point Sampler, open position. Canted roof minimizes splashing into funnel and prevents snow accumulation.

- POWER (Double Underline)
- ELEMENTS (Italics)
- CIRCUITS & DESCRIPTIONS (Single Underline)

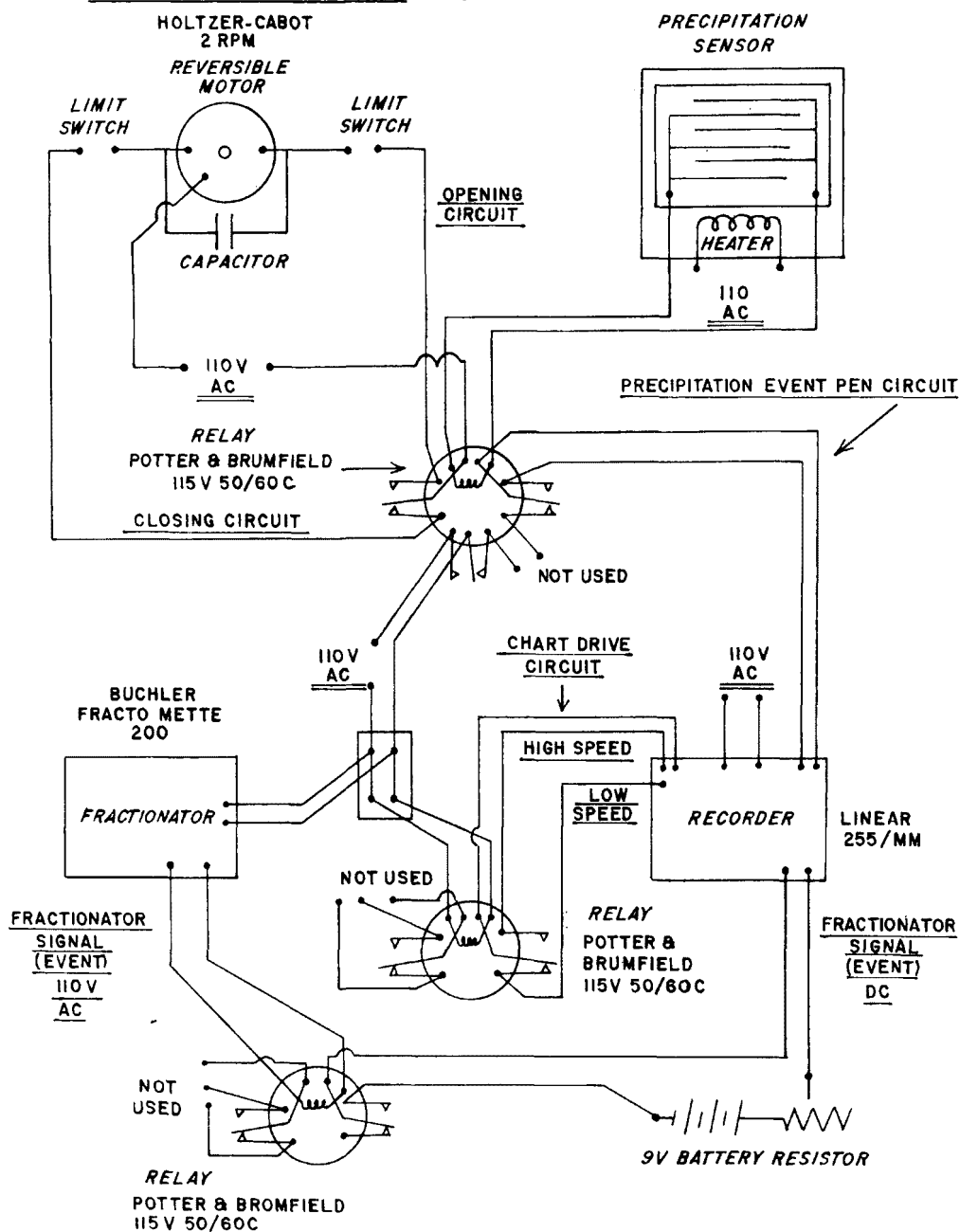


FIGURE 5. WIRING DIAGRAM FOR THE WEST POINT SAMPLER.

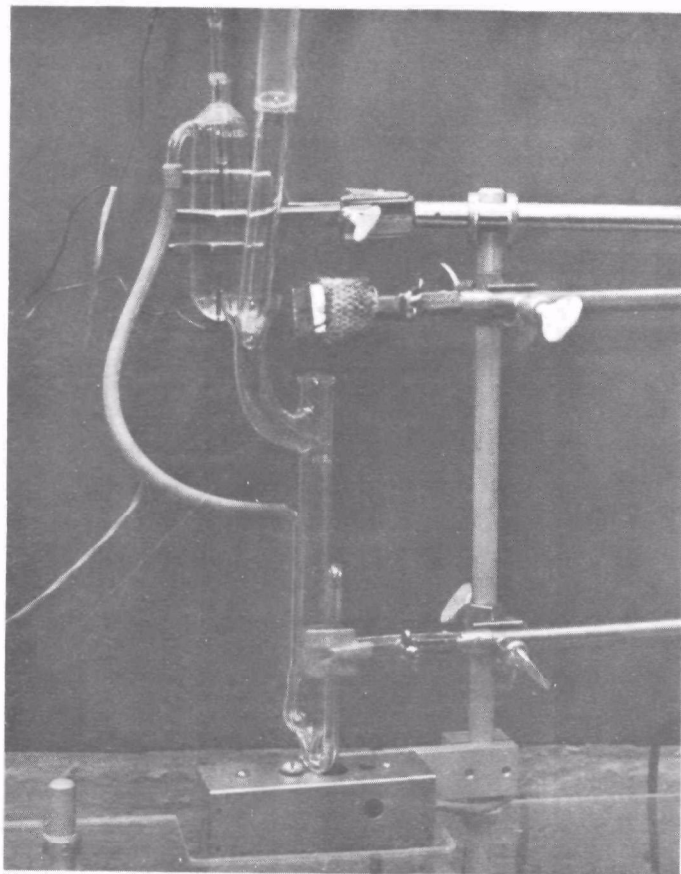


Fig 6. Siphon and switch for the West Point Sampler tube from above drains funnel on roof.

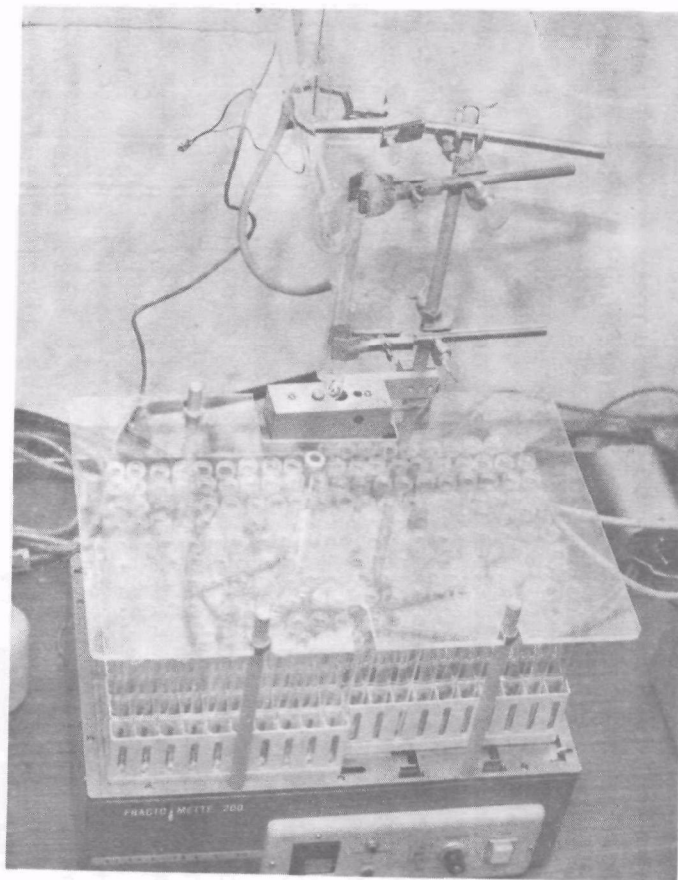


Fig 7. Fractionator with test tubes in place. Two hundred test tubes is a standard load. Magnet in last tube activates a sensor which shuts down the instrument.

hour during sample collection and provides a resolution of 0.2 to 0.4 minutes. When the funnel is closed, the recorder operates at a speed of 2.2 cm per hour. The event pen provides a record of the opening or closing of the funnel and simultaneously the change in chart speed.

A heater (j in Figure 3) provides heat to the funnel to melt snow and sleet. The heater is controlled by a temperature controller which activates the heater at 2°C. The heater is three laboratory heater tapes (Fisher 11-463-49c) linked in series and taped to the underside of the funnel. It was necessary to cover the full extent of the funnel and not just the lower cone to prevent bridging of the collector by snow. The funnel housing was insulated to prevent freeze up in the Tygon line. Heat from the room below the funnel is circulated into the housing by a blower to aid the heating process.

STATION LOCATION AND OPERATION

The sampler is located on the roof of the fifth floor tower of Bartlett Hall, at the U.S. Military Academy, West Point, New York. This is a convenient location logistically, but its use as a sampling location may not be good. The stack for the West Point steam plant is 300 meters southeast of the collector, but downwind in the predominant wind direction. Bartlett Hall houses the Academy's chemistry laboratories, but again the discharge from the laboratory ventilators is downwind from the collector. Data taken to date does not appear to be influenced by either of these sources. Wind speed/wind direction instruments colocated with the sampler since the summer of 1978 will allow more complete evaluation of these as sources of contaminants in the future.

Earlier versions of the sampler are reflected in the data presented. The earliest sampler was a simple 8 inch polyethylene funnel 18 inches above the roof but below the parapet wall. It was in operation from October 1976 until January 1977. It was replaced in January 1977 with a glass funnel of the same diameter when the polyethylene funnel was accidentally melted by the heater tapes. The glass funnel stayed in operation until October 1977. At that time the data trends were promising enough that the funnel was rebuilt using polyethylene. The funnel is now 18 inches above the parapet; no longer shielded from the wind nor subject to possible contamination from the parapet wall or loose material on the roof.

In November 1978, the autoclosure device described previously was added to the funnel. The fraction collector and siphon mechanism has remained unchanged from 1976 to the present time. The sampler was out of operation from May 1978 to September 1978 due to repair work being done to the roof.

Prior to the addition of the autoclosure mechanism, the funnel was opened and closed manually. The funnel was opened at the onset of precipitation during the normal workday. In some instances, if precipitation was predicted, the funnel was opened at the end of the workday allowing a period of dry deposition on the funnel prior to the beginning of precipitation. The funnel remained open until the precipitation event ceased. The funnel, tubing, and siphon were washed with distilled water after each precipitation event. The last washing was collected and analyzed to insure cleanliness.

Culture tubes are washed in an ultrasonic bath with Contrad-70 soap (Scientific Products C6327), rinsed in 1% nitric acid, then in distilled water before being placed in the sampler. Samples are removed each morning, again at noon, and at the end of the day. Culture tubes are capped and refrigerated at 4°C until analysis.

During operation, drops of sample remain on the siphon walls, but the volume of these drops is small compared to the siphon volume. Carry over between samples is considered negligible. Discussions with Stensland, who operated a similar sampler containing a glass siphon, led to agreement that carry over between samples was negligible. In no case was storm intensity high enough to cause continuous siphoning to occur.

The pH of samples was initially determined manually using an Orion model 407A specific ion meter and Orion model 91-02 combination electrode. This combination was bedeviled with static electricity problems after several measurements. A Corning model 476050 semimicro combination electrode was tried and solved the problem for 30 minutes to an hour, after which static electricity again became a problem. Static electricity was eliminated by use of a Microelectrodes, Inc. model MI-410 microcombination pH probe. The manual rinsing and wiping of electrodes proved to be slow and consumed too many technician man-hours. In January 1978 a Technicon Ion Selective Electrode system which utilized a thermostated flow-through combination pH electrode was put in use. This system is used to run 30 samples per hour without static electricity effects and with improved precision. All pH systems were standardized daily against commercially available pH 4.0 and pH 7.0 buffers. The time between sample collection and pH measurement varies from storm to storm and from sample to sample within a storm. Storms collected on weekdays will normally be analyzed for pH within 6 hours after collection of the last sample. Storms collected on Friday evening or a weekend will normally be analyzed for pH by noon on the 1st workday after the weekend. Other analyses on the refrigerated samples are performed as soon as instrument time is available (normally within a week or two, but in heavy rain periods it may take a month to analyze all samples).

Ion chemistries were determined initially using Hach powder pillows and a Hach DR-2 spectrophotometer. Each Hach test required 25 ml of sample, requiring combination of samples to achieve this volume. Once a sample was reacted for a particular colorimetric test it was not usable for further testing. These procedures allowed some preliminary determination that measurable differences were present. New analytical methods were sought and in August 1977 a Dionex model 14 Ion Chromatograph replaced the Hach powder pillows. Initially the ion chromatograph was used to determine only anions, but in January 1978 cation columns were added. The ion chromatograph is now utilized to analyze for Na^+ , K^+ , NH_4^+ , Ca^{+2} , Mg^{+2} , F^- , Cl^- , PO_4^{-3} , NO_3^- , and SO_4^{-2} . The above analyses require only 9 ml of sample and the ion chromatograph allows multiple analysis from the same sequential sample, a great improvement over our previous techniques. Preliminary work is underway to determine organic acids in the samples utilizing the ion chromatograph.

Quality control on the Dionex ion chromatograph was ensured by daily injections of a minimum of three standards which encompassed the range of concentrations expected in the samples. Calibration curves are prepared by plotting concentration vs peak height for these standards. Standards were prepared gravimetrically from reagent grade chemicals, dried to constant weight, and diluted to a known volume with Milli-Q deionized water (conductance > 10 megohm). Appendix D contains a list of reagents used for specific analytes. A sample of known concentration was injected and peak height compared to the calibration curve approximately every tenth sample. A blank was injected daily to detect possible contamination.

Some heavy metal analyses were performed on the sequential samples. These were made using a Varian model 1280 atomic absorption spectrophotometer equipped with a Varian model 90 carbon rod atomizer and Varian model 53 automatic sampling device. A new non-threaded tube furnace (Varian 56-100157-00) was used daily. A gas mixture of 99.5% argon-0.5% methane at a flow rate of 5.0 liter/minute was used to prevent oxidation of the carbon rod and to refresh the pyrolytic carbon coating thus prolonging furnace lifetime. The average of four absorbance readings on each sample was used in determining concentration. Absorbance data from the 1280 was converted to concentration values automatically utilizing a data link between the spectrophotometer and a Hewlett Packard 9815 calculator driven by a Varian supplied curve fitting program.

A 10 μl sample was used routinely for each analysis. Instrument parameters and temperature programs for the carbon-rod furnace are given in Table 2. Working standards were prepared daily for concentrations below 10 ppm following the recommendations of Begnoche and Risby.²⁶ 10 ppm standards were prepared from AA standards bought from Varian-Techtron.

TABLE 2. OPERATING CONDITIONS USED FOR THE ATOMIC ABSORPTION
SPECTROPHOTOMETER AND CARBON ROD FURNACE

ELEMENT	LAMP Current mA	SPECTRAL Bandwidth nm	SPECTRAL Line* nm	DRY Temp/Time C Sec	ASH Temp/Time C Sec	ATOMIZE Temp/Time C Sec
Aluminum	5	0.5	309.27(5)	110/50	1700/20	2500/2/600
Copper	3	0.5	324.75(1)	110/50	500/20	1200/2/400
Iron	5	0.2	371.99(2)	110/50	600/20	2200/2/600
Manganese	5	0.2	232.00(1)	110/50	700/20	1900/2/400
Nickel	5	0.2	232.00(1)	110/50	900/20	2200/2/600
Lead	5	1.0	217.00(1)	110/50	500/20	1200/2/400

*Numbers in parentheses are ranking of sensitivity of spectral line (1 = prime, 2 - 2nd most sensitive, etc.).

SECTION 6

EXPERIMENTAL DATA

Data from 22 precipitation events sampled over a 2-year period are tabulated in Appendix A. Time between samples was measured by converting the distance between sampling marks from the chart recorder into time in minutes. The elapsed time is the cumulative sum of the times between samples. Intensity is calculated from the time between samples and the number of millimeters of precipitation represented by the culture tube volume according to the following equation:

$$\text{Intensity, mm/hr} = \frac{\text{mm of precipitation} \times 60 \text{ min/hr}}{\text{Time between samples, min}}$$

This calculated intensity assumes a collection efficiency of 100%. The efficiency of collection will be evaluated against a tipping bucket rain gauge in the future. Galloway's⁵ results show that collectors of similar design have collection efficiencies of about 85% for rain and 80% for snow. If this holds true for the West Point Sampler then the intensities calculated above are low. The pH and ion chemistry values are those obtained as stated in Section 5. The data presented show the progression in improved techniques and equipment. Early storms (Tables 3 through 5) present just pH data. Then Tables 6 through 12 add chemical determinations using the Hach test kits. Three or more consecutive samples were combined to allow these tests to be made. The results are shown opposite each separate sample and represent the average concentration for the three samples. Table 13 is the first of the ion chromatograph data. Tables 13 through 18 present pH, nitrate, and sulfate data. Tables 19 thru 22 add light metals. Tables 23 and 24 are the most extensive containing pH, anion, light metal, and heavy metal data.

Plots of the data from two storms are presented in this section to illustrate and explain our plotting conventions. Figure 8 is a plot of the data from the rainstorm on 2 June 1977 (Table 10). The upper half of the figure is a hyetograph based on the calculated intensities and the elapsed time. Intensity values are shown as the average for the time period during which they were collected. Plotting difficulties forced plotting of intensities

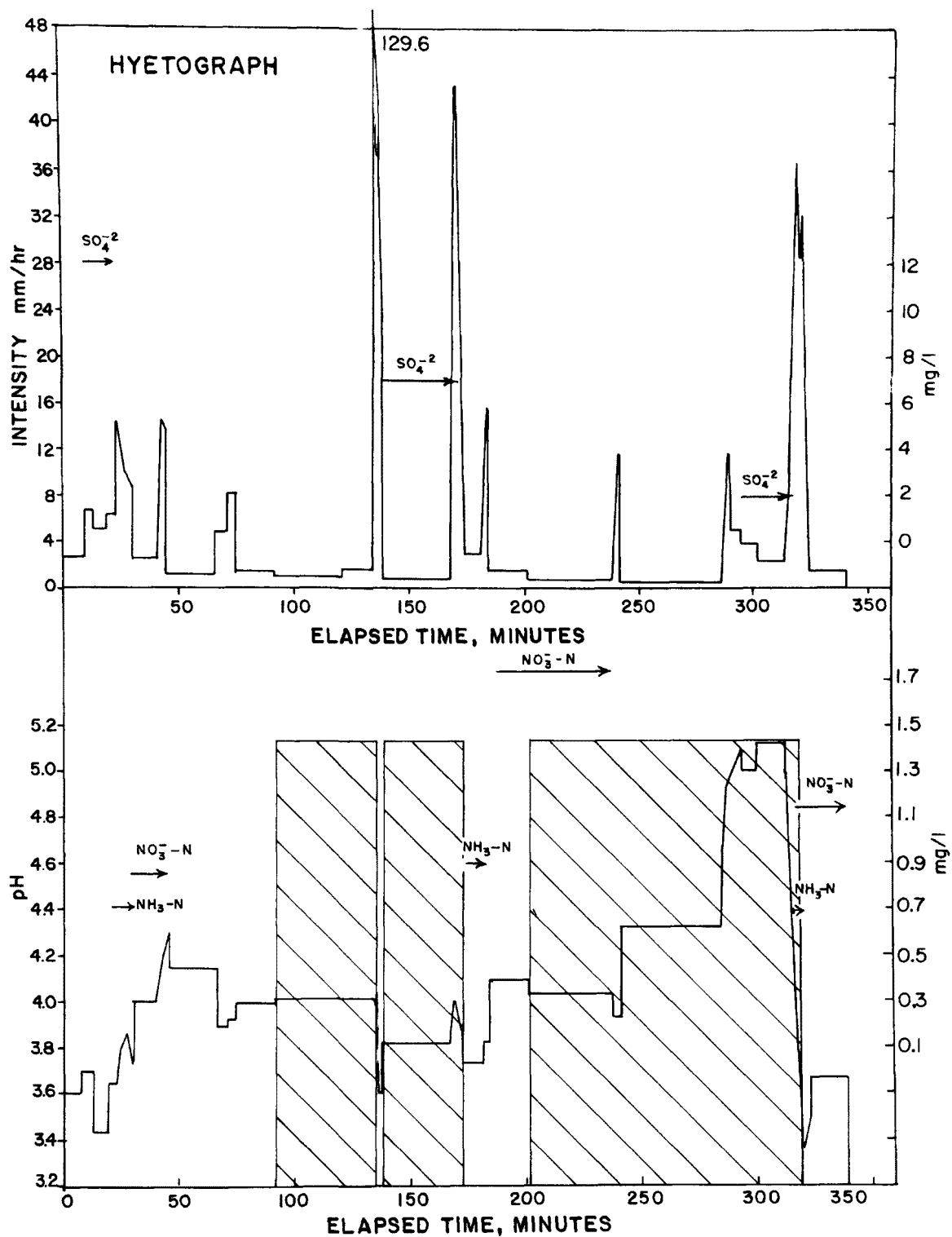


FIGURE 8. CHANGES IN STORM CHEMISTRY AND INTENSITY, RAINSTORM, 2 JUNE 1977.

for very short periods (period varies from plot to plot) as points even though they are average values for the shorter period. The lower half of the figure is a plot of pH versus elapsed time. Again pH is shown as the average for its period of collection except where resolution caused points to be used. Superposed on the two halves of the figure are the chemical data (in this case Hach powder pillow tests). Chemical data is shown over its period of collection as the average value for the period. Arrows indicate direction to the concentration scale used. The grid on the lower half of the figure indicates interpreted periods of contamination by dry deposition (see Section 7).

Figure 9 is a plot of the data from the storm on 19 Oct 1977 (Table 18). It is basically the same as Figure 8 except that more samples were analyzed by ion chromatography. In this example, sulfate and nitrate values for individual samples are plotted as the average value for the time of collection (other plots use points where necessary because of time scales). Sulfate and nitrate values are linked by a broken line to lead the observer from one reading to another, not to indicate that this is the chemical trend followed (on other plots where consecutive samples were analysed, values are linked by solid line to indicate the trend). In the early exploratory work, every 5th to 10th sample, samples at points where pH increased or decreased markedly, samples at extended time between samples, or samples at very short time between samples were analyzed. This was necessary because it was too costly and time consuming to analyze all samples in large storms. Criteria are being evaluated which will enable one to pick which samples will be analyzed to give a good representation of the species trends even though there are gaps in the chemical data. This is being done by analyzing complete storms and comparing the chemical trends produced using the selection strategy with the trends produced using the full storm chemistry.

Data for all storms are plotted and discussed in Section 7.

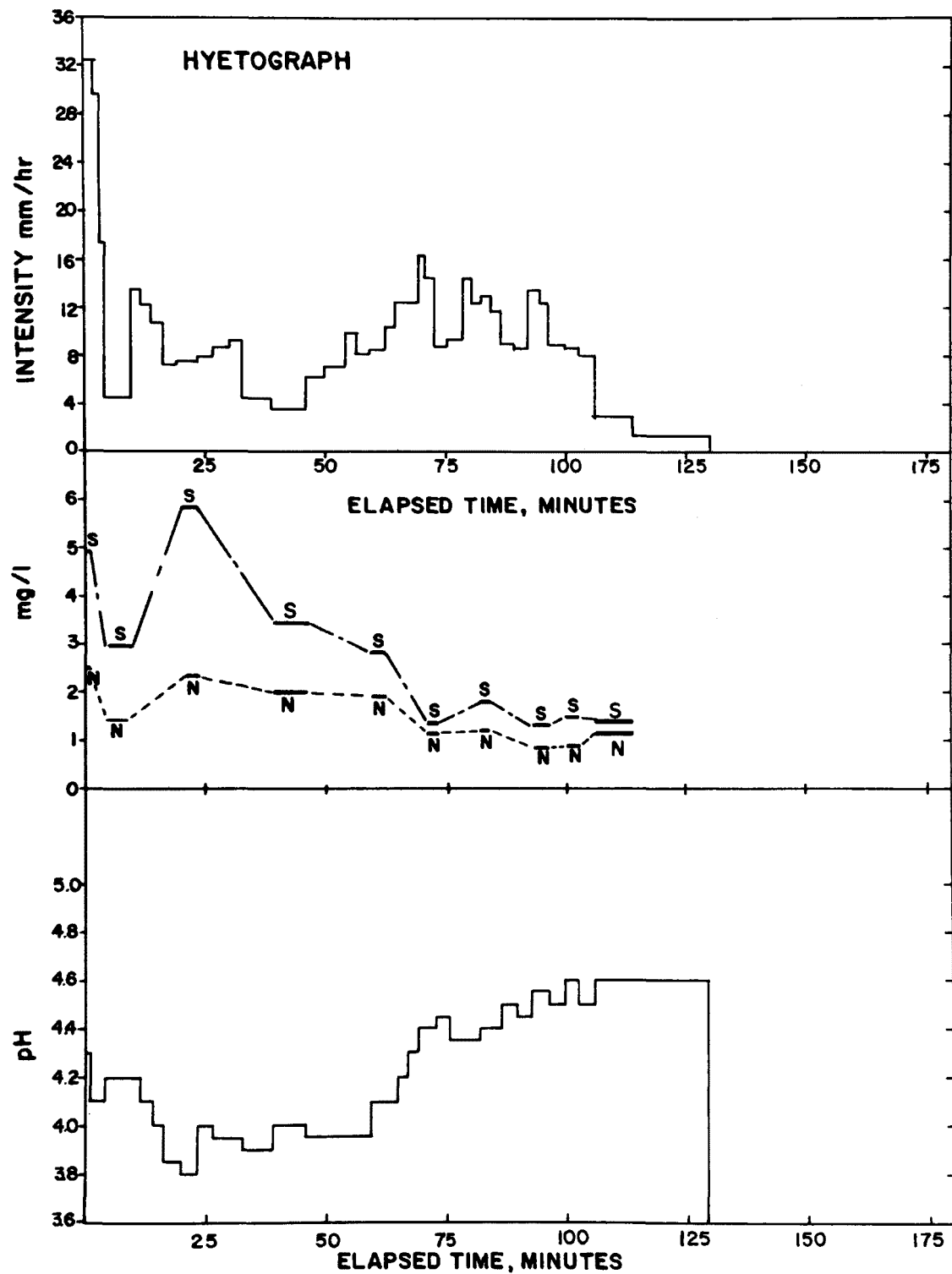


FIGURE 9. CHANGES IN STORM CHEMISTRY AND INTENSITY, RAINSTORM, 19 OCTOBER 1977. S = sulfate; N = nitrate.

SECTION 7

DISCUSSION

When one quickly reviews the plotted storm data (Figures 8, 9, and 10 to 29), several things immediately become apparent: (1) the chemistry of precipitation varies widely within a storm; (2) the chemistry within a storm can change very rapidly; (3) a suggestion that there is a linkage between storm intensity and precipitation chemistry; (4) a parallelism in the chemical trends within a storm when several chemical species are determined.

The following discussion will explore the above deductions and test our hypotheses (Section 1) against the plotted data (Figures 8, 9, and 10 through 29). Examples from the full range of storms will be cited where appropriate; however, the more recent storms will be used more frequently since there is more chemical data available from them to support the discussion.

FUNNEL CONTAMINATION

The manual opening/closing procedures for funnel operation represented in all the storms presented in this report are such that periods of exposure to contamination by dry deposition are present. It is believed that these contamination periods can be identified. Also, that a period of precipitation following a period of dry deposition will result in cleansing of the funnel by washing the contaminants into the next few sequential samples. This cleansing mechanism is highly efficient. A set of criteria has been developed for identifying periods of dry deposition contamination and for identifying the length of the cleansing period. Utilizing these criteria, each of the twenty-two storms has been analyzed for contamination and cleansing periods. Appendix C presents the evaluation of each storm with respect to the criteria. Only data from the contamination-free periods will be utilized in subsequent discussion sections.

Periods of dry deposition are most likely identified in the data by samples which have "long" times between samples. These dry deposition periods must be distinguished from periods of low intensity precipitation. Time alone will not make a good discriminator, but time and the chemical data together may serve this purpose. Since pH data is available for almost every sample

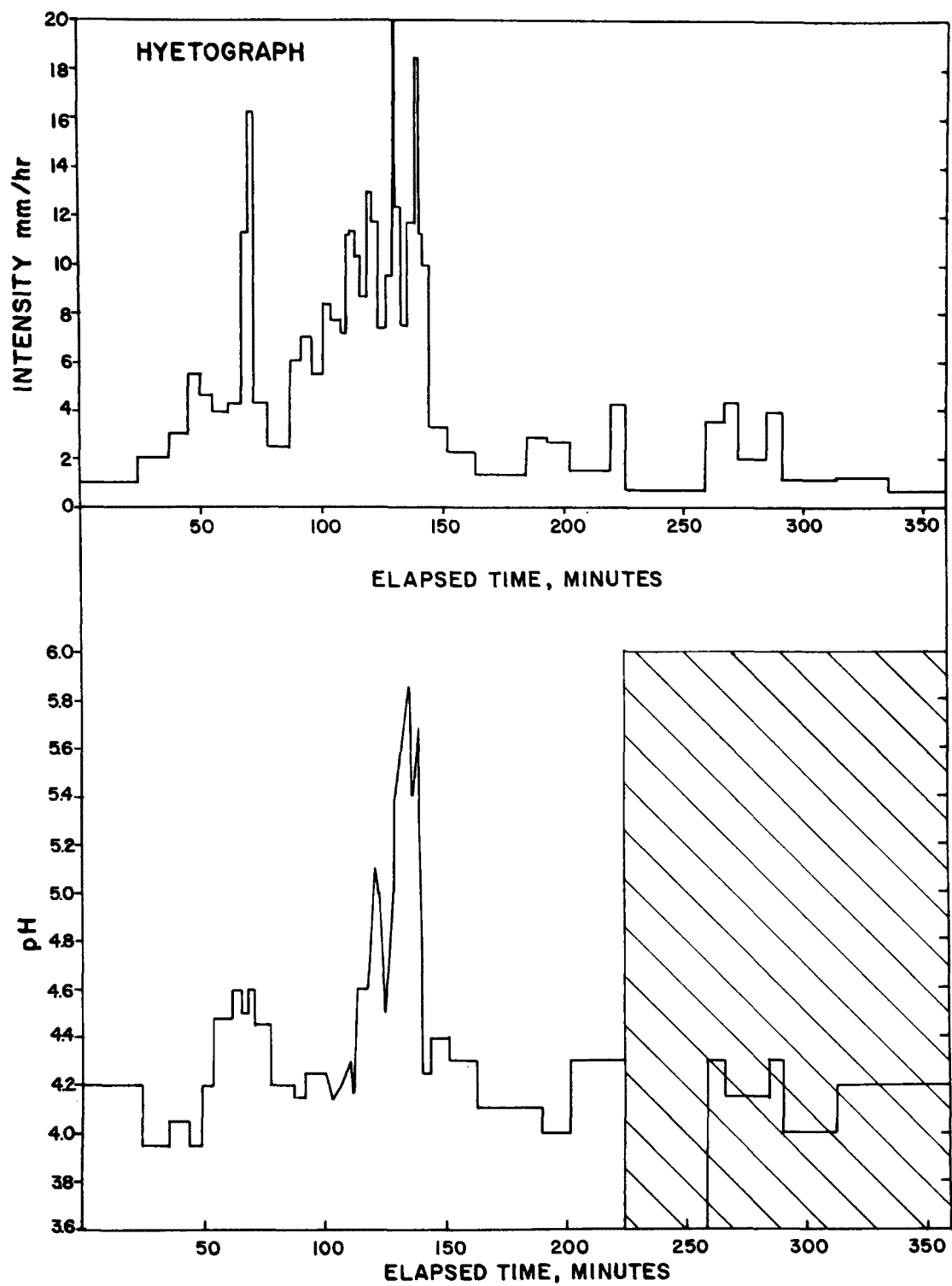


FIGURE 10. CHANGES IN STORM CHEMISTRY AND INTENSITY, RAINSTORM, 20 OCTOBER 1976.

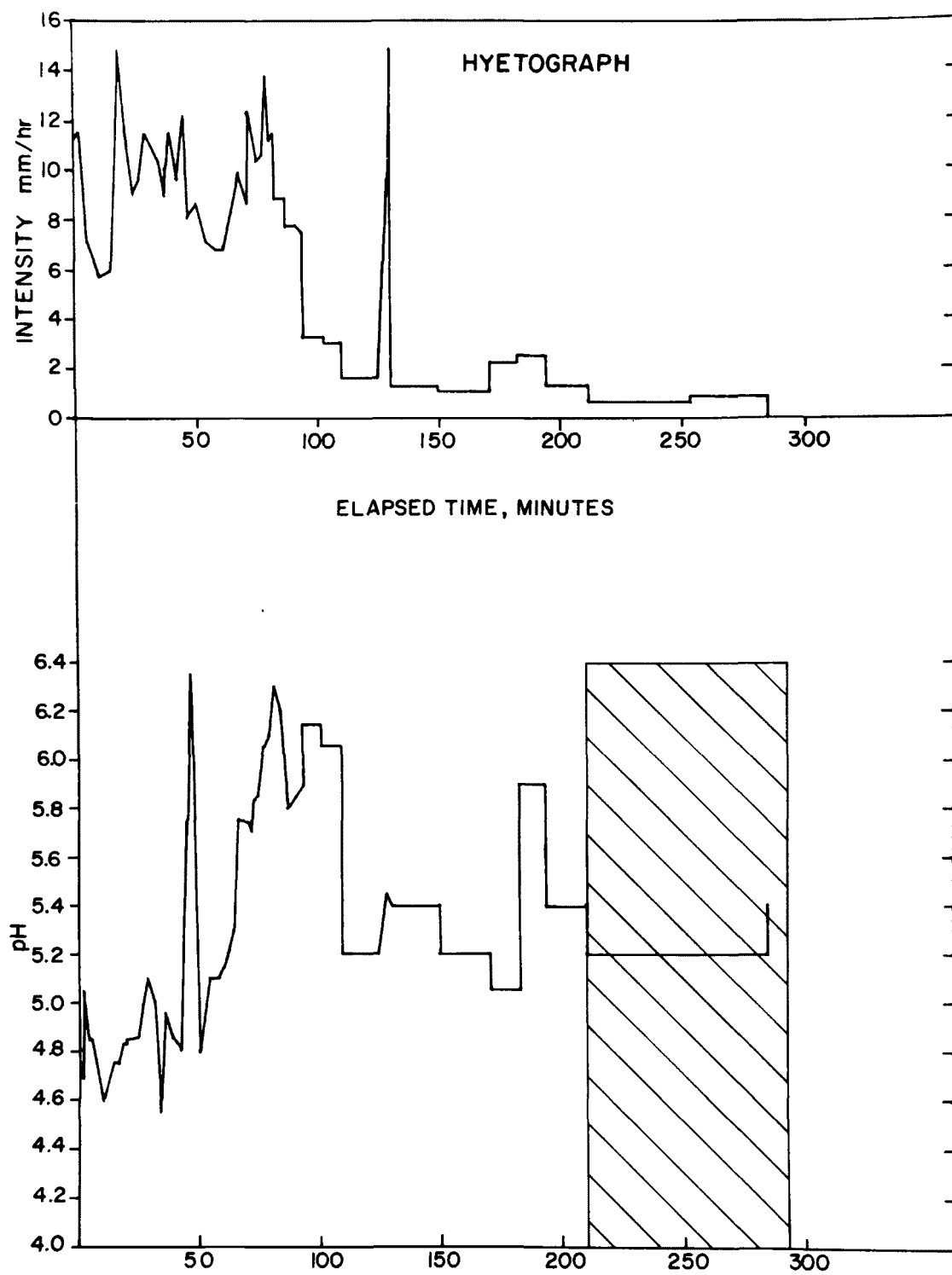


FIGURE 11. CHANGES IN STORM CHEMISTRY AND INTENSITY, RAINSTORM, 7 DECEMBER 1976.

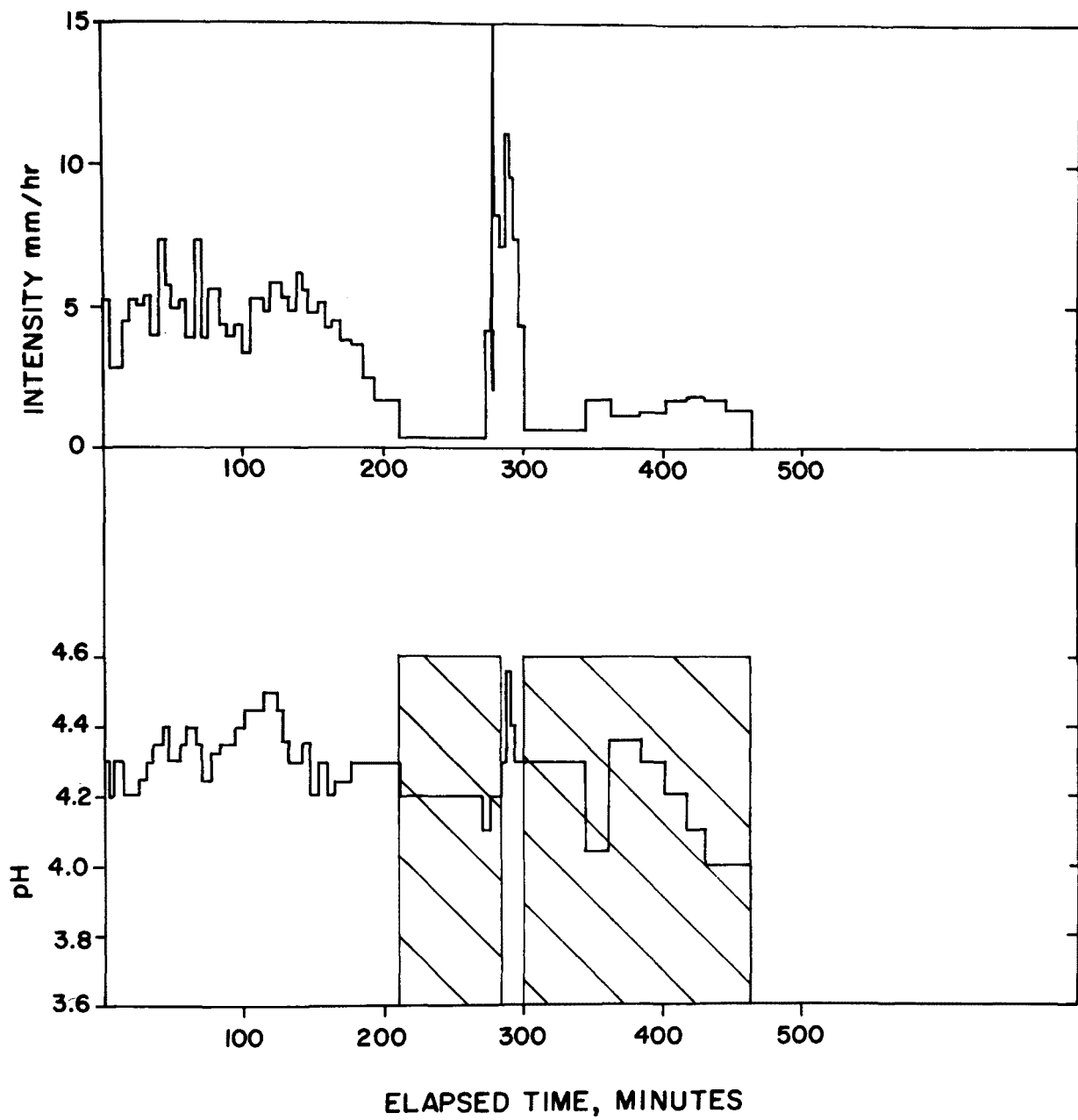


FIGURE 12. CHANGES IN STORM CHEMISTRY AND INTENSITY, SNOW/RAIN, 17-18 MARCH 1977.

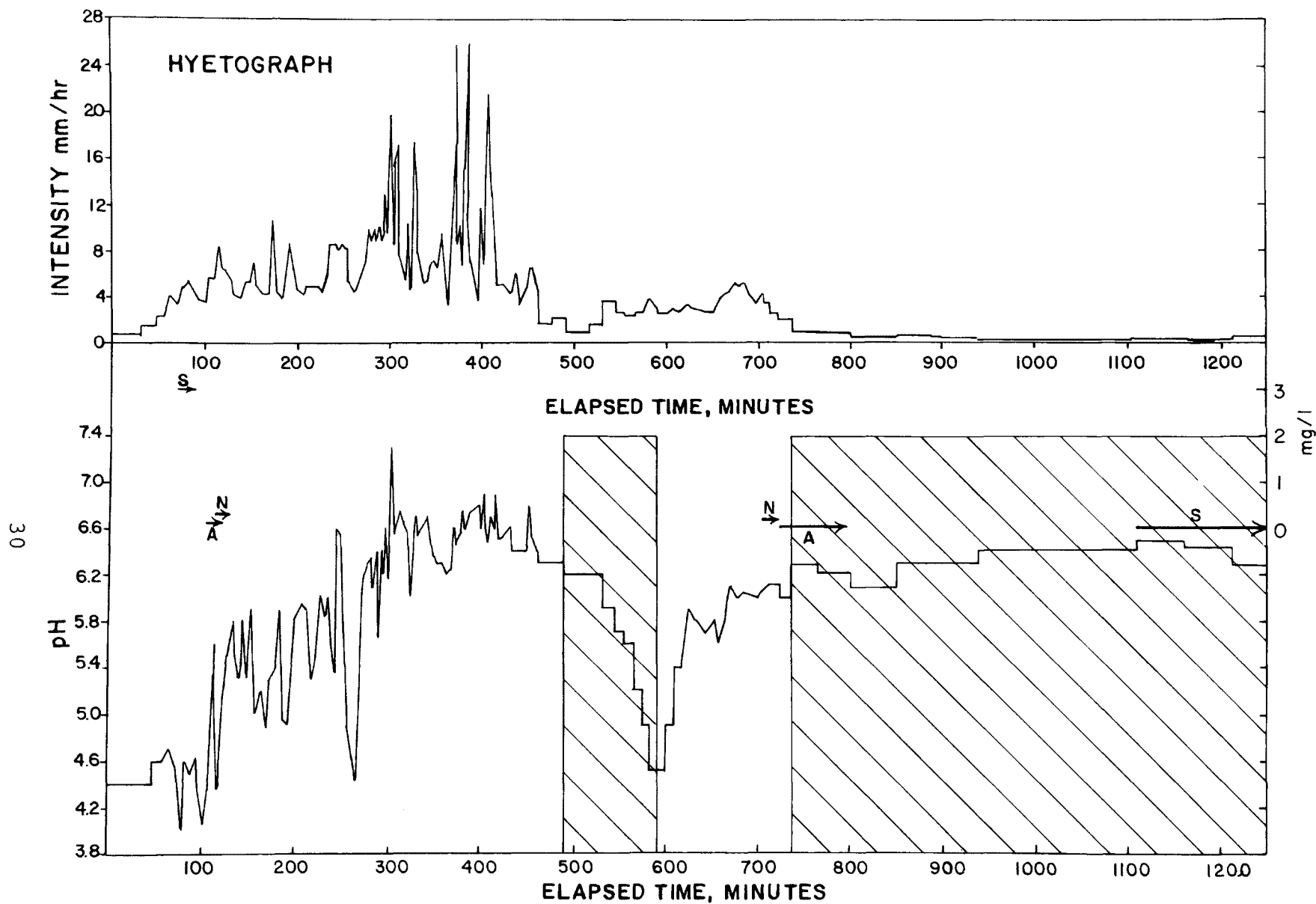


FIGURE 13. CHANGES IN STORM CHEMISTRY AND INTENSITY, RAINSTORM, 22 MARCH 1977.
 S = sulfate; A = ammonia as nitrogen; N = nitrate as nitrogen.

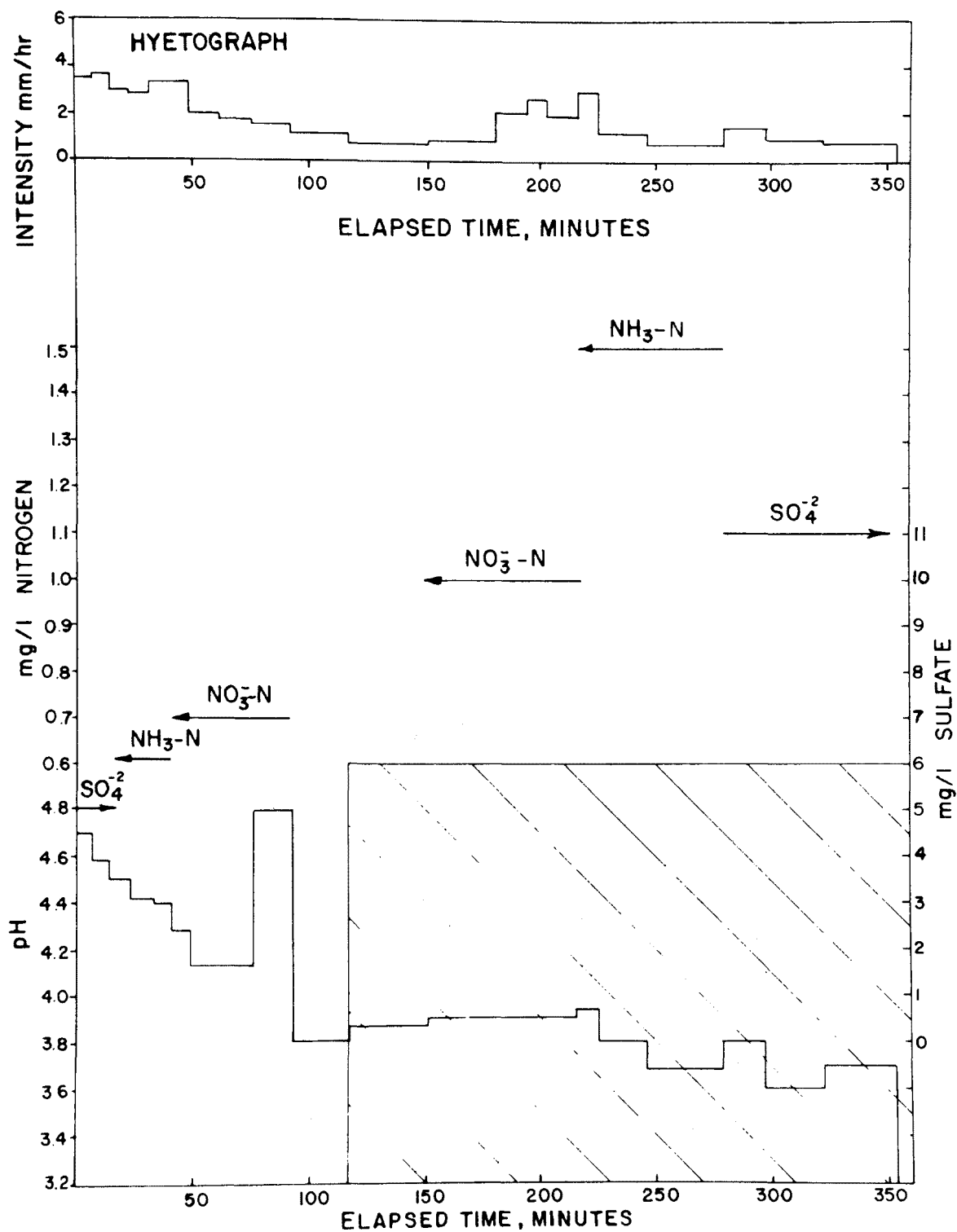


FIGURE 14. CHANGES IN STORM CHEMISTRY AND INTENSITY, RAINSTORM, 28 MARCH 1977.

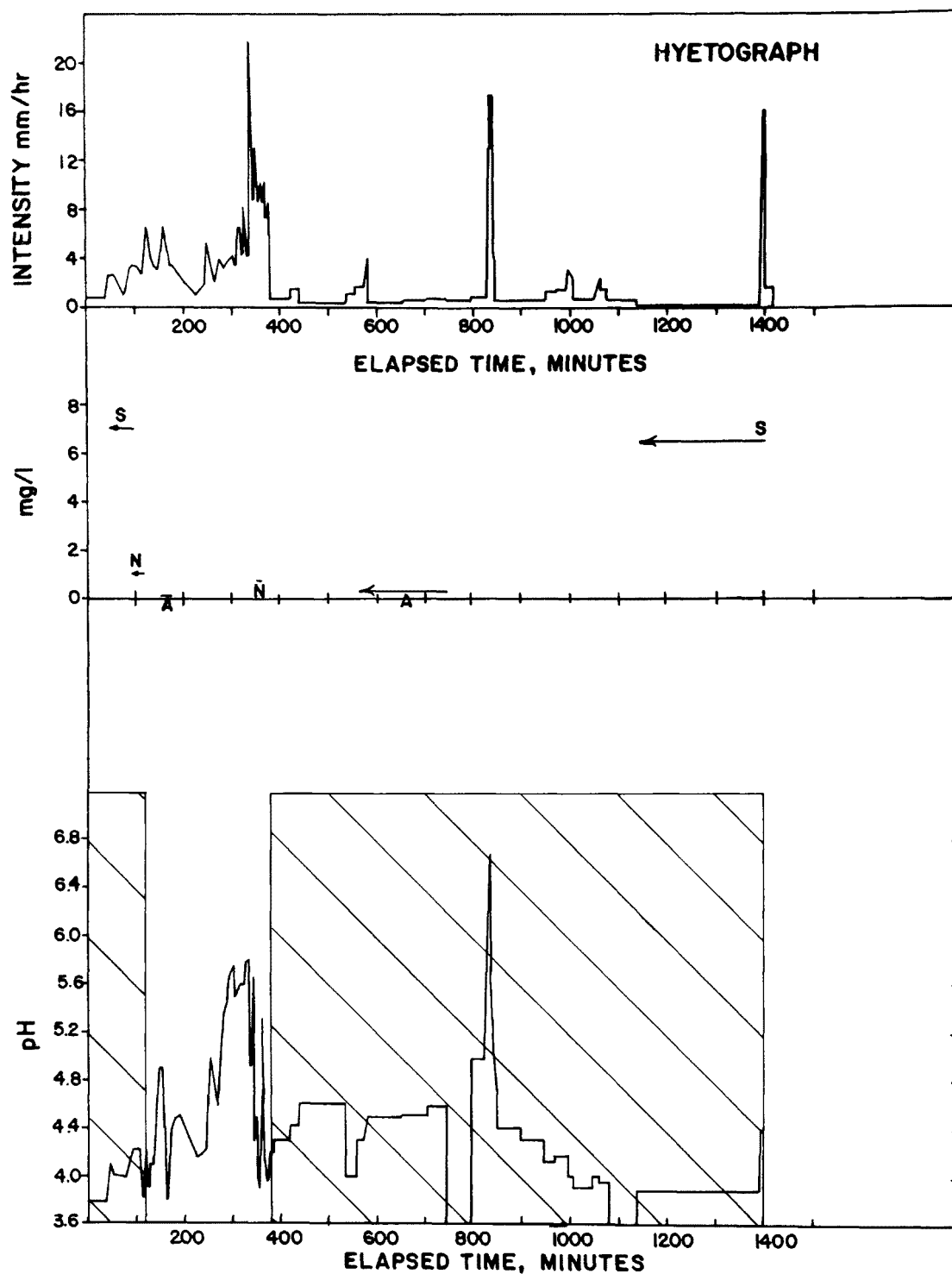


FIGURE 15. CHANGES IN STORM CHEMISTRY AND INTENSITY, RAINSTORM, 4-6 APRIL 1977. S = sulfate; A = ammonia as nitrogen; N = nitrate as nitrogen.

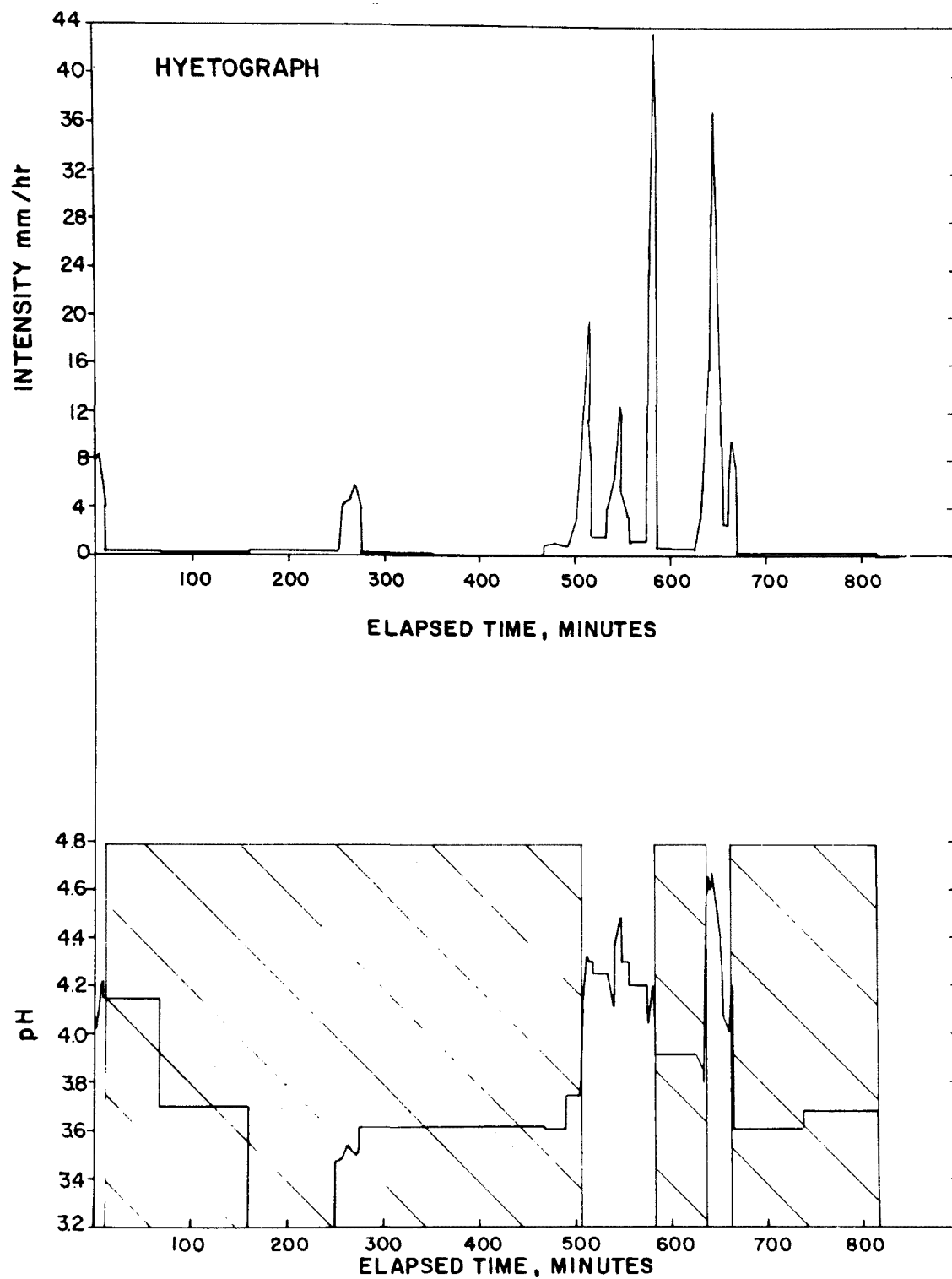


FIGURE 16. CHANGES IN STORM CHEMISTRY AND INTENSITY, RAINSTORM, 23-24 APRIL 1977.

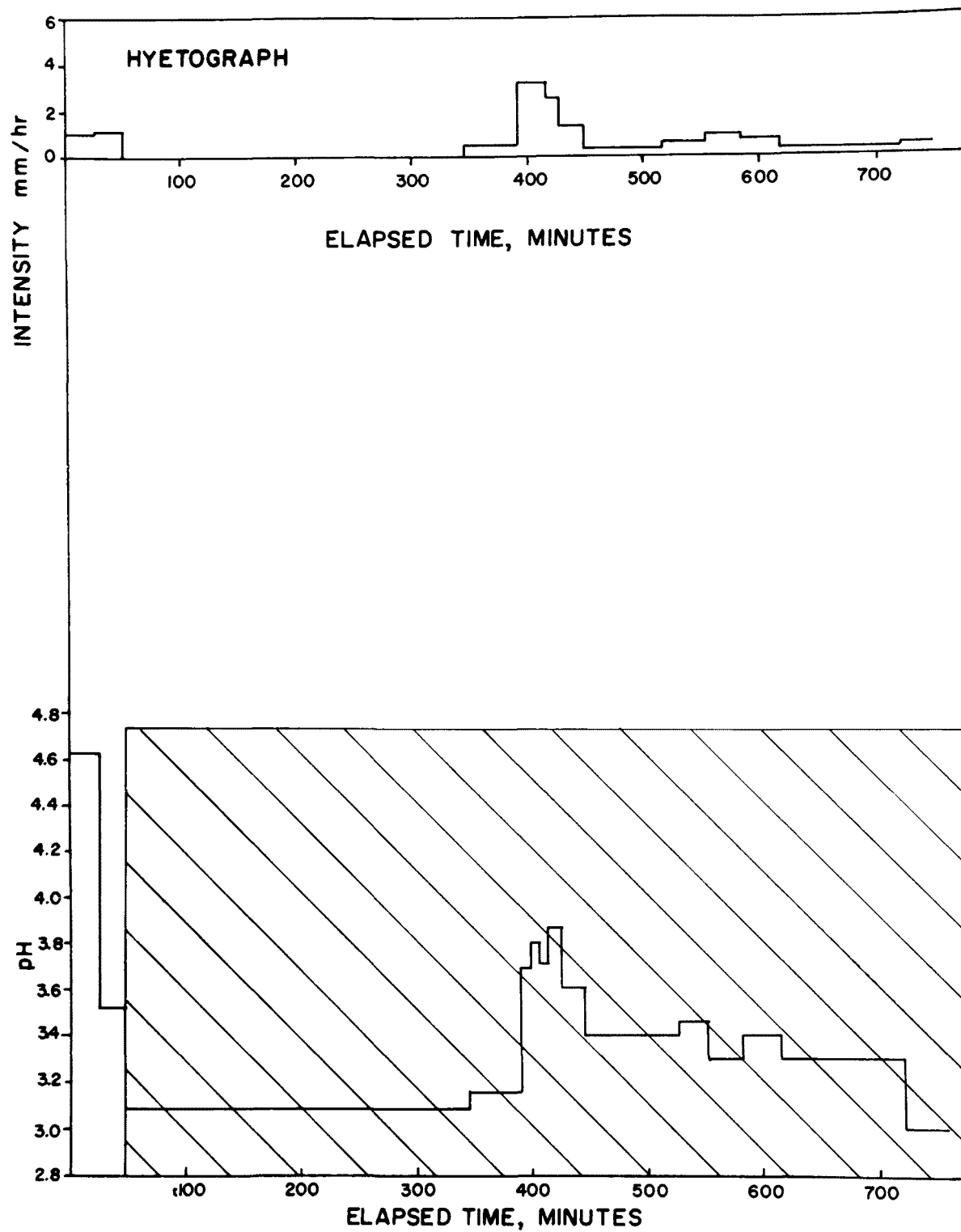


FIGURE 17. CHANGES IN STORM CHEMISTRY AND INTENSITY, RAINSTORM, 7 JUNE 1977.

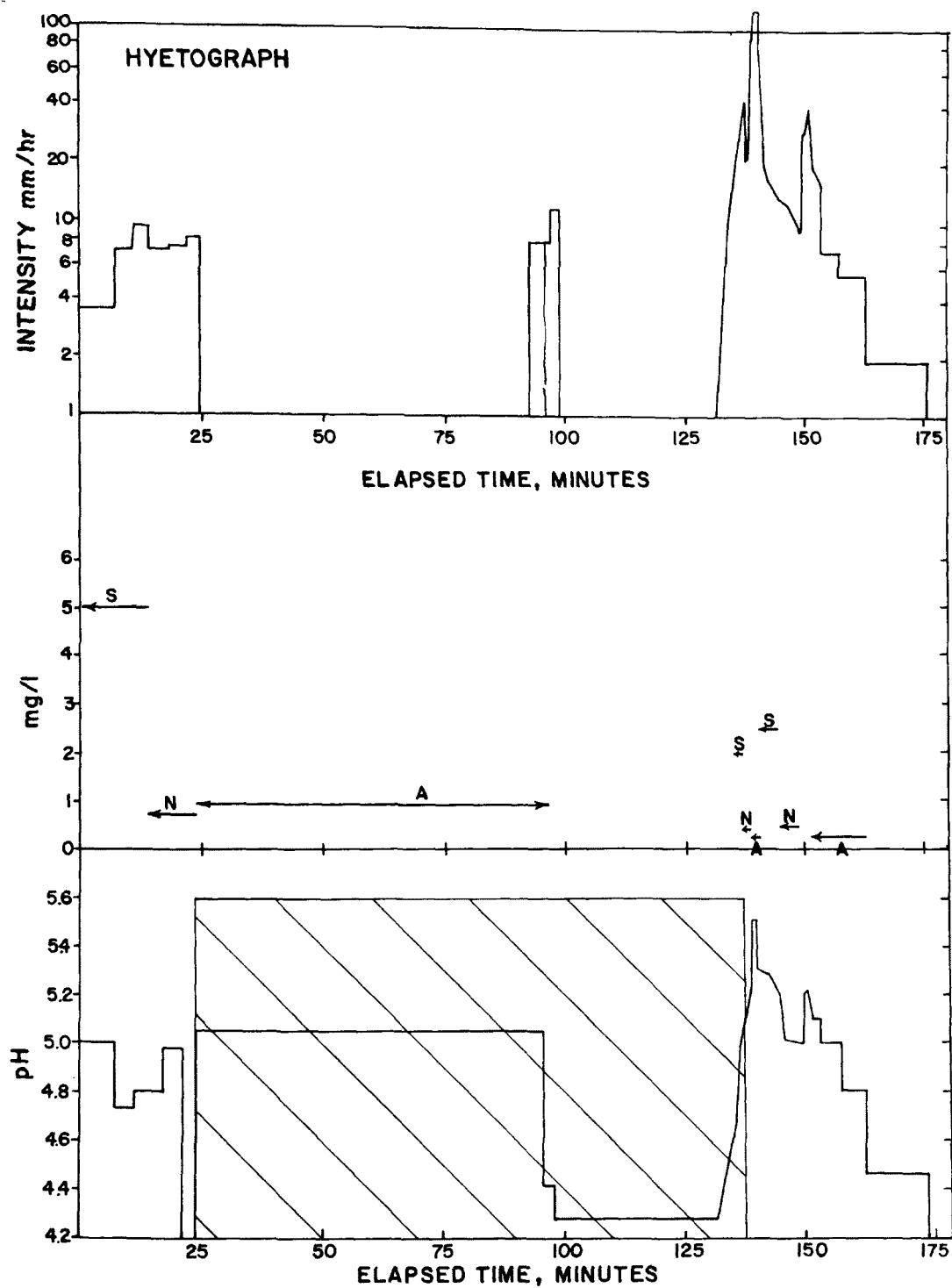


FIGURE 18. CHANGES IN STORM CHEMISTRY AND INTENSITY, RAINSTORM, 18 AUGUST 1977. S = sulfate; A = ammonia as nitrogen; N = nitrate as nitrogen.

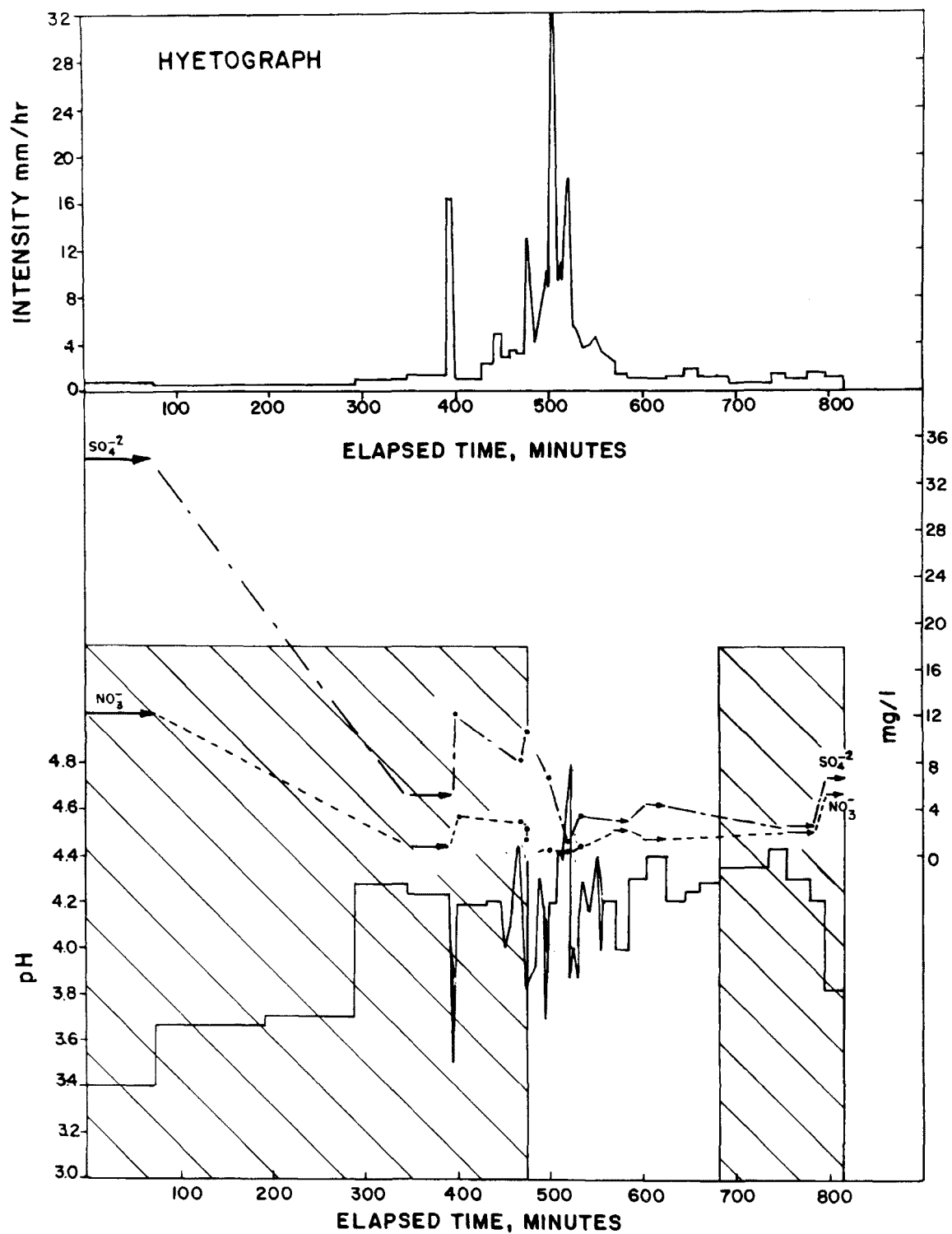


FIGURE 19. CHANGES IN STORM CHEMISTRY AND INTENSITY, RAINSTORM, 16-17 SEPTEMBER 1977.

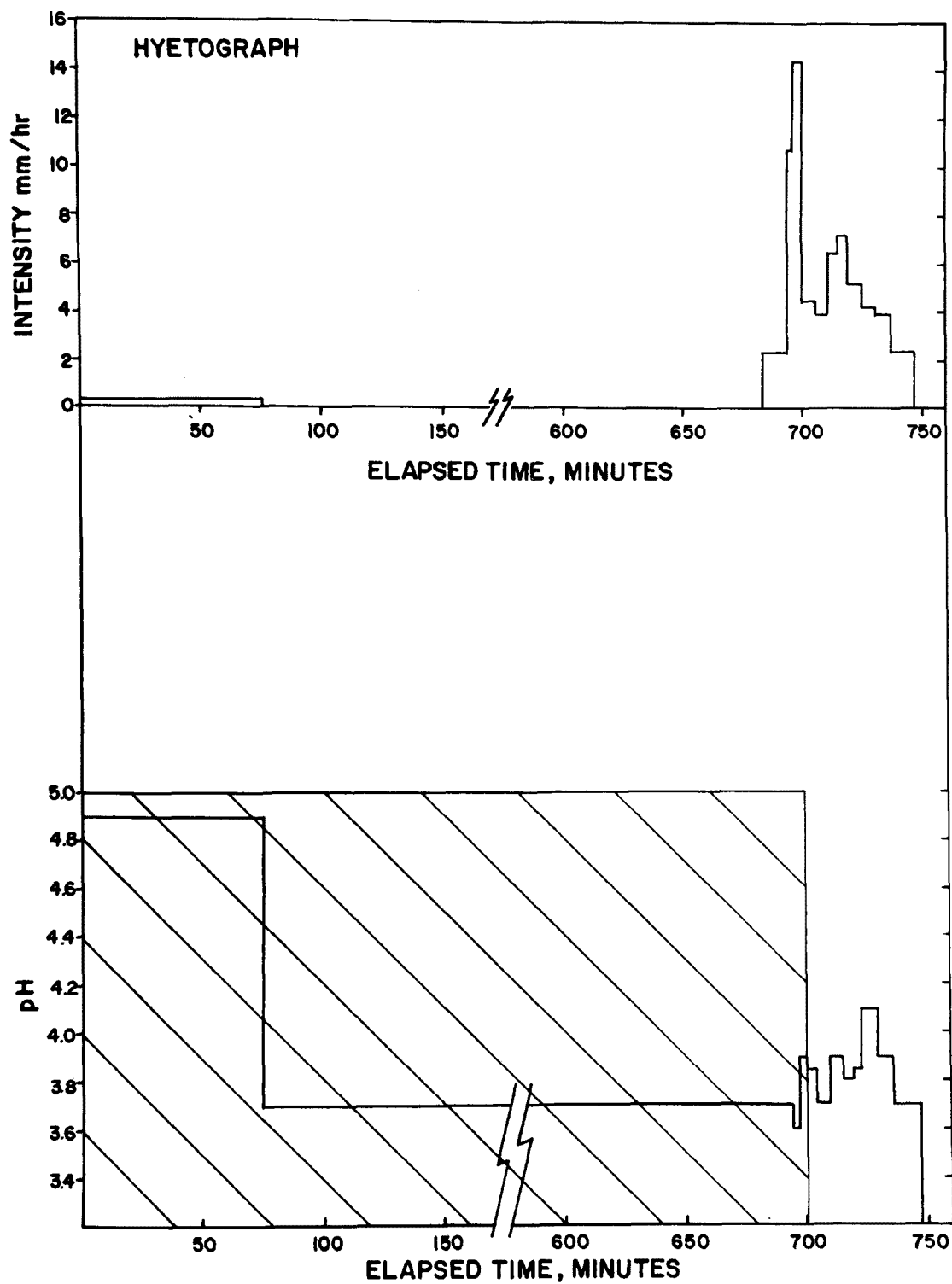


FIGURE 20. CHANGES IN STORM CHEMISTRY AND INTENSITY, RAINSTORM, 18 SEPTEMBER 1977.

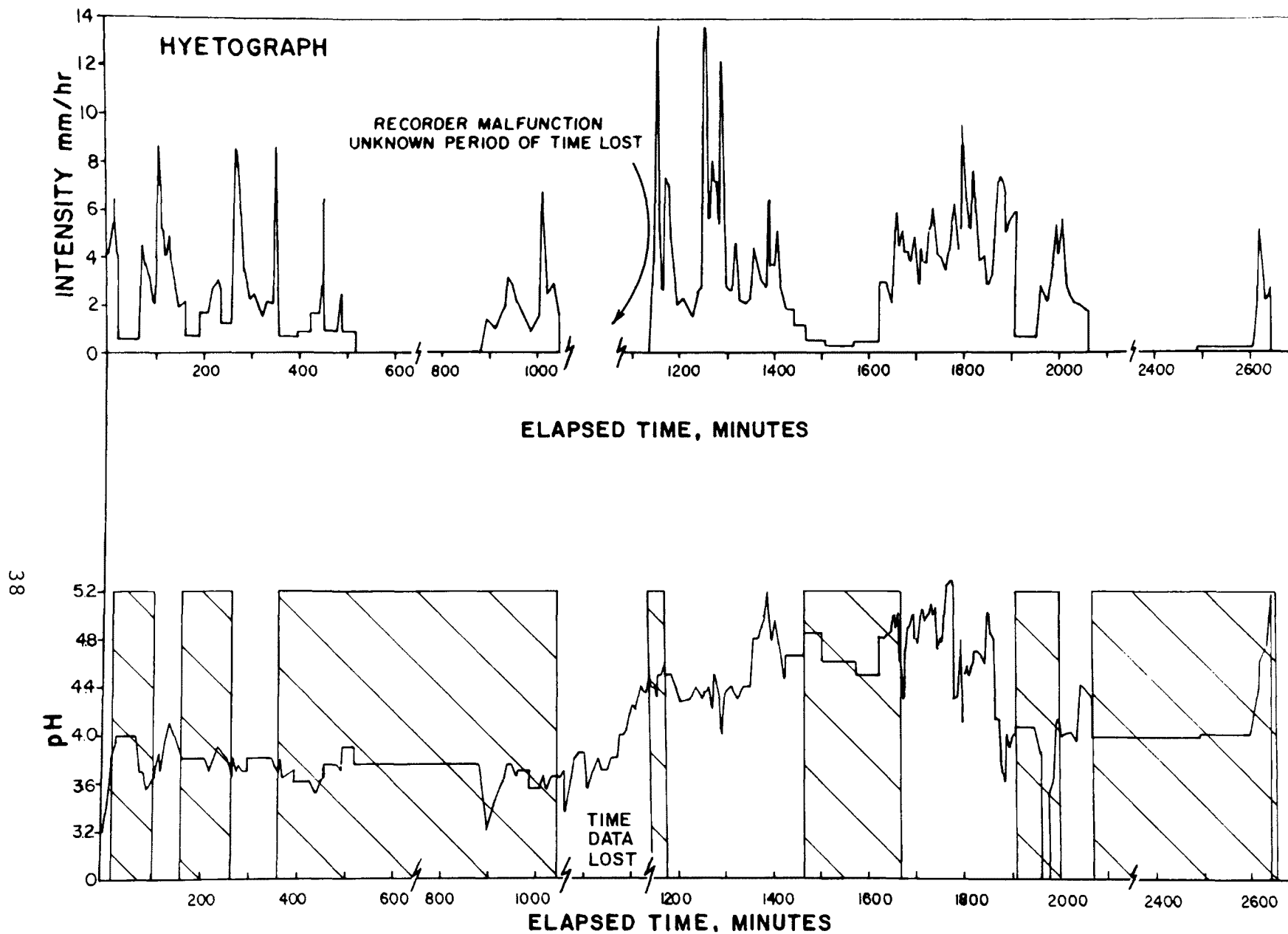


FIGURE 21. CHANGES IN STORM CHEMISTRY AND INTENSITY, RAINSTORM, 24-26 SEPTEMBER 1977. a. Hyetograph; b. pH data.

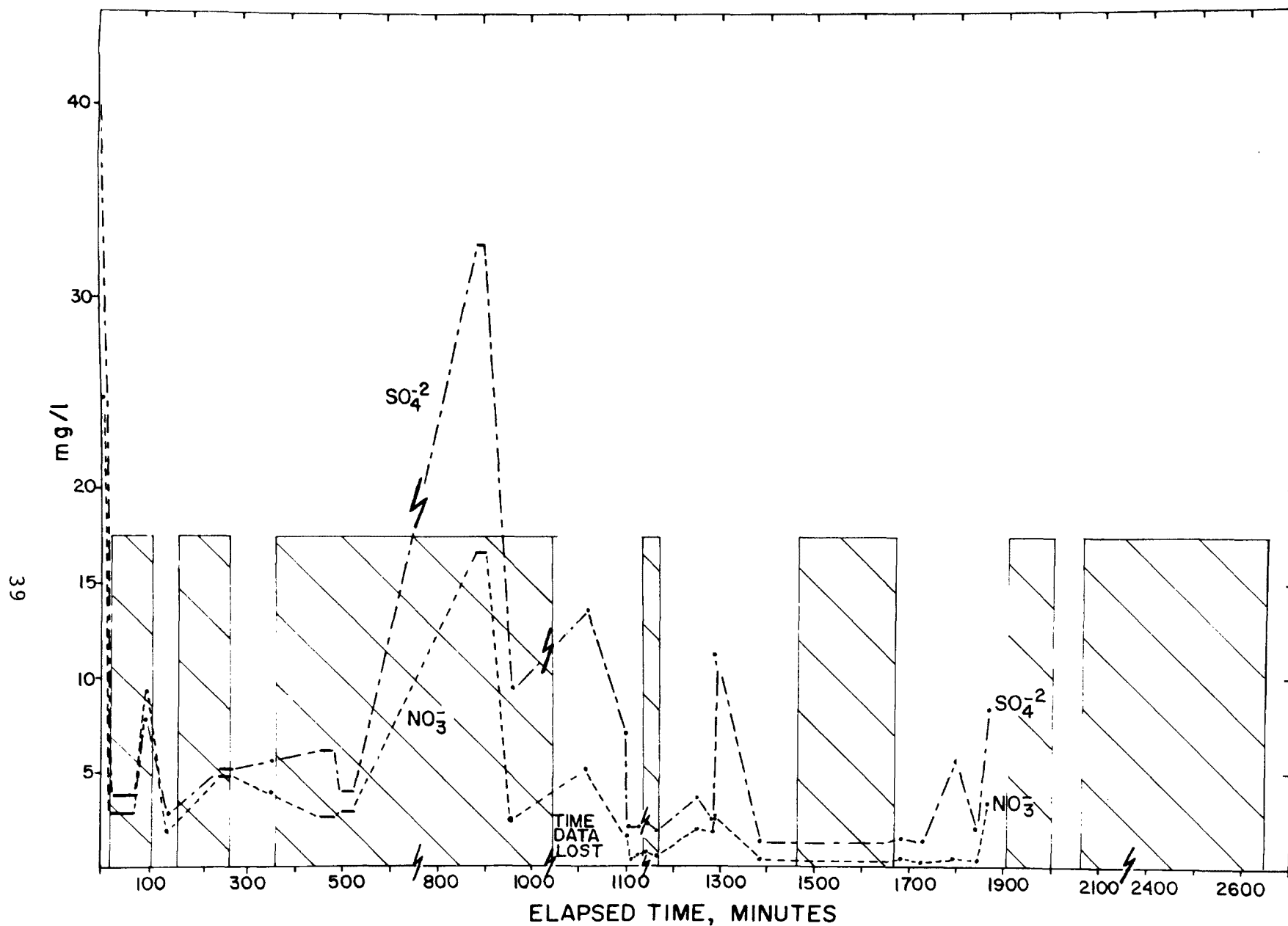


FIGURE 21. CHANGES IN STORM CHEMISTRY AND INTENSITY, RAINSTORM, 24-26 SEPTEMBER 1977. c. Ion chemistry.

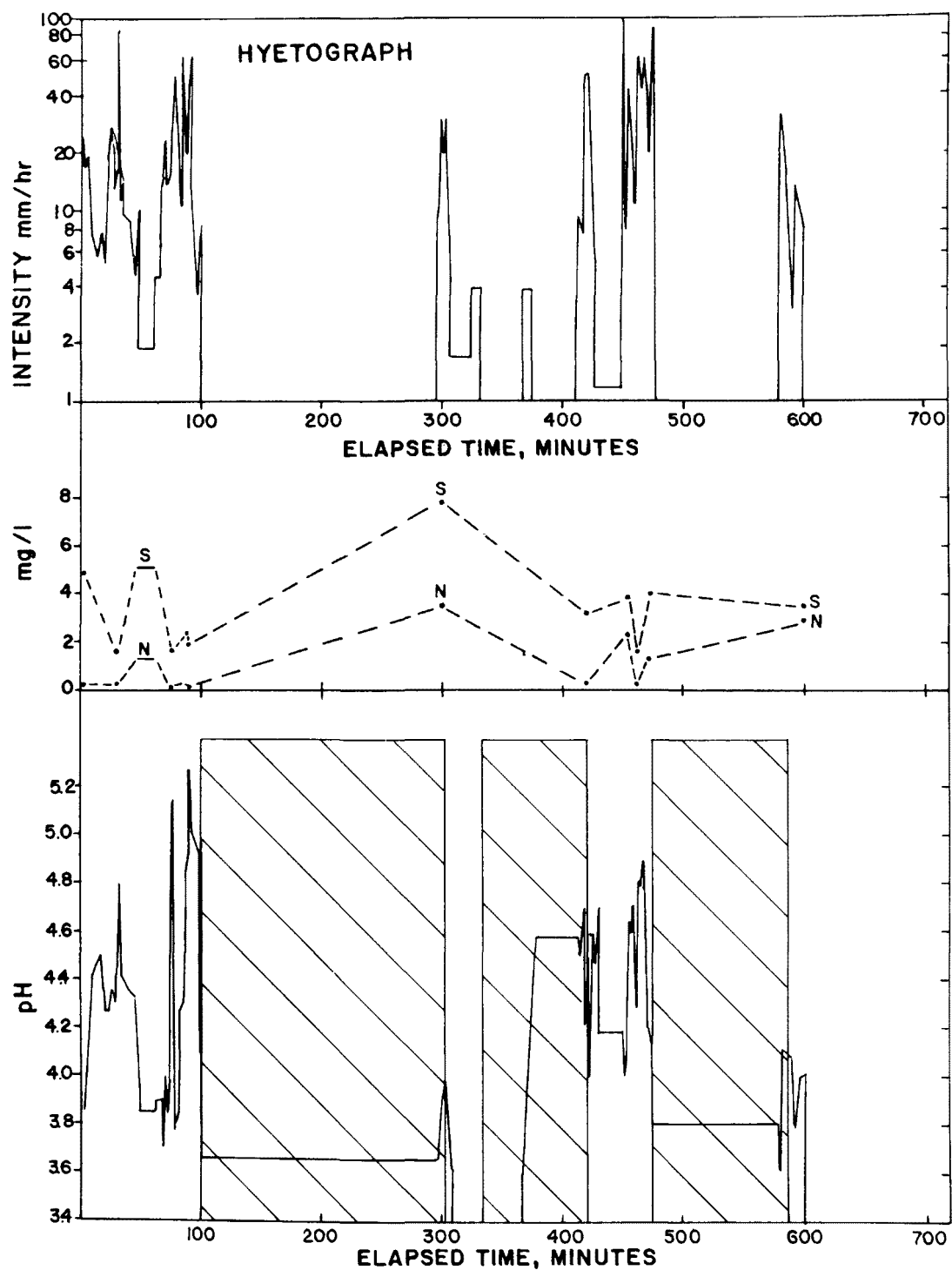


FIGURE 22. CHANGES IN STORM CHEMISTRY AND INTENSITY, RAINSTORM, 26 SEPTEMBER 1977. S = sulfate; N = nitrate.

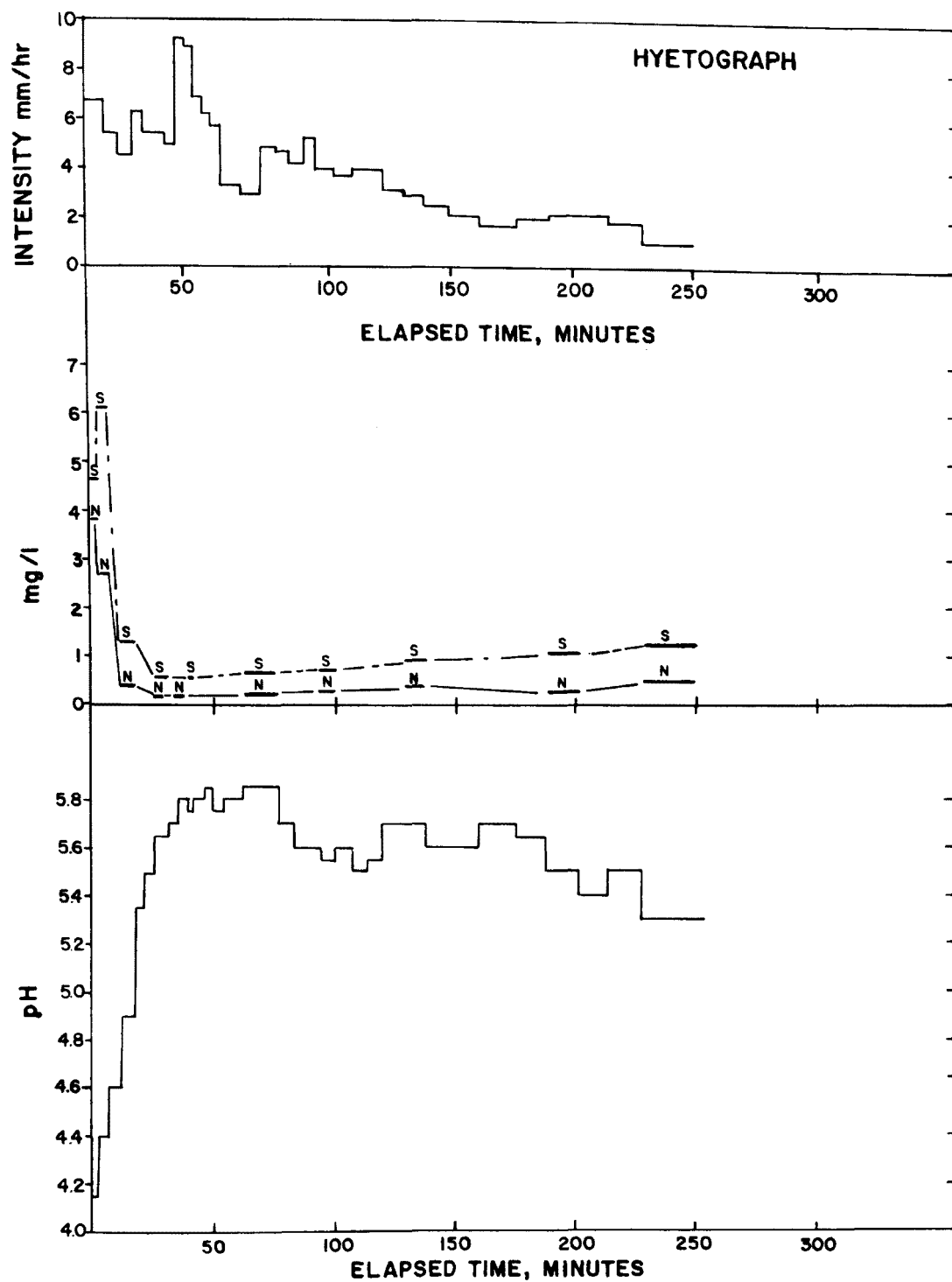


FIGURE 23. CHANGES IN STORM CHEMISTRY AND INTENSITY, RAINSTORM, 17 OCTOBER 1977. S = sulfate; N = nitrate.

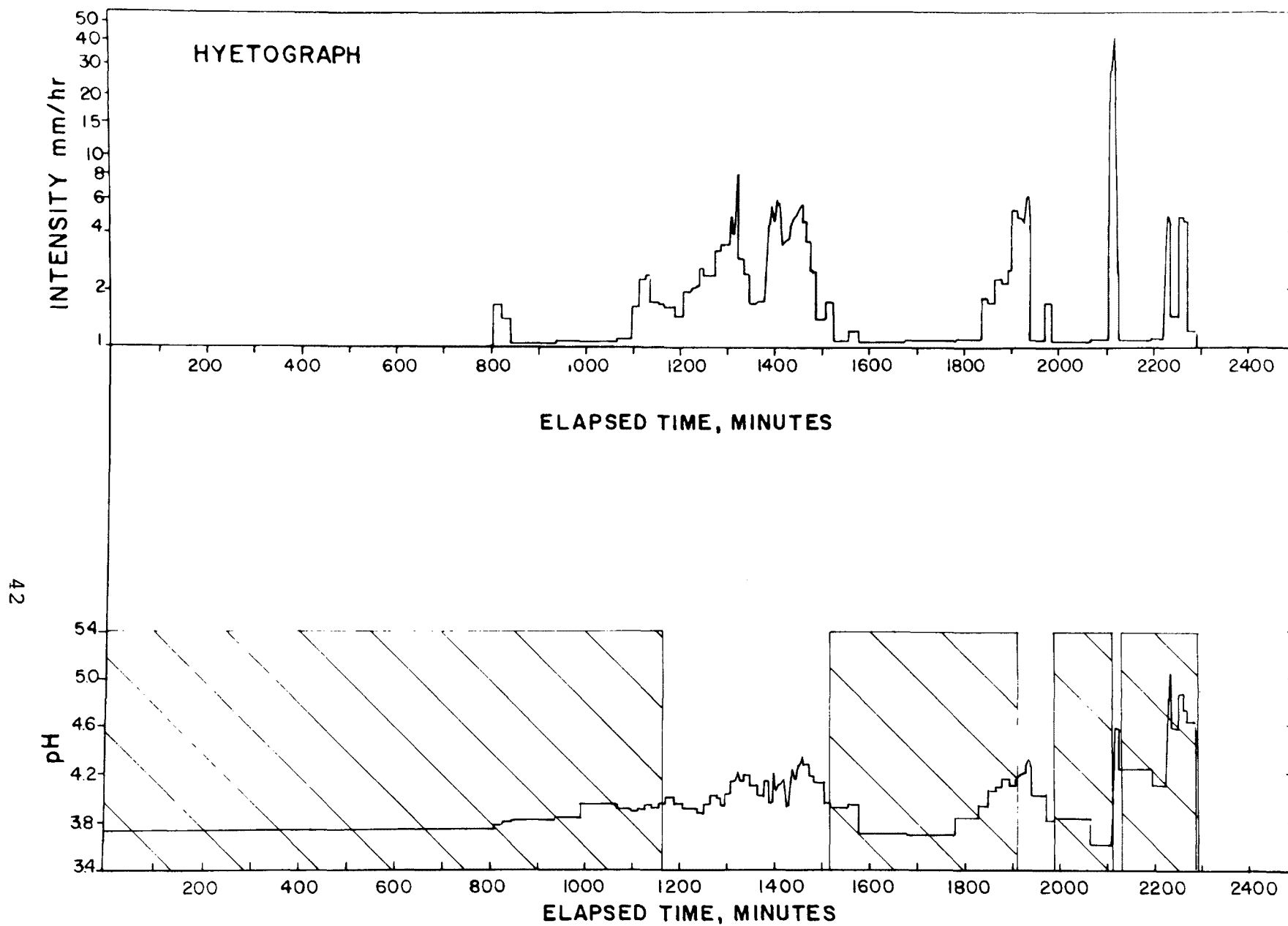


FIGURE 24. CHANGES IN STORM CHEMISTRY AND INTENSITY, RAINSTORM, 24-26 JANUARY 1978.
a. Hyetograph; b. pH data.

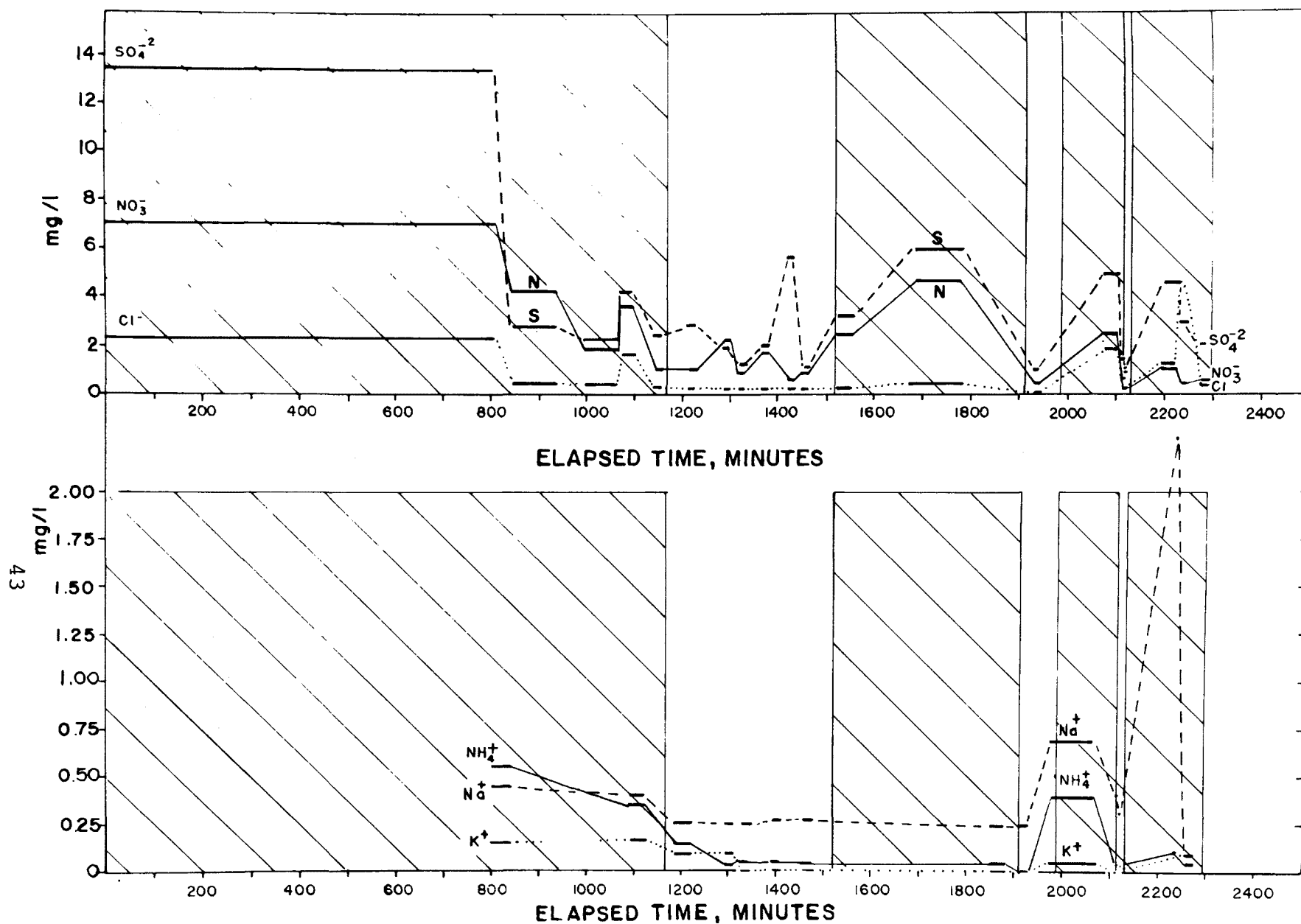


FIGURE 24. CHANGES IN STORM CHEMISTRY AND INTENSITY, RAINSTORM, 24-26 JANUARY 1978.
c. Anion chemistry; d. Cation chemistry. S = sulfate; N = nitrate.

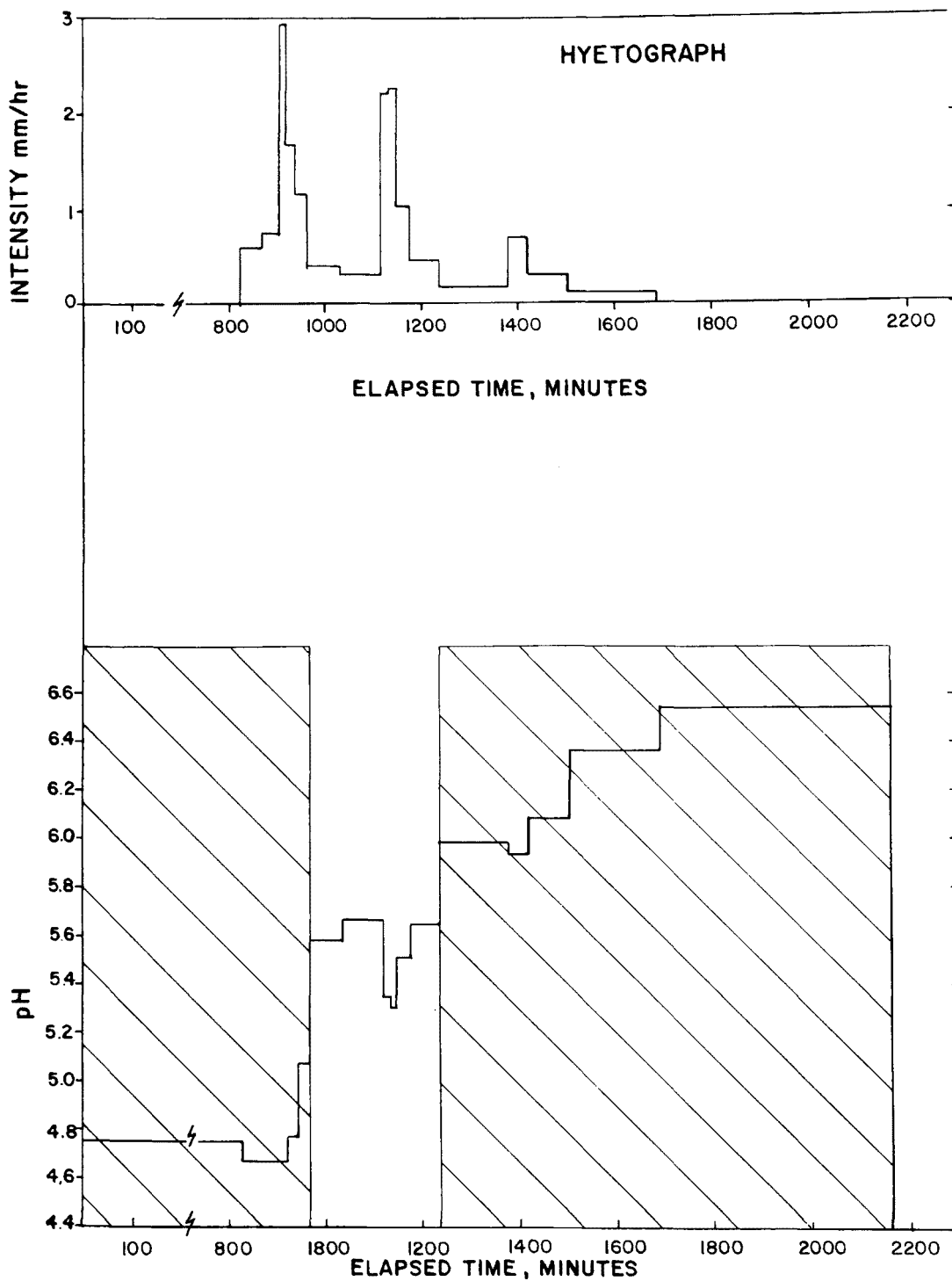


FIGURE 25. CHANGES IN STORM CHEMISTRY AND INTENSITY, SNOWSTORM, 6-7 FEBRUARY 1978. a. Hyetograph; b. pH data.

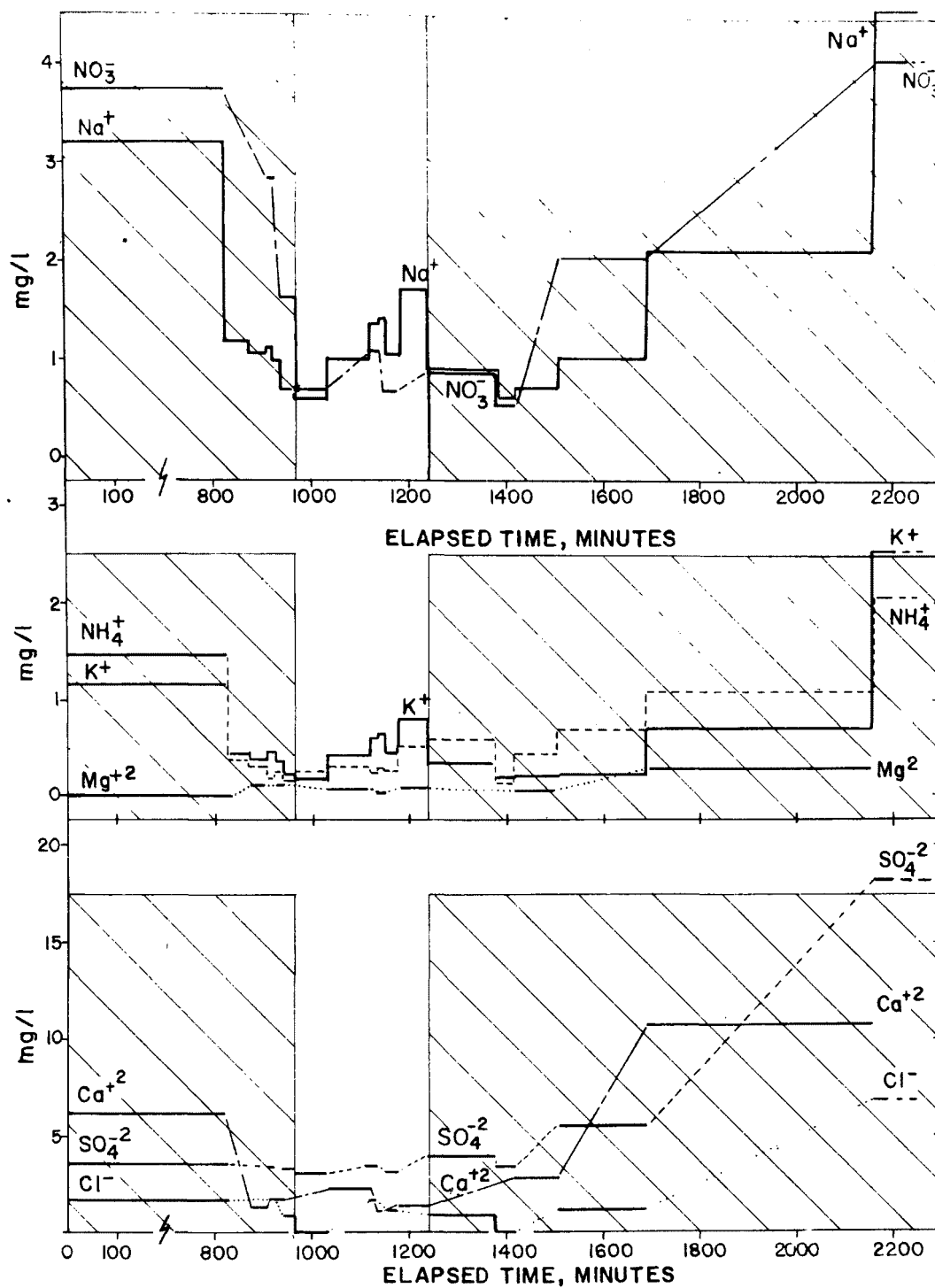


FIGURE 25. CHANGES IN STORM CHEMISTRY AND INTENSITY, SNOWSTORM, 6-7 FEBRUARY 1978. c. Ion chemistry.

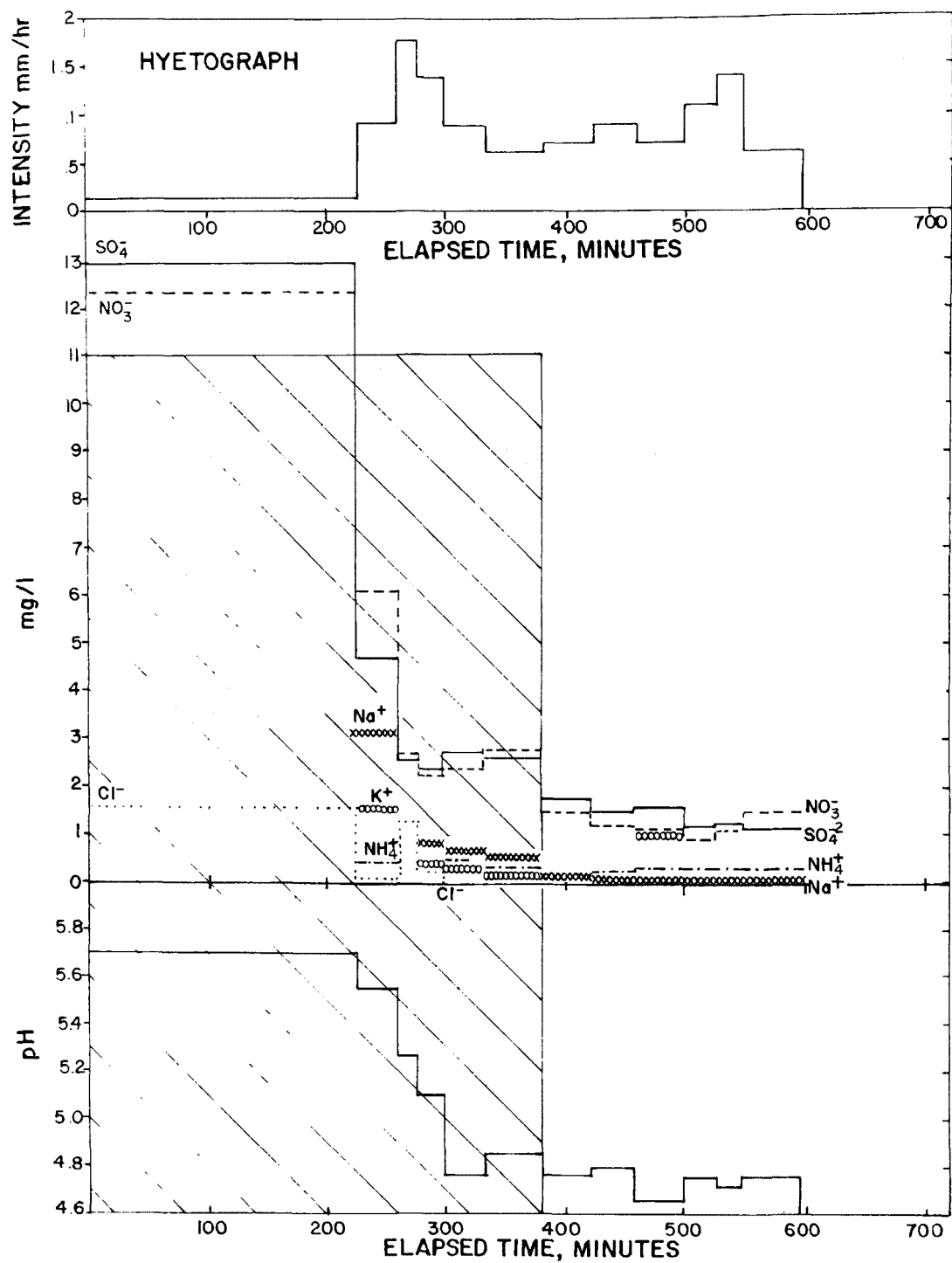


FIGURE 26. CHANGES IN STORM CHEMISTRY AND INTENSITY, SNOWSTORM, 3 MARCH 1978.

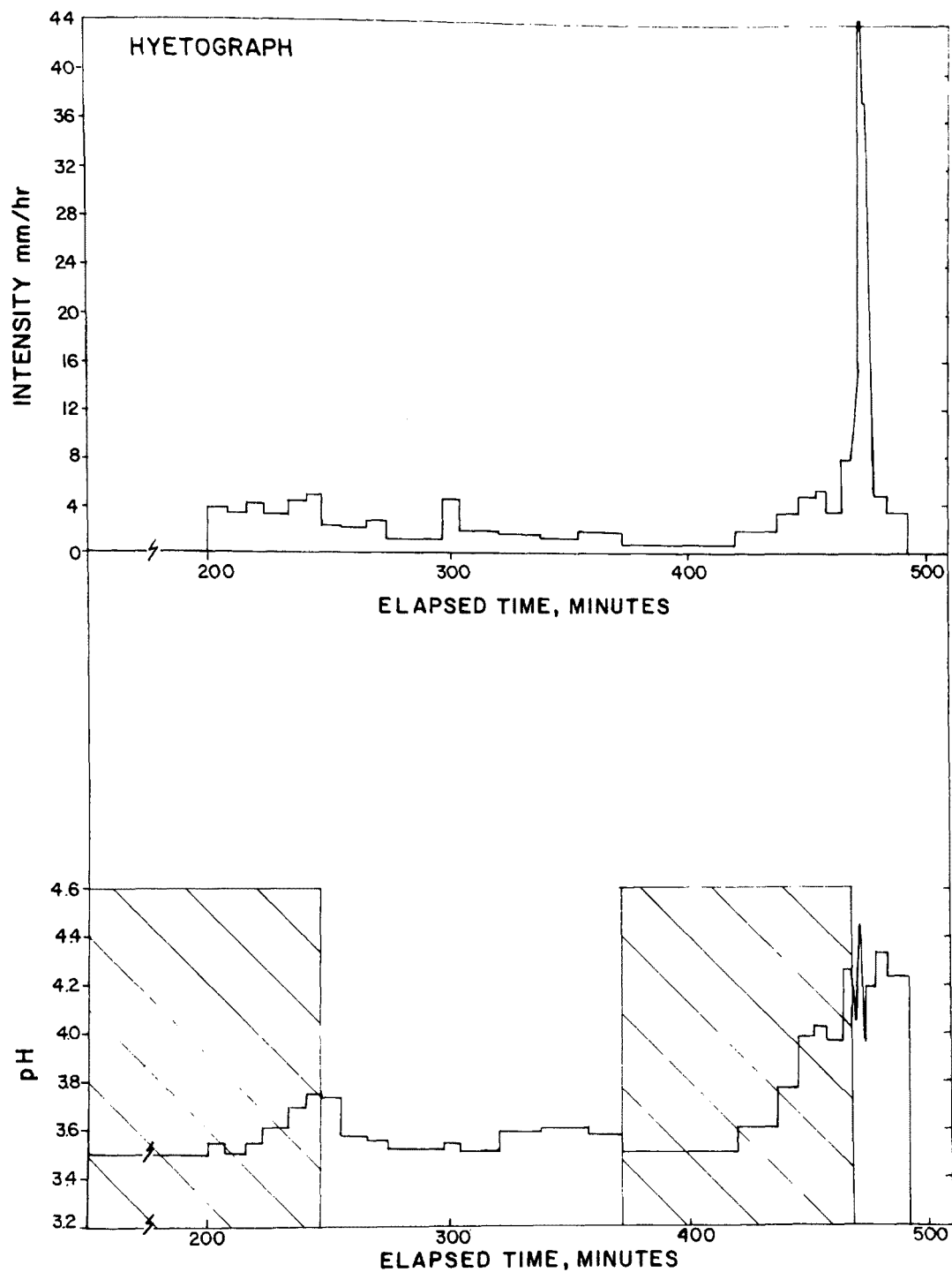


FIGURE 27. CHANGES IN STORM CHEMISTRY AND INTENSITY, RAINSTORM, 14-15 MARCH 1978. a. Hyetograph; b. pH data.

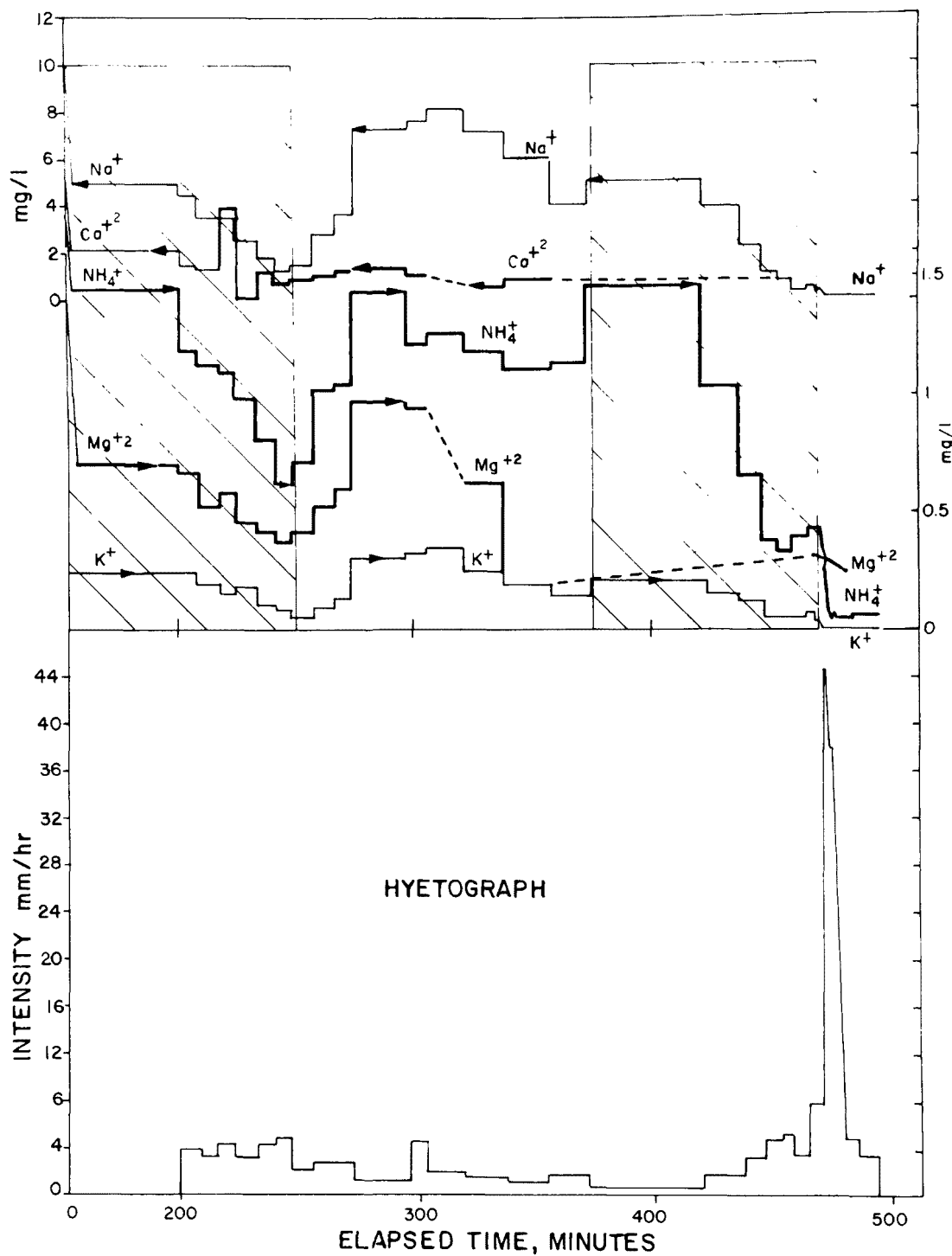


FIGURE 27. CHANGES IN STORM CHEMISTRY AND INTENSITY, RAINSTORM, 14-15 MARCH 1978. c. Ion chemistry.

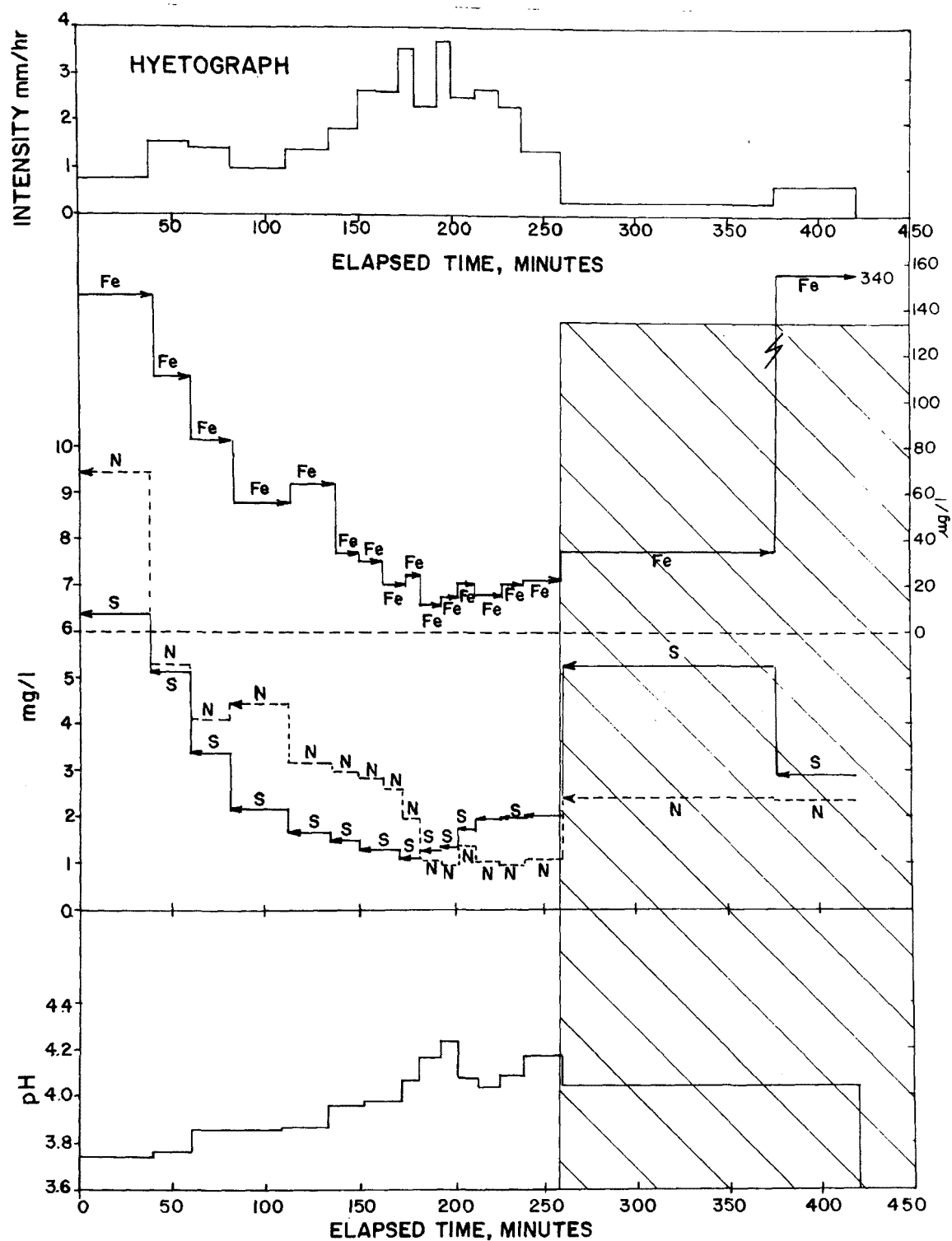


FIGURE 28. CHANGES IN STORM CHEMISTRY AND INTENSITY, SNOWSTORM, 16-17 MARCH 1978. S = sulfate; N = nitrate; Fe = iron.

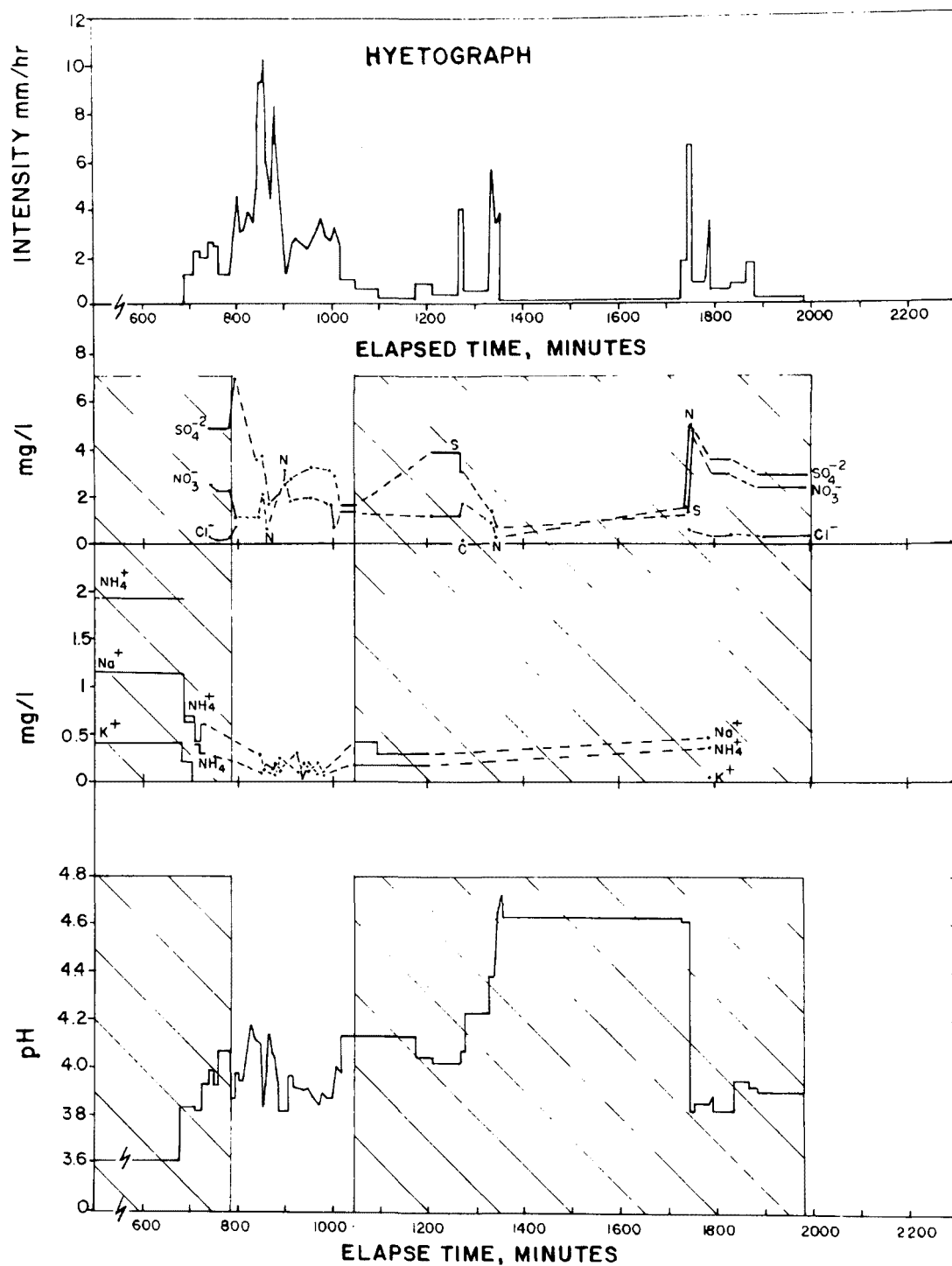


FIGURE 29. CHANGES IN STORM CHEMISTRY AND INTENSITY, RAINSTORM, 18-20 APRIL 1978.

collected, it would be convenient if the time-pH data would be sufficient to discriminate the contamination-free from the contamination periods. Another factor which must be considered is precipitation type. The intensity discriminator for a rainstorm will probably not work for snowstorms which have a much lower intensity.

The procedures used made contamination more likely at the start of a storm when the funnel was uncovered in anticipation of rain. As a first approximation, rainstorms with an elapsed time of greater than 50 minutes (~ 0.5 mm/hr intensity) before collection of the first sample were looked at for indications of contamination. Four rainstorms, 16-17 September 1977 (Figure 19, 24-26 January 1978 (Figure 24), 14-15 March 1978 (Figure 27), and 18-20 April 1978 (Figure 29) had elapsed times greater than 50 minutes at the start. In the samples following this possible period of contamination, the pH starts from a low of 3.4 to 3.8 and rises slowly (16-17 Sep and 24-26 Jan are complicated by several early periods in excess of 50 minutes). Galloway and Likens²⁷ have shown that dry deposition in the northeastern U.S. is acidic in nature, containing sulfate and nitrate salts. If dry deposition occurred, one would expect the earliest samples coming from the funnel to be very acid, and then as acid material is washed off, the pH should rise. This expectation is borne out in the four storms. In addition, chemical data from the storms show high early sulfate and nitrate concentrations (16-17 Sept and 24-26 Jan) and high early metal concentrations (14-15 Mar and 18-20 April). It appears that long (>50 min) elapsed time and pH data are sufficient indicators for dry deposition contamination at the beginning of a storm.

The above pH and elapsed time tests were extended to rainstorms with elapsed times between 25 minutes (1.0 mm/hr intensity) and 50 minutes (~ 0.5 mm/hr intensity). Three rainstorms, 22 March 1977 (Figure 13), 4-6 April 1977 (Figure 15), and 7 June 1977 (Figure 17) fit in this category. Two, 22 March 1977, and 4-6 April 1977 show the slowly rising pH trend. Supportive chemical data for the two storms are indicative of high early sulfate and nitrate, but the sparseness of data does not allow a definitive conclusion to be drawn. The other storm, 7 June, has high early pH that drops following the initial "long" period. No supporting chemical data are available. Rainstorms with an initial collection period less than 25 minutes (intensity greater than 1.0 mm/hr) have a random pH and chemistry pattern. Further analysis of future storms is needed, but it appears that a working hypothesis can be advanced which states that rainstorms with initial periods of intensity greater than 1.0 mm/hr are contamination free during this period and those with intensity less than 1.0 mm/hr are contaminated by dry deposition.

There is no reason why application of the intensity discriminator should be confined to the early period of a storm only.

Therefore, all rainstorms with periods of intensity less than 1.0 mm/hr during the course of the storm were identified. Of all the rainstorms collected, only two, 17 October 1977 (Figure 23) and 19 October 1977 (Figure 9) show no possible period of contamination. The others generally show a sharp drop in the pH following a contamination period, which is indicative of the acidic nature of dry deposition. Following the drop, the gradual rise seen in the initial contamination period was exhibited (See Figure 21 for example). Sulfate and nitrate data support this conclusion, but are not plentiful enough to provide the desired level of confidence. The intensity of 1 mm/hr for rainstorms is a good discriminator for discerning periods of dry deposition contamination throughout a rainstorm.

Dry deposition contamination in snowstorms was explored. Four snowstorms are represented in our data, 17-18 March 1977 (Figure 12), 6-7 February 1978 (Figure 25), 3 March 1978 (Figure 26), and 16-17 March 1978 (Figure 28). All have periods with intensity (using the water equivalent of snow) less than 1.0 mm/hr. The 6-7 February data has been used to establish an intensity limit for snowstorms of 0.25 mm/hr (See Appendix C for the interpretation of the data). There are no periods in the other three storms with intensity greater than 0.25 mm/hr which could be interpreted as contaminated nor are there periods with intensity less than 0.25 mm/hr which do not show evidence of dry deposition contamination.

The cleansing period is harder to quantify. Assuming a uniform deposition flux, more material will need to be removed from the funnel the longer the period of exposure. Intensity of rainfall will play a role too. A light drizzle will collect on the funnel and remain longer as droplets coalesce to drops and run down the funnel. Light rain will promote solution of soluble materials as it will have a longer contact period. On the other hand, heavy rain will tend to flush particulates because of the impact energy of the drops. A complicating factor is a succession of contamination periods each with samples between.

Examination of several storms indicates that the dry deposition flux must not be uniform. In the 14-15 March 1978 rainstorm (Figure 27), sodium ion concentration for a 200-minute period is almost 5 mg/l whereas the rainstorm on 18-20 April 1978 (Figure 29) had a 678-minute period yielding a sodium ion concentration of 1.15 mg/l. Ammonium ion concentration was 1.45 mg/l and 1.93 mg/l in the two storms respectively and potassium ion concentration was 0.24 mg/l and 0.35 mg/l. The trend for K^+ and NH_4^+ is as expected with the longer exposure time having the higher concentration, but the Na^+ data cannot be reconciled with this interpretation. If the constant flux hypothesis were to hold then one would expect 18-20 April to have three times more contaminant than 14-15 March since the contamination period is three times longer.

Storms with high intensity rain after periods of contamination (e.g. 2 June 77, Figure 8) appear to wash their dry deposits off the funnel in the 2 or 3 samples following contamination (e.g. the intensity spike at 136 minutes of the 2 June data produces an acid condition which recovers quickly). On the other hand during less intense periods following contamination 5 or more samples may be needed to cleanse the funnel. For example, the contamination period stretching from 372 to 420 minutes in the 14-15 March storm (Figure 27) is followed by rains of low intensity which slowly raise the pH and lower the pollutant concentrations. Pollutants are not finally removed until the intensity spike at 472 minutes.

There does not appear to be any single discriminator which will allow quantification of the cleansing period. The pH is not suited for use. The ion concentrations for many samples from a storm make interpretation easier, but not certain. Perhaps laboratory experiments under controlled conditions would produce a useful discriminator. The chemical data, when available, has been used or in the absence of such data deletion of an arbitrary 3-8 samples following the suspected dry deposition depending upon the intensity of rain. The deletion of these samples is to account for cleansing of dry deposition from the funnel.

This problem of funnel contamination will be eliminated with the automated closure device, providing that the precipitation sensor is sensitive enough to react quickly to rain stoppages. This will be a function of the speed at which the sensor heater evaporates the rain. This heating rate cannot be too high, however, or in very light rain the funnel may be closed prematurely.

A MODEL FOR INTERPRETING SEQUENTIAL PRECIPITATION CHEMISTRY DATA

Sequential precipitation chemistry data show the chemical composition of samples collected beneath a changing air column during a storm event. The goal is to relate the changes in the chemistry of these samples to processes occurring in the atmosphere above the collector. The model below looks at atmospheric processes which affect the number of aerosol particles or drops and the composition of aerosols present in the atmosphere.

Clean dry air is composed of gases with relatively long residence times, (N_2 , O_2 , He, Ne, Ar, Kr, Xe, H_2 , CO_2 , O_3 , N_2O , and CH_4). Pollutant gases (H_2O vapor, NO_2 , NO, NH_3 , SO_2 , H_2S , CO, HCl, and I_2) from natural and anthropogenic sources; and aerosols of solid and liquid particles suspended in the gaseous medium are also present. These aerosols are typically extraterrestrial stony and metallic meteoric material; volcanic material (ash); biological material (bacteria, spores, and pollen); metal oxides; organic combustion products; acids (H_2SO_4 , HNO_3); and salts ($NaCl$, $MgCl_2$, $MgSO_4$, Na_2SO_4 , $NaNO_3$, $(NH_4)_2SO_4$, NH_4Cl , NH_4NO_3). The aerosol particles can be divided into water soluble and not soluble³⁰.

A number of processes (Figure 30) affect the number, size, and composition of the particles of the aerosols present. The processes can be divided into those which bring particles into the parcel, the input processes; those which remove particles from the parcel, the output processes; and those processes which operate within the parcel to change the makeup of the aerosol population, the internal processes. The inputs to the air column result from material entering from an adjacent column due to: 1) diffusional transport by either thermal agitation (Brownian movement) or turbulent eddying of the air; 2) dry gravitational processes from above (deposition, fallout, sedimentation); 3) hydrometeors (rain, snow, drizzle, fog, sleet, hail, ice) carried into the parcel by gravity or air turbulence.

Many processes occur that affect the size, composition, and number of aerosol particles within the air parcel. A complete review has been presented by Pruppacher.³¹ The following are examples of these processes: 1) vapors condense to produce a liquid aerosol particle; 2) condensed material evaporates, leaving dry particulate aerosol; 3) gases are adsorbed on solids; 4) particles, both liquid and solid, collide to produce larger aggregate particles or perhaps breakup into smaller particles; 5) chemical reactions occur between gases and solids, liquids and solids, etc. to produce differing chemical composition; and 6) water vapor nucleates on particles. In all of these processes the material involved remains within the parcel.

Of prime interest to the precipitation chemist are the output processes which remove aerosols from the parcel. These processes will have the largest effect on the chemistry observed on the ground. The dominant process is rainout, the removal of gases or aerosols in a cloud by capture on cloud droplets or raindrops in a cloud. Sedimentation occurs when particles have obtained sufficient mass to fall out of the air parcel. The next two processes are the scavenging of aerosol particles by other aerosol particles falling through the parcel from above and by hydrometeors falling through the air column from above (washout). A number of mechanisms have been proposed to explain how the material is scavenged and incorporated into the falling mass. Studies by Beard³², Dana and Hales³³, and Adam and Semonin³⁴ have shown that the scavenging efficiency is related to drop and particle size. Some authors have proposed wake capture as an important process.³⁵ Hydrometeor type will affect scavenging efficiency^{36,37}. Electrostatic processes play a role but the extent is not known. The last output process is impaction on buildings, trees, mountains, etc. as the wind impinges liquid and solid aerosols on a surface. Impaction is largely a near surface process.

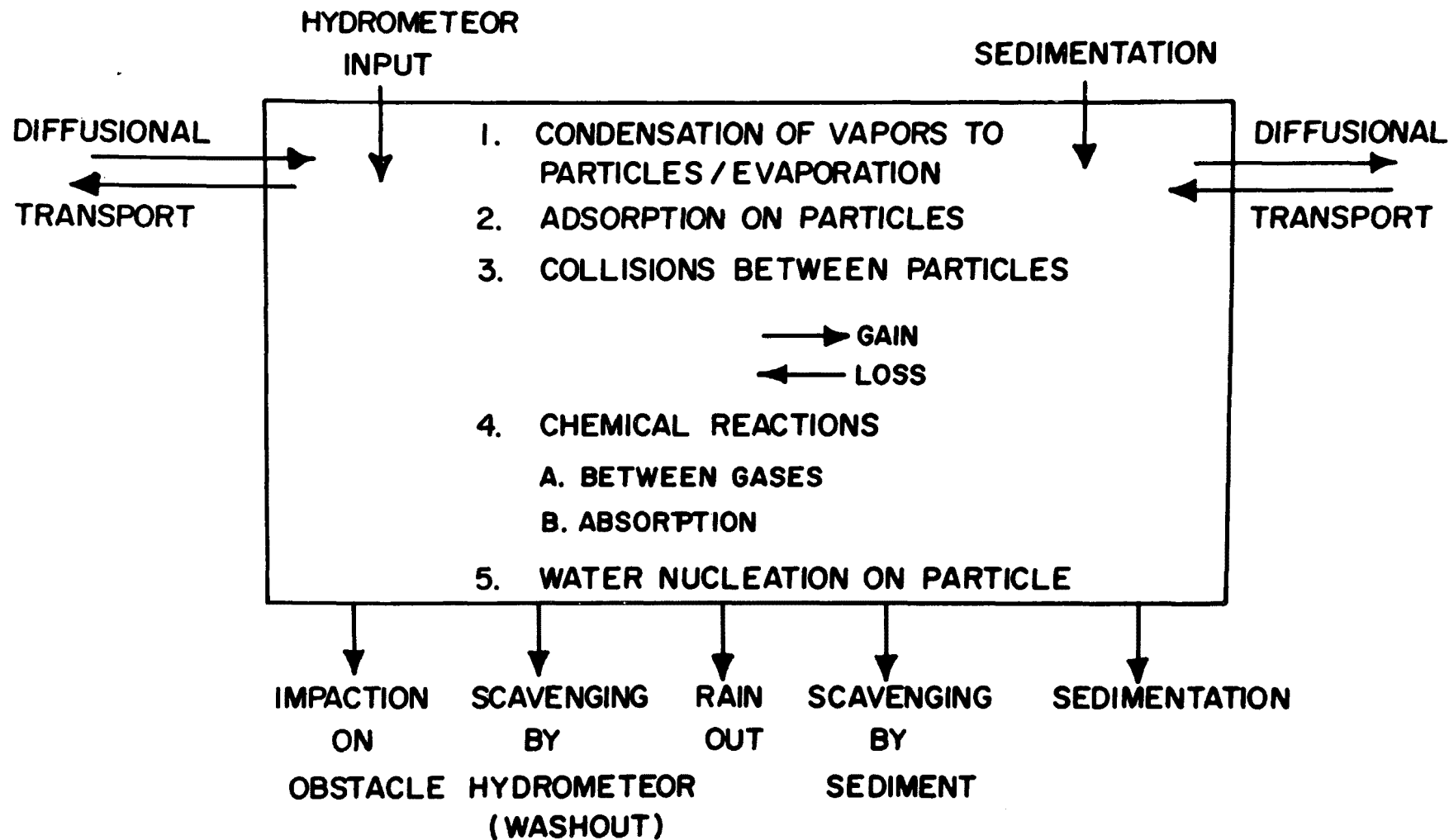


FIGURE 30. PROCESSES EFFECTING THE NUMBER OF AEROSOL (LIQUID AND SOLID) PARTICLES IN THE AIR COLUMN.

The contents of the precipitation chemistry samples is the sum of a number of processes operating above the sampling site. The sample chemistry represents the integration of nucleation, scavenging, dry deposition and impaction on the funnel. Gatz and Dingle⁶ have summed this up as "the sum of (1) individual changes within moving rain parcels, and (2) horizontal and vertical advection of concentration gradients in the three-dimensional rain field."

THE VARIATION OF CHEMISTRY WITHIN A STORM

One of the more interesting observations to come from the data is the range of concentrations of dissolved constituents within the precipitation of any storm. It is not unusual for pH to jump from 1 to 2 pH units representing a 10 to 100X increase/decrease in the hydrogen ion concentration of the rain. One storm, 22 March 1977 (Figure 13) has a 3-unit jump in pH, representing a 1000X increase in hydrogen ion concentration. Increases of 100X or more are not found in the anion analyses. It is not unusual for a change of 10 to 20X for sulfate or 5 to 10X for nitrate. The cations show a similar pattern with sodium and calcium varying 5 to 10X, magnesium 2 to 5X, and potassium and ammonium 1 to 2X.

The pH data show significant jumps in level over the relatively short period of minutes or fractions of minutes. The ion concentration data show differences in levels but there is not sufficient data to ascertain the rapidity of the changes.

INTENSITY AS A FACTOR IN PRECIPITATION CHEMISTRY

The sudden variations in rain water impurity concentrations from convective storms have been previously observed.⁶ These observations pertain mainly to particulates. The data presented in this paper extends the observations to frontal storms (See Appendix B) and deals mainly with dissolved constituents.

There appears to be a correlation between peaks in pH and intensity maxima. Regression and correlation analyses have been made using this data (contamination periods excluded) with pH as the dependent variable and intensity the independent variable. Correlation coefficients were surprisingly low. The pH was converted into hydrogen ion concentration and the coefficients improved slightly. This was difficult to understand. A second attempt was made using intensity and elapsed time as independent variables and pH as the dependent variable. Multivariate regression analysis yielded correlation coefficients in some cases of better than 0.7. Again using hydrogen ion concentrations rather than pH yielded correlation coefficients that were improved from 5 to 10 percent. This better fit can be explained by the nature of pH and hydrogen ion concentration - the first, pH, is a log function, while hydrogen ion concentration is linear.

Periods of high intensity precipitation, for example the 70 and 140 minute peaks of 20 Oct 76 (Figure 10), or the 2100 minute peak of 24-26 Jan 78 (Figure 24) have a marked effect on the precipitation chemistry. In almost every instance, pH jumps several tenths of a pH unit, indicating a lowering of the acidity. At the same time storms with additional chemical data show a drastic lowering of the concentration of the dissolved constituents (See the 2100 minute peak of Figure 24). This suggests confirmation of the first hypothesis that intensity is inversely proportional to the concentration of dissolved constituents. Due to the limited data available positive confirmation is not possible at this time.

THE ACIDITY OF PRECIPITATION

An effort was made to try to correlate the concentrations of dissolved constituents with the pH of the sample. Problems arise in the application of multiple linear regression techniques to the data. As mentioned previously, better regression coefficients are obtained if hydrogen ion concentration is used instead of pH. There is a high correlation between the concentrations of individual ionic species, a property called multi-collinearity. A data set exhibiting multi-collinearity cannot properly use the multiple linear regression technique because of violation of the underlying assumptions. Techniques exist to manipulate the data to reduce multi-collinearity²⁸. One successful manipulation involves conversion of nitrate and sulfate data from mg/l to microequivalents and adding them together to form a single dependent variable against either pH or pH converted to microequivalents of H^+ . The pH values produced are close to those expected for CO_2 gas in equilibrium with distilled water at the mean temperature during the storm. No tests were made to see that autocorrelation or heteroskedasticity assumptions are not violated.

EQUILIBRIUM OF PRECIPITATION WITH THE ATMOSPHERE

Distilled water in equilibrium with atmospheric CO_2 should have a pH in the range 5.6 to 5.75 depending on the atmospheric temperature. If acidic species dissolve in the rain, then the pH should be more acid (lower). One could expect then, that rain falling through an air mass containing acidic pollutants should produce early samples which are acidic. Subsequent samples should gradually show lower acidity as more and more pollutants are removed from the air mass. The pH of the sequential samples should gradually rise to an equilibrium value governed by the CO_2 water equilibrium. One storm, 17 October 1977 (Figure 23) shows such a relationship. As long as equilibrium is maintained one would not expect to find pH values above 5.75. There are many occurrences in the data of pH values of 6.0 or higher (e.g. 22 March 1977, Figure 13).

If disequilibrium is important, then the experimental techniques would not allow the values to be detected. Once collected the samples remain in open test tubes for several hours before capping and refrigeration. During this time one would expect CO_2 from the laboratory air to enter the solution and bring the sample to an equilibrium pH. As Galloway et al.²⁹ point out, CO_2 is more soluble in basic solutions and this would tend to bring a high pH solution toward the equilibrium 5.6-5.75 value. Acid solutions in the pH range 3 to 5 do not dissolve CO_2 and would therefore maintain a stable pH value. That pH values of six or more are found suggests that something other than disequilibrium is important.

Cooper et al.¹³ present data from Texas which shows pH values in the range 6.5 to above 7.0. They attribute this high pH to basic components in the rain, mainly calcium and magnesium. New York State has significant limestone and dolomite industries to the north of West Point at Kingston and to the south of West Point at Stony Point. As stated previously the predominant wind direction at West Point is from the north. Wind data are lacking for the period of data presented, but some calcium and magnesium data are available for 6-7 February 1978 (Figure 25) and 14-15 March 1978 (Figure 27). Definitive conclusions cannot be drawn from the data because of sparseness and dry deposition contamination.

THE SECTION 3 HYPOTHESES

Two of the hypotheses have been discussed indirectly to this point. There does appear to be an inverse relationship between concentration and intensity. Disequilibrium has pretty well been eliminated. The other hypotheses mentioned in Section 3 lack supporting or contradictory data. It is clear that chemical analyses must be performed on every sample, that dry deposition must be excluded, and that meteorological data are needed if the hypotheses are to be fully tested.

SECTION 8

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SECTION 9

APPENDICES

- A. Tabulations of Measured Concentrations
- B. Tabulation of Storm Information
- C. Interpretation of Periods of Contamination for the 22 Storms.
- D. Reagents Used for Standards

APPENDIX A

TABULATIONS OF MEASURED CONCENTRATIONS

In the following tables, pH, time between samples, and ion concentrations are all measured quantities. Elapsed time is calculated by summing the time between samples. Intensity is calculated from the time between samples and the number of millimeters of precipitation represented by the culture tube volume according to the following equation:

$$\text{Intensity} = \frac{\text{mm of precip} \times 60 \text{ min/hr}}{\text{Time between samples, min}}$$

Missing data indicate no measurement was made or measurement (sample) lost. A pH of 0.0 indicates either a lost sample or that an empty culture tube was in the rack at that position due to wind pressure triggering the siphon switch and advancing the tube rack. Using ion chromatography, the presence of ions will show as a peak at the proper retention time. The symbol BDL indicates that the analysis was below the established detection limit for the analyte.

Symbols in the remarks column indicate the contamination and cleansing periods detailed in Appendix C. Symbols used are:

X = Contamination

Cl= Cleansing

TABLE 3. INTENSITY AND pH OF RAINSTORM, 20 OCTOBER 1976

SAMPLE NUMBER	TIME BETWEEN (Min)	ELAPSED TIME (Min)	INTENSITY (mm/hr)	pH	REMARKS
1		0.0			
2	24.1	24.1	1.08	4.20	
3	12.2	36.3	2.12	3.95	
4	8.2	44.5	3.16	4.05	
5	4.7	49.2	5.51	3.95	
6	5.5	54.7	4.71	4.20	
7	6.5	61.2	3.99	4.48	
8	6.1	67.3	4.25	4.60	
9	2.3	69.6	11.27	4.50	
10	1.6	71.2	16.20	4.60	
11	6.1	77.3	4.25	4.45	
12	10.3	87.6	2.52	4.20	
13	4.3	91.9	6.03	4.15	
14	3.7	95.6	7.01	4.25	
15	4.7	100.3	5.51	4.25	
16	3.1	103.4	8.36	4.15	
17	3.4	106.8	7.62	4.20	
18	3.6	110.4	7.20	4.30	
19	2.3	112.7	11.27	4.15	
20	2.5	115.2	10.37	4.60	
21	3.0	118.2	8.64	4.60	
22	2.0	120.2	12.96	5.10	
23	2.2	122.4	11.78	5.00	
24	3.5	125.9	7.41	4.50	
25	2.7	128.6	9.60	5.00	
26	1.3	129.9	19.94	5.40	
27	2.1	132.0	12.34	5.60	
28	3.5	135.5	7.41	5.85	
29	2.2	137.7	11.78	5.40	
30	1.4	139.1	18.51	5.70	
31	2.3	141.4	11.27	5.00	
32	2.6	144.0	9.97	4.25	
33	7.8	151.8	3.32	4.40	
34	12.0	163.8	2.16	4.30	
35	20.4	184.2	1.27	4.10	
36	8.9	193.1	2.91	4.10	
37	9.6	202.7	2.70	4.00	
38	16.6	219.3	1.56	4.30	
39	6.0	225.3	4.32	4.30	
40	34.0	259.3	0.76		X

Continued

TABLE 3 Continued

SAMPLE NUMBER	TIME BETWEEN (Min)	ELAPSED TIME (Min)	INTENSITY (mm/hr)	pH	REMARKS
41	7.2	266.5	3.60	4.30	C1
42	5.9	272.4	4.39	4.15	C1
43	12.8	285.2	2.03	4.15	C1
44	6.5	291.7	3.99	4.30	C1
45	22.0	313.7	1.18	4.00	C1
46	20.7	334.4	1.25	4.20	C1
47	33.5	367.9	0.77	4.20	X

TABLE 4. INTENSITY AND pH OF RAINSTORM,
7 DECEMBER 1976

SAMPLE NUMBER	TIME BETWEEN (Min)	ELAPSED TIME (Min)	INTENSITY (mm/hr)	pH	REMARKS
1		0.0			
2	2.3	2.3	11.27	5.05	
3	3.6	5.9	7.20	4.85	
4	4.5	10.4	5.76	4.60	
5	4.4	14.8	5.89	4.75	
6	2.8	17.6	9.26	4.75	
7	1.8	19.4	14.40	4.83	
8	2.3	21.7	11.27	4.85	
9	2.9	24.6	8.94	4.85	
10	2.7	27.3	9.60	4.98	
11	2.3	29.6	11.27	5.10	
12	2.4	32.0	10.80	5.00	
13	2.5	34.5	10.37	4.55	
14	2.9	37.4	8.94	4.95	
15	2.3	39.7	11.27	4.85	
16	2.8	42.5	9.26	4.80	
17	2.1	44.6	12.34	5.30	
18	3.2	47.8	8.10	6.35	
19	3.0	50.8	8.64	4.80	
20	3.6	54.4	7.16	5.10	
21	3.8	58.2	6.82	5.10	
22	3.8	62.0	6.82	5.15	
23	3.1	65.1	8.31	5.30	
24	2.6	67.7	9.89	5.75	
25	3.0	70.7	8.64	5.73	
26	2.0	72.7	12.96	5.70	
27	2.5	75.2	10.37	5.85	
28	2.4	77.7	10.62	6.05	
29	1.9	79.5	13.86	6.10	
30	2.3	81.8	11.27	6.30	
31	2.2	84.0	11.52	6.20	
32	2.9	87.0	8.82	5.80	
33	3.3	90.3	7.83	5.85	
34	3.4	93.7	7.53	5.90	
35	7.8	101.5	3.34	6.15	
36	8.4	109.9	3.07	6.05	
37	15.9	125.9	1.63	5.20	
38	2.7	128.5	9.64	5.45	
39	1.8	130.3	14.81	5.40	
40	19.8	150.0	1.31	5.40	

Continued

TABLE 4 Continued

SAMPLE NUMBER	TIME BETWEEN (Min)	ELAPSED TIME (Min)	INTENSITY (mm/hr)	pH	REMARKS
41	21.0	171.0	1.23	5.20	
42	11.3	182.3	2.30	5.05	
43	10.7	193.0	2.42	5.90	
44	18.9	211.9	1.37	5.40	
45	40.8	252.6	0.64	5.20	X
46	32.6	285.2	0.79	5.20	X
47		285.2		5.40	

TABLE 5. INTENSITY AND pH OF SNOW FOLLOWED BY RAIN, 17-18 MARCH 1977

SAMPLE NUMBER	TIME BETWEEN (Min)	ELAPSED TIME (Min)	INTENSITY (mm/hr)	pH	REMARKS
1					
2		0.0		4.30	
3	5.0	5.0	5.18	4.20	
4	9.2	14.2	2.82	4.30	
5	5.8	20.0	4.47	4.20	
6	5.0	25.0	5.18	4.20	
7	5.1	30.1	5.08	4.25	
8	4.9	35.0	5.29	4.30	
9	6.5	41.5	3.99	4.35	
10	3.5	45.0	7.41	4.40	
11	4.6	49.6	5.63	4.30	
12	5.2	54.8	4.98	4.30	
13	5.0	59.8	5.18	4.35	
14	6.7	66.5	3.87	4.40	
15	3.5	70.0	7.41	4.35	
16	6.7	76.7	3.87	4.25	
17	4.7	81.4	5.51	4.32	
18	6.0	87.4	4.32	4.35	
19	6.5	93.9	3.99	4.35	
20	6.0	99.9	4.32	4.40	
21	8.0	107.9	3.24	4.45	
22	5.0	112.9	5.18	4.45	
23	5.3	118.2	4.89	4.50	
24	4.5	122.7	5.76	4.50	
25	4.5	127.2	5.76	4.45	
26	5.0	132.2	5.18	4.35	
27	5.3	137.5	4.89	4.30	
28	4.3	141.8	6.03	4.30	
29	4.7	146.5	5.51	4.35	
30	5.5	152.0	4.71	4.20	
31	5.1	157.1	5.08	4.30	
32	6.4	163.5	4.05	4.20	
33	5.8	169.3	4.47	4.25	
34	7.0	176.3	3.70	4.25	
35	7.1	183.4	3.65	4.30	
36	10.8	194.2	2.40	4.30	
37	16.0	210.2	1.62	4.30	
38	61.3	271.5	0.42	4.20	X
39	6.0	277.5	4.32	4.10	C1
40	1.7	279.2	15.25	4.20	C1

Continued

TABLE 5 Continued

SAMPLE NUMBER	TIME BETWEEN (Min)	ELAPSED TIME (Min)	INTENSITY (mm/hr)	pH	REMARKS
41	3.1	282.3	8.36	3.90	C1
42	3.7	286.0	7.01	4.30	C1
43	2.3	288.3	11.27	4.55	
44	2.7	291.0	9.60	4.40	
45	3.5	294.5	7.41	4.30	
46	5.9	300.4	4.39	4.30	
47	45.2	345.6	0.57	4.30	X
48	15.0	360.6	1.73	4.05	C1
49	22.6	383.2	1.15	4.35	C1
50	19.3	402.5	1.34	4.30	C1
51	15.6	418.1	1.66	4.20	C1
52	14.0	432.1	1.85	4.10	C1
53	14.2	446.3	1.83	4.00	C1
54	18.5	464.8	1.40	4.00	C1

TABLE 6. INTENSITY, pH, AND CHEMISTRY OF SELECTED SAMPLES
RAINSTORM, 22 MAR 1977

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	IONS (mg/l)		NH ₃ -N	REMARKS
					NO ₃ ⁻ -N	SO ₄ ⁻²		
1		0.0						
2	32.0	32.0	0.81	4.40				X
3	15.6	47.6	1.66	4.40				C1
4	10.9	58.5	2.38	4.60				C1
5	6.0	64.5	4.32	4.70				C1
6	8.0	72.5	3.24	4.55		3		C1
7	5.4	77.9	4.80	4.00		3		C1
8	4.7	82.6	5.51	4.60		3		C1
9	5.3	87.9	4.89	4.50				C1
10	6.7	94.6	3.87	4.62				C1
11	6.9	101.5	3.76	4.10				
12	4.4	105.9	5.89	4.35			0.08	
13	4.5	110.4	5.76	5.30			0.08	
14	3.0	113.4	8.64	5.60			0.08	
15	3.9	117.3	6.65	4.38	0.3			
16	4.0	121.3	6.48	5.10	0.3			
17	4.7	126.0	5.51	5.50	0.3			
18	6.0	132.0	4.32	5.80				
19	6.3	138.3	4.11	5.32				
20	5.0	143.3	5.18	5.80				
21	5.0	148.3	5.18	5.30				
22	3.5	151.8	7.41	5.90				
23	5.2	157.0	4.98	5.00				
24	6.0	163.0	4.32	5.20				
25	6.0	169.0	4.32	4.90				
26	2.4	171.4	10.80	5.25				
27	6.0	177.4	4.32	5.40				
28	6.5	183.9	3.99	5.90				
29	4.0	187.9	6.48	4.95				
30	3.0	190.9	8.64	4.90				

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Continued

TABLE 6 Continued

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	IONS (mg/l)		NH ₃ -N	REMARKS
					NO ₃ ⁻ -N	SO ₄ ⁻²		
31	4.0	194.9	6.48	5.20				
32	5.5	200.4	4.71	5.80				
33	6.0	206.4	4.32	5.95				
34	5.1	211.5	5.08	5.90				
35	5.2	216.7	4.98	5.30				
36	5.2	221.9	4.98	5.48				
37	5.5	227.4	4.71	6.02				
38	5.2	232.6	4.98	5.84				
39	3.0	235.6	8.64	6.00				
40	3.0	238.6	8.64	5.60				
41	3.0	241.6	8.64	5.35				
42	3.2	244.8	8.10	6.60				
43	3.0	247.8	8.64	6.55				
44	3.1	250.9	8.36	5.70				
45	5.0	255.9	5.18	4.90				
46	6.0	261.9	4.32	4.60				
47	4.5	266.4	5.76	4.43				
48	3.8	270.2	6.82	6.07				
49	3.7	273.9	7.01	6.20				
50	2.6	276.5	9.97	6.30				
51	3.0	279.5	8.64	6.35				
52	2.6	282.1	9.97	6.10				
53	3.0	285.1	8.64	6.40				
54	2.5	287.6	10.37	5.65				
55	3.0	290.6	8.64	6.21				
56	2.7	293.3	9.60	6.40				
57	2.0	295.3	12.96	6.60				
58	2.3	297.6	11.27	6.15				
59	1.5	299.1	17.28	6.48				
60	1.3	300.4	19.94	7.30				

Continued

TABLE 6 Continued

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	IONS (mg/l)		NH ₃ -N	REMARKS
					NO ₃ ⁻ -N	SO ₄ ⁻²		
61	2.5	302.9	10.37	6.85				
62	1.7	304.6	15.25	6.85				
63	1.5	306.1	17.28	6.55				
64	1.5	307.6	17.28	6.65				
65	3.5	311.1	7.41	6.75				
66	5.5	316.6	4.71	6.62				
67	2.5	319.1	10.37	6.55				
68	5.5	324.6	4.71	6.00				
69	1.5	326.1	17.28	6.42				
70	2.0	328.1	12.96	6.65				
71	3.4	331.5	7.62	6.54				
72	5.0	336.5	5.18	6.60				
73	4.7	341.2	5.51	6.70				
74	3.8	345.0	6.82	6.47				
75	3.5	348.5	7.41	6.35				
76	4.0	352.5	6.48	6.30				
77	2.7	355.2	9.60	6.30				
78	9.5	364.7	2.73	6.20				
79	2.7	367.4	9.60	6.25				
80	3.0	370.4	8.64	6.62				
81	1.0	371.4	25.92	6.46				
82	1.5	372.9	17.28	6.60				
83	2.5	375.4	10.37	6.50				
84	3.6	379.0	7.20	6.75				
85	1.7	380.7	15.25	6.75				
86	2.3	383.0	11.27	6.60				
87	1.5	384.5	17.28	6.68				
88	1.0	385.5	25.92	6.73				
89	3.7	389.2	7.01	6.73				
90	7.3	396.5	3.55	6.80				

Continued

TABLE 6 Continued

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	IONS (mg/l)		NH ₃ -N	REMARKS
					NO ₃ ⁻ -N	SO ₄ ⁻²		
91	2.2	398.7	11.78	6.60				
92	3.7	402.4	7.01	6.90				
93	2.3	404.7	11.27	6.60				
94	1.2	405.9	21.60	6.50				
95	1.5	407.4	17.28	6.60				
96	2.0	409.4	12.96	6.70				
97	2.3	411.7	11.27	6.60				
98	3.2	414.9	8.10	6.90				
99	5.0	419.9	5.18	6.50				
100	5.0	424.9	5.18	6.50				
101	6.2	431.1	4.18	6.60				
102	4.3	435.4	6.03	6.40				
103	7.5	442.9	3.46	6.40				
104	5.2	448.1	4.98	6.40				
105	4.0	452.1	6.48	6.80				
106	4.0	456.1	6.48	6.50				
107	5.7	461.8	4.55	6.40				
108	13.8	475.6	1.88	6.30				
109	11.5	487.1	2.25	6.30				
110	27.6	514.7	0.94	6.20				X
111	16.0	530.7	1.62	6.20				C1
112	7.0	537.7	3.70	6.20				C1
113	7.0	544.7	3.70	5.90				C1
114	9.7	554.4	2.67	5.70				C1
115	10.5	564.9	2.47	5.60				C1
116	9.6	574.5	2.70	5.20				C1
117	6.5	581.0	3.99	4.90				C1
118	7.5	588.5	3.46	4.50				C1
119	10.2	598.7	2.54	4.50				
120	8.5	607.2	3.05	4.90				

Continued

TABLE 6 Continued

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	IONS (mg/l)		NH ₃ -N	REMARKS
					NO ₃ ⁻ -N	SO ₄ ⁻²		
121	9.0	616.2	2.88	5.40				
122	8.0	624.2	3.24	5.90				
123	8.6	632.8	3.01	5.80				
124	9.5	642.3	2.73	5.70				
125	9.3	651.6	2.79	5.80				
126	6.5	658.1	3.99	5.63				
127	6.0	664.1	4.32	5.80				
128	5.7	669.8	4.55	6.10				
129	5.0	674.8	5.18	6.05				
130	5.1	679.9	5.08	6.00				
131	5.0	684.9	5.18	6.05				
132	6.4	691.3	4.05	6.02				
133	7.3	698.6	3.55	6.00				
134	6.0	704.6	4.32	6.05	0.2			
135	7.5	712.1	3.46	6.10	0.2			
136	10.7	722.8	2.42	6.10	0.2			
137	12.5	735.3	2.07	6.00			0.06	
138	29.5	764.8	0.88	6.30			0.06	X
139	31.5	796.3	0.82	6.20			0.06	X
140	54.0	850.3	0.48	6.10				X
141	34.0	884.3	0.76	6.30				X
142	53.0	937.3	0.49	6.30				X
143	172.5	1109.8	0.15	6.41				X
144	50.5	1160.3	0.51	6.50		BDL		X
145	53.0	1213.3	0.49	6.45		BDL		X
146	43.0	1256.3	0.60	6.30		BDL		X

TABLE 7. INTENSITY, pH, AND CHEMISTRY OF SELECTED SAMPLES
RAINSTORM, 28 MARCH 1977

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	IONS (mg/l)		NH ₃ -N	REMARKS
					NO ₃ ⁻ -N	SO ₄ ⁻²		
1		0.0						
2	7.5	7.5	3.46	4.70		5.0		
3	7.2	14.7	3.60	4.58		5.0		
4	8.7	23.4	2.98	4.50			0.6	
5	9.0	32.4	2.88	4.42			0.6	
6	8.0	40.4	3.24	4.40			0.6	
7	8.0	48.4	3.24	4.28	0.7			
8	13.5	61.9	1.92	4.13	0.7			
9	14.5	76.4	1.79	4.13	0.7			
10	16.5	92.9	1.57	4.80	0.7			
11	24.0	116.9	1.08	3.80				
12	34.0	150.9	0.76	3.87				X
13	31.0	181.9	0.84	3.90	1.0			X
14	12.3	194.2	2.11	3.90	1.0			Cl
15	9.5	203.7	2.73	3.90	1.0			Cl
16	13.0	216.7	1.99	3.90	1.0			Cl
17	8.5	225.2	3.05	3.94			1.5	Cl
18	21.0	246.2	1.23	3.80			1.5	Cl
19	33.0	279.2	0.79	3.68			1.5	X
20	17.5	296.7	1.48	3.80		11.0		Cl
21	26.5	323.2	0.98	3.60		11.0		X
22	31.0	354.2	0.84	3.70		11.0		X

TABLE 8. INTENSITY, pH, AND CHEMISTRY OF SELECTED SAMPLES
RAINSTORM, 4-6 APRIL 1977

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	IONS (mg/l)		NH ₃ -N	REMARKS
					NO ₃ ⁻ -N	SO ₄ ⁻²		
1		0.0						
2	34.5	34.5	0.75	3.79				X
3	10.3	44.8	2.52	4.10				C1
4	10.2	55.0	2.54	4.00				C1
5	23.0	78.0	1.13	3.99		7.0		C1
6	8.6	86.6	3.01	4.12		7.0		C1
7	7.8	94.4	3.32	4.22		7.0		C1
8	8.0	102.4	3.24	4.23	1.0			C1
9	9.5	111.9	2.73	3.81	1.0			C1
10	5.5	117.4	4.71	4.21	1.0			C1
11	4.0	121.4	6.48	3.90				
12	5.0	126.4	5.18	4.10				
13	6.5	132.9	3.99	4.10				
14	7.5	140.4	3.46	4.60				
15	8.3	148.7	3.12	4.90				
16	6.2	154.9	4.18	4.91				
17	4.0	158.9	6.48	4.40			0.12	
18	4.5	163.4	5.76	3.81			0.12	
19	8.0	171.4	3.24	4.40			0.12	
20	8.0	179.4	3.24	4.48				
21	9.3	188.7	2.79	4.50				
22	14.0	202.7	1.85	4.33				
23	26.0	228.7	1.00	4.15				
24	15.0	243.7	1.73	4.22				
25	5.0	248.7	5.18	4.60				
26	6.5	255.2	3.99	4.99				
27	13.5	268.7	1.92	4.58				
28	6.6	275.3	3.93	4.90				
29	8.3	283.6	3.12	5.35				
30	7.0	290.6	3.70	5.44				

Continued

TABLE 8 Continued

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	IONS (mg/l)		NH ₃ -N	REMARKS
					NO ₃ ⁻ -N	SO ₄ ⁻²		
31	4.7	295.3	5.51	5.63				
32	6.4	301.7	4.05	5.75				
33	8.0	309.7	3.24	5.50				
34	4.0	313.7	6.48	5.59				
35	4.0	317.7	6.48	5.58				
36	6.0	323.7	4.32	5.58				
37	3.2	326.9	8.10	5.77				
38	6.3	333.2	4.11	5.80				
39	2.3	335.5	11.27	5.50				
40	2.3	337.8	11.27	5.38				
41	1.2	339.0	21.60	4.90				
42	1.5	340.5	17.28	5.65				
43	2.0	342.5	12.96	5.60				
44	2.5	345.0	10.37	4.31				
45	3.0	348.0	8.64	4.50				
46	2.0	350.0	12.96	4.00				
47	2.6	352.6	9.97	3.95	0.7			
48	2.7	355.3	9.60	3.90	0.7			
49	3.0	358.3	8.64	4.60	0.7			
50	2.5	360.8	10.37	5.30				
51	3.0	363.8	8.64	5.20				
52	2.5	366.3	10.37	4.75				
53	3.5	369.8	7.41	4.13				
54	3.5	373.3	7.41	3.98				
55	3.0	376.3	8.64	4.10				
56	4.5	380.8	5.76	4.10				
57	40.5	421.3	0.64	4.30				X
58	17.0	438.3	1.52	4.42				C1
59	96.5	534.8	0.27	4.60				X
60	22.5	557.3	1.15	3.98				C1

Continued

TABLE 8 Continued

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	IONS (mg/l)		NH ₃ -N	REMARKS
					NO ₃ ⁻ -N	SO ₄ ⁻²		
61	15.0	572.3	1.73	4.30				C1
62	6.6	578.9	3.93	4.50				C1
63	74.6	653.5	0.35	4.48			0.39	X
64	50.0	703.5	0.52	4.50			0.39	X
65	42.5	746.0	0.61	4.58			0.39	X
66	47.7	793.7	0.54					X
67	35.7	829.4	0.73	4.97				X
68	1.5	830.9	17.28	5.75				C1
69	2.0	832.9	12.96	6.68				C1
70	1.5	834.4	17.28	5.30				C1
71	5.5	839.9	4.71	5.02				C1
72	6.6	846.5	3.93	4.72				C1
73	51.5	898.0	0.50	4.40				X
74	50.5	948.5	0.51	4.30				X
75	20.5	969.0	1.26	4.12				C1
76	18.0	987.0	1.44	4.18				C1
77	8.6	995.6	3.01	4.18				C1
78	11.0	1006.6	2.36	4.00				C1
79	42.5	1049.1	0.61	3.90				X
80	11.0	1060.1	2.36	4.00				C1
81	21.3	1081.4	1.22	3.95				C1
82	53.5	1134.9	0.48					X
83	255.5	1390.4	0.10	3.89		6.5		X
84	3.5	1393.9	7.41	4.18		6.5		C1
85	1.6	1395.5	16.20	4.42		6.5		C1
86	2.3	1397.8	11.27	4.40				C1
87	16.0	1413.8	1.62					C1

TABLE 9. INTENSITY, pH, AND CHEMISTRY OF SELECTED SAMPLES
RAINSTORM, 23-24 APRIL 1977

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	IONS (mg/l)		NH ₃ -N	REMARKS
					NO ₃ ⁻ -N	SO ₄ ⁻²		
1		0.0						
2	3.2	3.2	8.10	4.00				
3	5.0	8.2	5.18	4.22		12		
4	59.8	68.0	0.43	4.14		12		X
5	93.7	161.7	0.28	3.70		12		X
6	90.7	252.4	0.29					X
7	6.2	258.6	4.18	3.48			>2.0	C1
8	5.8	264.4	4.47	3.53			>2.0	C1
9	4.5	268.9	5.76	3.51			>2.0	C1
10	6.6	275.5	3.93	3.50	2.5			C1
11	193.0	468.5	0.13	3.61	2.5			X
12	25.9	494.4	1.00	3.60	2.5			C1
13	9.6	504.0	2.70	3.74			2.0	C1
14	3.2	507.2	8.10	3.75			2.0	C1
15	1.8	509.0	14.40	4.10			2.0	C1
16	2.3	511.3	11.27	4.23				
17	2.0	513.3	12.96	4.32				
18	1.3	514.6	19.94	4.30				
19	3.2	517.8	8.10	4.30				
20	16.6	534.4	1.56	4.25				
21	4.7	539.1	5.51	4.10				
22	3.6	542.7	7.20	4.37				
23	4.9	547.6	5.29	4.48				
24	2.1	549.7	12.34	4.30				
25	8.2	557.9	3.16	4.30				
26	21.9	579.8	1.18	4.20				
27	1.1	580.9	23.56	4.00				
28	0.6	581.5	43.20	4.20				
29	0.8	582.3	32.40	4.00				
30	46.8	629.1	0.55	3.91				X

Continued

TABLE 9 Continued

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	IONS (mg/l)		NH ₃ -N	REMARKS
					NO ₃ ⁻ -N	SO ₄ ⁻²		
31	5.4	634.5	4.80	3.84				C1
32	1.7	636.2	15.25	3.98				C1
33	1.3	637.5	19.94	4.36				C1
34	0.7	638.2	37.03	4.58				
35	0.9	639.1	28.80	4.65				
36	1.0	640.1	25.92	4.60				
37	2.8	642.9	9.26	4.67				
38	9.2	652.1	2.82	4.40				
39	2.7	654.8	9.60	4.07				
40	5.2	660.0	4.98	4.01				
41	3.7	663.7	7.01	4.20				
42	72.4	736.1	0.36	3.60				X
43	81.8	817.9	0.32	3.68				X

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Storm continued for several hours. Time data lost due to recorder malfunction.

TABLE 10. INTENSITY, pH, AND CHEMISTRY OF SELECTED SAMPLES
RAINSTORM, 2 JUNE 1977

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	IONS (mg/l)		NH ₃ -N	REMARKS
					NO ₃ ⁻ -N	SO ₄ ⁻²		
1		0.0						
2	9.7	9.7	2.67	3.60				
3	3.9	13.6	6.65	3.70		12		
4	5.2	18.8	4.98	3.43		12		
5	4.1	22.9	6.32	3.65		12		
6	1.8	24.7	14.40	3.80			0.7	
7	2.6	27.3	9.97	3.86			0.7	
8	3.0	30.3	8.64	3.70			0.7	
9	10.7	41.0	2.42	4.00	0.85			
10	1.8	42.8	14.40	4.20	0.85			
11	1.9	44.7	13.64	4.30	0.85			
12	21.6	66.3	1.20	4.15				
13	5.4	71.7	4.80	3.88				
14	3.2	74.9	8.10	3.92				
15	17.0	91.9	1.52	3.99				
16	28.7	120.6	0.90	4.05				X
17	14.2	134.8	1.83	4.04				C1
18	0.2	135.0	129.60	3.98				C1
19	0.6	135.6	43.20	3.66				C1
20	0.7	136.3	37.03	3.63				
21	1.1	137.4	23.56	3.46				
22	31.4	168.8	0.83	3.82		7		X
23	0.6	169.4	43.20	4.00		7		C1
24	0.7	170.1	37.03	3.95		7		C1
25	1.3	171.4	19.94	3.87			0.9	C1
26	2.1	173.5	12.34	3.65			0.9	C1
27	9.0	182.5	2.88	3.73			0.9	
28	1.7	184.2	15.25	3.82	1.73			
29	17.0	201.2	1.52	4.09	1.73			
30	37.7	238.9	0.69	4.03	1.73			X

Continued

TABLE 10 Continued

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	IONS (mg/l)		NH ₃ -N	REMARKS
					NO ₃ ⁻ -N	SO ₄ ⁻²		
31	2.2	241.1	11.78	3.93				C1
32	46.5	287.6	0.56	4.32				X
33	2.2	289.8	11.78	4.93				C1
34	5.1	294.9	5.08	5.08				C1
35	6.8	301.7	3.81	5.00		2		C1
36	12.4	314.1	2.09	5.12		2		C1
37	2.8	316.9	9.26	4.52		2		C1
38	1.3	318.2	19.94	3.98			0.7	C1
39	0.7	318.9	37.03	3.78			0.7	C1
40	0.9	319.8	28.80	3.18			0.7	
41	0.8	320.6	32.40	3.36	1.15			
42	3.7	324.3	7.01	3.50	1.15			
43	16.5	340.8	1.57	3.66	1.15			

TABLE 11. INTENSITY, pH, AND CHEMISTRY OF SELECTED SAMPLES
RAINSTORM, 7 JUNE 1977

SAMPLE NUMBER	TIME BETWEEN (Min)	ELAPSED TIME (Min)	INTENSITY (mm/hr)	pH	REMARKS
1		0.0			
2	25.6	25.6	1.01	4.63	
3	22.4	48.0	1.16	3.52	
4	298.2	346.2	0.09	3.08	X
5	47.2	393.4	0.55	3.16	X
6	8.0	401.4	3.24	3.69	C1
7	8.1	409.5	3.20	3.80	C1
8	8.2	417.7	3.16	3.70	C1
9	10.0	427.7	2.59	3.86	C1
10	19.3	447.0	1.34	3.60	C1
11	69.0	516.0	0.38	3.40	X
12	39.4	555.4	0.66	3.46	X
13	29.4	584.8	0.88	3.30	X
14	32.7	617.5	0.79	3.40	X
15	103.9	721.4	0.25	3.30	X
16	53.5	774.9	0.48	3.00	X

TABLE 12. INTENSITY, pH, AND CHEMISTRY OF SELECTED SAMPLES
RAINSTORM, 18 AUG 1977

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	IONS (mg/l)		NH ₃ -N	REMARKS
					NO ₃ ⁻ -N	SO ₄ ⁻²		
1		0.0						
2	7.5	7.5	3.46	5.00		5.0		
3	3.7	11.2	7.01	4.73		5.0		
4	2.8	14.0	9.26	4.80		5.0		
5	3.7	17.7	7.01	4.80	0.7			
6	3.5	21.2	7.41	4.98	0.7			
7	3.2	24.4	8.10		0.7			
8	68.0	92.4	0.38	5.05			0.9	X
9	3.2	95.6	8.10	4.41			0.9	C1
10	2.2	97.8	11.78	4.41			0.9	C1
11	34.5	132.3	0.75	4.28				X
12	2.6	134.9	9.97	4.50				C1
13	1.5	136.4	17.28	4.72				C1
14	0.8	137.2	32.40	4.95				C1
15	0.6	137.8	43.20	4.95		2.0		
16	0.8	138.6	32.40	5.20		2.0		
17	0.3	138.9	86.40	5.20		2.0		
18	0.2	139.1	129.60	5.50	0.4			
19	0.2	139.3	129.60	5.31	0.4			
20	0.2	139.5	129.60	5.50	0.4			
21	0.3	139.8	86.40	5.45			0.25	
22	0.4	140.1	64.80	5.45			0.25	
23	0.9	141.0	28.80	5.43			0.25	
24	1.5	142.5	17.28	5.28		2.5		
25	1.8	144.3	14.40	5.20		2.5		
26	2.0	146.3	12.96	5.05		2.5		
27	2.8	149.1	9.26	5.00				
28	0.9	150.0	28.80	5.20	0.5			
29	0.8	150.8	32.40	5.22	0.5			
30	1.0	151.8	25.92	5.10	0.5			

Continued

TABLE 12 Continued

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	IONS (mg/l)		NH ₃ -N	REMARKS
					NO ₃ ⁻ -N	SO ₄ ⁻²		
31	1.6	153.4	16.20	5.09			0.3	
32	3.9	157.3	6.65	4.97			0.3	
33	4.7	162.0	5.51	4.80			0.3	
34	13.5	175.5	1.92	4.46				

TABLE 13. INTENSITY, pH, AND CHEMISTRY OF SELECTED SAMPLES
RAINSTORM, 16-17 SEPT 1977

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	IONS (mg/l)		REMARKS
					NO ₃	SO ₄ ⁻²	
1		0.0					
2	74.0	74.0	0.35	3.40	12.2	34.3	X
3	112.0	186.0	0.23	3.66			X
4	106.0	292.0	0.24	3.71			X
5	56.0	348.0	0.46	4.28			X
6	42.0	390.0	0.62	4.24	0.87	5.20	X
7	1.6	391.6	16.20	4.20			C1
8	1.6	393.2	16.20	3.90			C1
9	1.6	394.8	16.20	3.52	3.68	12.1	C1
10	4.0	398.8	6.48	3.73			C1
11	32.5	431.3	0.80	4.19			X
12	12.0	443.3	2.16	4.20			C1
13	5.4	448.7	4.80	3.97			C1
14	9.0	457.7	2.88	4.09			C1
15	7.8	465.5	3.32	4.46	3.04	8.09	C1
16	8.2	473.7	3.16	3.90			C1
17	2.0	475.7	12.96	3.80	1.49	10.86	C1
18	2.8	478.5	9.26	3.87			
19	6.6	485.1	3.93	3.91			
20	4.2	489.3	6.17	4.32			
21	3.0	492.3	8.64	4.14			
22	2.4	494.7	10.80	3.70			
23	2.9	497.6	8.94	4.09			
24	2.3	499.9	11.27	4.22			
25	1.0	500.9	25.92	3.99	0.49	6.89	
26	0.8	501.7	32.40	4.01			
27	1.0	502.7	25.92	4.43			
28	3.0	505.7	8.64	4.40			
29	2.4	508.1	10.80	3.99			
30	3.2	511.3	8.10	4.78	0.36	1.63	
31	3.0	514.3	8.64	4.41			
32	1.4	515.7	18.51	3.90			
33	2.0	517.7	12.96	3.98			
34	3.0	520.7	8.64	3.89			
35	4.6	525.3	5.63	4.30	0.61	3.57	
36	5.0	530.3	5.18	4.20			
37	7.0	537.3	3.70	4.17			
38	6.8	544.1	3.81	4.18			
39	6.0	550.1	4.32	4.40			
40	7.8	557.9	3.32	3.99			

Continued

TABLE 13 Continued

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED		INTENSITY (mm/hr)	pH	IONS (mg/l)		REMARKS
		TIME	TIME			NO ₃ ⁻	SO ₄ ⁻²	
41	10.0	567.9	2.59	4.20				
42	17.0	584.9	1.52	4.00	2.12		3.34	
43	17.6	602.5	1.47	4.30				
44	22.0	624.5	1.18	4.40	1.79		3.48	
45	20.0	644.5	1.30	4.21				
46	16.0	660.5	1.62	4.25				
47	21.0	681.5	1.23	4.28				
48	55.0	736.5	0.47	4.35				X
49	17.0	753.5	1.52	4.43				C1
50	22.6	776.1	1.15	4.29	2.40		2.55	C1
51	17.0	793.1	1.52	4.20				C1
52	21.0	814.1	1.23	3.82	5.37		6.64	C1

TABLE 14. INTENSITY AND pH OF RAINSTORM,
18 SEPT 1977

SAMPLE NUMBER	TIME BETWEEN (Min)	ELAPSED TIME (Min)	INTENSITY (mm/hr)	pH	REMARKS
1		0.0			
2	75.0	75.0	0.35	4.90	X
3	608.0	683.0	0.04	3.70	X
4	11.0	694.0	2.36	3.70	C1
5	2.4	696.4	10.80	3.60	C1
6	1.8	698.2	14.40	3.90	C1
7	5.8	704.0	4.47	3.85	
8	6.6	710.6	3.93	3.70	
9	4.0	714.6	6.48	3.90	
10	3.6	718.2	7.20	3.80	
11	5.0	723.2	5.18	3.85	
12	6.2	729.4	4.18	4.10	
13	6.6	736.0	3.93	3.90	
14	11.0	747.0	2.36	3.70	

TABLE 15. INTENSITY, pH, AND CHEMISTRY OF SELECTED SAMPLES
RAINSTORM, 24-26 SEPT 1977

SAMPLE NUMBER	TIME BETWEEN (min)	TIME ELAPSED		INTENSITY (mm/hr)	pH	IONS (mg/l)		REMARKS
						NO ₃ ⁻	SO ₄ ⁻²	
1	0.0	0.0						
2	0.0	0.0		3.25	24.9	61.6		
3	6.2	6.2	4.18	3.35				
4	4.8	11.0	5.40	3.60	9.25	7.59		
5	4.0	15.0	6.48	3.82				
6	6.3	21.3	4.11	3.95				
7	45.0	66.3	0.58	3.99	2.78	3.89		X
8	5.8	72.1	4.47	3.70				C1
9	6.9	79.0	3.76	3.70				C1
10	7.9	86.9	3.28	3.55	9.36	7.87		C1
11	11.8	98.7	2.20	3.60				C1
12	6.7	105.4	3.87	3.65				C1
13	3.0	108.4	8.64	3.75				C1
14	3.7	112.1	7.01	3.85				
15	5.0	117.1	5.18	3.75				
16	6.3	123.4	4.11	3.95				
17	5.2	128.6	4.98	4.00				
18	6.8	135.4	3.81	4.10	1.92	2.76		
19	13.2	148.6	1.96	4.00				
20	12.6	161.2	2.06	3.80				
21	32.7	193.9	0.79	3.80				X
22	14.7	208.6	1.76	3.80				C1
23	9.9	218.5	2.62	3.70				C1
24	8.3	226.8	3.12	3.80				C1
25	9.6	236.4	2.70	3.90				C1
26	20.4	256.8	1.27	3.80	4.85	5.03		C1
27	8.0	264.8	3.24	3.65				C1
28	3.0	267.8	8.64	3.80				C1
29	3.3	271.1	7.85	3.70				
30	4.4	275.5	5.89	3.75				
31	7.3	282.8	3.55	3.70				
32	11.4	294.2	2.27	3.70				
33	10.3	304.5	2.52	3.70				
34	16.4	320.9	1.58	3.80				
35	12.0	332.9	2.16	3.80				
36	12.6	345.5	2.05	3.80	3.99	5.60		
37	5.5	351.0	4.71	3.72				
38	3.0	354.0	8.64	3.70				
39	3.5	357.5	7.41	3.80				
40	3.4	360.9	7.62	3.65				

Continued

TABLE 15 Continued

SAMPLE NUMBER	TIME BETWEEN (min)	TIME ELAPSED		INTENSITY (mm/hr)	pH	IONS (mg/l)		REMARKS
		(min)	(min)			NO ₃ ⁻	SO ₄ ⁻²	
41	32.8		393.7	0.79	3.70			X
42	30.6		424.3	0.85	3.60			X
43	15.0		439.3	1.73	3.50			C1
44	9.2		448.5	2.82	3.60			C1
45	4.0		452.5	6.48	3.65			C1
46	27.3		479.8	0.95	3.75	2.65	6.02	X
47	10.4		490.2	2.49	3.70			C1
48	28.2		518.4	0.92	3.90	2.78	3.89	X
49	360.0		878.4	0.07	3.75			X
50	17.0		895.4	1.52	3.20	16.67	32.76	C1
51	21.6		917.0	1.20	3.45			C1
52	13.2		930.2	1.96	3.60			C1
53	8.0		938.2	3.24	3.75			C1
54	9.0		947.2	2.88	3.75			C1
55	11.8		959.0	2.20	3.65	2.29	9.44	C1
56	27.7		986.7	0.94	3.70			X
57	16.0		1002.7	1.62	3.55			C1
58	6.9		1009.6	3.76	3.55			C1
59	3.8		1013.4	6.82	3.65			C1
60	10.5		1023.9	2.47	3.55			C1
61	8.9		1032.8	2.91	3.65			C1
62	15.0		1047.8	1.73	3.65			C1
63	0.0				3.65			
64	0.0				3.70			
65	0.0	R			3.40	5.04	13.6	
66	0.0	E			3.60			
67	0.0	C			3.80			
68	0.0	O			3.85			
69	0.0	R			3.85			
70	0.0	D			3.55			
71	0.0	E			3.70			
72	0.0	R			3.80			
73	0.0				3.75			
74	0.0	Q			3.75			
75	0.0	U			3.80	1.56	6.73	
76	0.0	I			3.80			
77	0.0	T			4.00			
78	0.0				4.00			
79	0.0				4.05			
80	0.0				4.15			

Continued

TABLE 15 Continued

SAMPLE NUMBER	TIME BETWEEN (min)	TIME ELAPSED		pH	IONS (mg/l)		REMARKS
		TIME (min)	INTENSITY (mm/hr)		NO ₃ ⁻	SO ₄ ⁻²	
81	0.0			4.25	0.34	2.05	
82	0.0			4.25			
83	0.0			4.20			
84	0.0			4.40	0.54	2.02	
85	0.0			4.35			
86	0.0			4.35			
87	90.0	1137.8	0.29	4.50	0.65	2.16	X
88	6.7	1144.5	3.87	4.40			C1
89	3.0	1147.5	8.64	4.40			C1
90	2.0	1149.5	12.96	4.35			C1
91	1.9	1151.4	13.64	4.50			C1
92	5.0	1156.4	5.18	4.50			C1
93	9.6	1166.0	2.70	4.60	0.54	1.88	C1
94	3.5	1169.0	7.41	4.50			
95	3.6	1173.1	7.20	4.50			
96	5.4	1178.5	4.80	4.50			
97	6.4	1184.9	4.05	4.50			
98	12.3	1197.2	2.11	4.35			
99	11.2	1208.4	2.31	4.28			
100	16.7	1225.1	1.55	4.30			
101	10.0	1235.1	2.59	4.40			
102	9.0	1244.1	2.88	4.35			
103	4.3	1248.4	6.03	4.30	1.83	3.53	
104	1.9	1250.3	13.64	4.30			
105	2.0	1252.3	12.96	4.35			
106	2.8	1255.1	9.26	4.35			
107	3.8	1258.9	6.82	4.40			
108	4.6	1263.5	5.63	4.30			
109	3.2	1266.7	8.10	4.20			
110	3.6	1270.3	7.20	4.50			
111	3.6	1273.9	7.20	4.50			
112	4.8	1278.9	5.40	4.40			
113	3.7	1282.4	7.01	4.35	1.79	2.43	
114	2.3	1284.7	11.27	4.30			
115	2.1	1286.8	12.34	4.00	2.56	11.20	
116	2.9	1289.7	8.94	4.10			
117	9.2	1298.9	2.82	4.35			
118	9.9	1308.8	2.62	4.40			
119	5.6	1314.4	4.63	4.35			
120	11.9	1326.3	2.18	4.30			

Continued

TABLE 15 Continued

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	IONS (mg/l)		REMARKS
					NO ₃ ⁻	SO ₄ ⁻²	
121	12.4	1338.7	2.09	4.40			
122	11.0	1349.7	2.36	4.40			
123	5.8	1355.5	4.47	4.80			
124	7.2	1362.7	3.60	4.80			
125	8.6	1371.3	3.01	4.89			
126	9.3	1380.6	2.79	4.95			
127	4.0	1384.6	6.48	5.20	0.28	1.24	
128	7.0	1391.6	3.70	4.99			
129	6.9	1398.5	3.76	4.80			
130	5.0	1403.5	5.18	4.95			
131	9.2	1412.7	2.82	4.75			
132	13.8	1426.5	1.88	4.50			
133	14.4	1440.9	1.80	4.65			
134	21.7	1462.6	1.19	4.65			
135	43.5	1506.1	0.60	4.85			X
136	69.9	1576.0	0.37	4.60			X
137	50.5	1626.5	0.51	4.50			X
138	8.7	1635.2	2.98	4.80			C1
139	12.0	1647.2	2.16	4.85			C1
140	5.0	1652.2	5.18	5.00			C1
141	4.4	1656.6	5.89	4.90			C1
142	5.6	1662.2	4.63	5.00			C1
143	5.0	1667.2	5.18	4.60			C1
144	6.0	1673.2	4.32	4.30			
145	6.0	1679.2	4.32	4.70			
146	6.7	1685.9	3.87	4.90	0.35	1.40	
147	5.4	1691.3	4.80	5.00			
148	9.0	1700.3	2.88	4.80			
149	5.9	1706.2	4.39	4.75			
150	6.8	1713.0	3.81	5.05			
151	6.8	1719.8	3.81	4.95			
152	5.0	1724.8	5.18	4.99			
153	4.9	1729.7	5.29	5.10	0.17	1.33	
154	4.3	1734.0	6.03	5.00			
155	4.8	1738.8	5.40	5.05			
156	6.3	1745.1	4.11	4.70			
157	6.5	1751.6	3.99	4.80			
158	7.5	1759.1	3.46	4.90			
159	6.4	1765.5	4.05	5.25			
160	4.7	1770.2	5.51	5.30			

Continued

TABLE 15 Continued

SAMPLE NUMBER	TIME BETWEEN (min)	TIME ELAPSED		INTENSITY (mm/hr)	pH	IONS (mg/l)		REMARKS
		(min)	(min)			NO ₃ ⁻	SO ₄ ⁻²	
161	5.0		1775.2	5.18	5.25			
162	4.1		1779.3	6.32	4.30			
163	5.9		1785.2	4.39	4.30			
164	5.0		1790.2	5.18	4.70			
165	2.7		1792.9	9.60	4.80			
166	3.0		1795.9	8.64	4.10	0.39	5.64	
167	3.2		1799.1	8.10	4.50			
168	4.1		1803.2	6.32	4.57			
169	3.9		1807.1	6.65	4.49			
170	4.9		1812.0	5.29	4.55			
171	4.5		1816.5	5.76	4.60			
172	3.4		1819.9	7.62	4.70			
173	4.0		1823.9	6.48	4.70			
174	4.3		1828.2	6.03	4.71			
175	6.6		1834.8	3.93	4.69			
176	6.4		1841.2	4.05	4.62			
177	9.1		1850.3	2.85	5.01	0.28	1.97	
178	7.8		1858.1	3.32	4.84			
179	5.6		1863.7	4.63	4.80			
180	5.5		1869.2	4.71	4.12			
181	3.6		1872.8	7.20	4.10	3.30	8.48	
182	3.5		1876.3	7.41	3.72			
183	3.6		1879.9	7.20	3.67			
184	3.9		1883.8	6.65	3.61			
185	5.1		1888.9	5.08	3.96			
186	4.7		1893.6	5.51	3.89			
187	8.8		1902.4	2.95	3.99			
188	5.2		1907.6	4.98	4.00			
189	42.0		1949.6	0.62	4.06			X
190	9.1		1958.7	2.85	3.85			C1
191	11.4		1970.1	2.27				C1
192	8.5		1978.6	3.05	3.51			C1
193	7.0		1985.6	3.70	3.61			C1
194	4.8		1990.4	5.40	4.13			C1
195	6.2		1996.6	4.18	4.09			C1
196	4.6		2001.2	5.63	3.97			
197	9.0		2010.2	2.88	4.00			
198	10.3		2020.5	2.52	4.01			
199	12.2		2032.7	2.12	3.95			
200	12.8		2045.5	2.03	4.42			

Continued

TABLE 15 Continued

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED		INTENSITY (mm/hr)	pH	IONS (mg/l)		REMARKS
		TIME (min)				NO_3^-	SO_4^{2-}	
201	14.8	2060.3	1.75	4.32				
202	430.0	2490.3	0.06	3.99				X
203	110.0	2600.3	0.24	4.00				X
204	14.3	2614.6	1.81	4.40				C1
205	5.0	2619.6	5.18	4.62				C1
206	11.7	2631.3	2.22	4.75				C1
207	9.5	2640.8	2.73	5.17				C1

TABLE 16. INTENSITY, pH, AND CHEMISTRY OF SELECTED SAMPLES
RAINSTORM, 26 SEPT 1977

SAMPLE NUMBER	TIME BETWEEN (min)	TIME ELAPSED		INTENSITY (mm/hr)	pH	IONS (mg/l)		REMARKS
		(min)				NO ₃ ⁻	SO ₄ ⁻²	
1		0.0						
2	0.5	0.5	51.84	4.20				
3	1.0	1.5	25.92	4.25				
4	1.5	3.0	17.28	3.85	0.25	4.89		
5	1.3	4.3	19.94	4.05				
6	1.7	6.0	15.25	4.20				
7	3.6	9.6	7.20	4.40				
8	4.5	14.1	5.76	4.45				
9	3.5	17.6	7.41	4.50				
10	4.8	22.4	5.40	4.25				
11	1.4	23.8	18.51	4.25				
12	0.9	24.7	28.80	4.25				
13	1.2	25.9	21.60	4.35				
14	2.0	27.9	12.96	4.30				
15	1.6	29.5	16.20	4.40				
16	0.3	29.8	86.40	4.45				
17	0.7	30.5	37.03	4.60				
18	2.3	32.8	11.27	4.80	0.25	1.74		
19	2.1	34.9	12.34	4.60				
20	2.6	37.5	9.97	4.40				
21	3.0	40.5	8.64	4.35				
22	5.6	46.1	4.63	4.33				
23	2.5	48.6	10.37	3.90				
24	13.2	61.8	1.96	3.85	1.37	5.11		
25	5.8	67.6	4.47	3.90				
26	2.1	69.7	12.34	3.70				
27	1.8	71.5	14.40	4.00				
28	1.1	72.6	23.56	3.84				
29	2.0	74.6	12.96	4.00				
30	1.7	76.3	15.25	5.02				
31	1.0	77.3	25.92	5.14	0.08	1.74		
32	0.5	77.8	51.84	4.50				
33	0.5	78.3	51.84	3.80				
34	0.5	78.8	51.84	3.84				
35	0.9	79.7	28.80	3.82				
36	1.0	80.7	25.92	4.10				
37	2.1	82.8	12.34	4.27				
38	2.4	85.2	10.80	4.30				
39	0.4	85.6	64.80	4.55				
40	0.9	86.5	28.80	4.50				

Continued

TABLE 16 Continued

SAMPLE NUMBER	TIME BETWEEN (min)	TIME ELAPSED		pH	IONS (mg/l)		REMARKS
		TIME (min)	INTENSITY (mm/hr)		NO ₃ ⁻	SO ₄ ⁻²	
41	1.3	87.8	19.94	4.84	0.20	2.28	
42	0.6	88.4	43.20	4.90			
43	0.5	88.9	51.84	4.93			
44	0.4	89.3	64.80	5.27	0.17	1.96	
45	1.8	91.1	14.40	5.00			
46	6.7	97.8	3.87	4.91			
47	3.0	100.8	8.64	4.09			
48	196.5	297.3	0.13	3.66			X
49	2.3	299.6	11.27	3.70			C1
50	0.9	300.5	28.80	3.91	3.50	7.80	C1
51	1.2	301.7	21.60	3.90			C1
52	0.9	302.6	28.80	3.98			
53	1.0	303.6	25.92	3.89			
54	6.0	309.6	4.32	3.62			
55	17.0	326.6	1.52				
56	6.5	333.1	3.99				
57	34.0	367.1	0.76	3.61			X
58	7.0	374.1	3.70	4.00			C1
59	39.0	413.1	0.66	4.58			X
60	2.8	415.9	9.26	4.50			C1
61	3.4	419.3	7.62	4.70	0.36	3.20	C1
62	0.6	419.9	43.20	4.22			C1
63	0.5	420.4	51.84	4.45			C1
64	0.5	420.9	51.84	4.49			
65	0.5	421.4	51.84	4.01			
66	0.7	422.1	37.03	4.60			
67	1.2	423.3	21.60	4.58			
68	4.8	428.1	5.40	4.71			
69	22.8	450.9	1.14	4.19			
70	0.2	451.1	129.60	4.01			
71	3.2	454.3	8.10	4.07	2.39	3.93	
72	1.0	455.3	25.92	4.05			
73	0.6	455.9	43.20	4.64			
74	1.0	456.9	25.92	4.60			
75	1.3	458.2	19.94	4.71			
76	2.2	460.4	11.78	4.39			
77	1.3	461.7	19.94	4.28			
78	0.6	462.3	43.20	4.44			
79	0.5	462.8	51.84	4.81			
80	0.4	463.2	64.80	4.79			

Continued

TABLE 16 Continued

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED		INTENSITY (mm/hr)	pH	IONS (mg/l)		REMARKS
		TIME (min)				NO ₃ ⁻	SO ₄ ⁻²	
81	0.5	463.7		51.84	4.90	0.32	1.60	
82	0.6	464.3		43.20	4.45			
83	0.5	464.8		51.84	4.79			
84	0.4	465.2		64.80	4.71			
85	0.6	465.8		43.20	4.57			
86	0.7	466.5		37.03	4.42			
87	0.8	467.3		32.40	4.35			
88	1.2	468.5		21.60	4.19			
89	0.6	469.1		43.20	4.20			
90	0.3	469.4		86.40	4.20			
91	4.0	473.4		6.48	4.14	1.38	4.02	
92	107.0	580.4		0.24	3.80			X
93	1.1	581.5		23.56	3.62			Cl
94	0.8	582.3		32.40	4.07			Cl
95	1.7	584.0		15.25	4.11			Cl
96	8.5	592.5		3.05	4.08			
97	2.0	594.5		12.96	3.80			
98	2.6	597.1		9.97	4.00			
99	3.2	600.3		8.10	4.01	2.95	3.47	

TABLE 17. INTENSITY, pH, AND CHEMISTRY OF SELECTED SAMPLES
RAINSTORM, 17 OCT 1977

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	IONS (mg/l)		REMARKS
					NO ₃ ⁻	SO ₄ ⁻²	
1		0.0					
2	3.9	3.9	6.65	4.15	3.76	4.65	N
3	3.9	7.8	6.65	4.40	2.63	6.02	O
4	4.8	12.6	5.40	4.60			
5	5.7	18.3	4.55	4.90	0.39	1.27	C
6	4.1	22.4	6.32	5.35			O
7	4.8	27.2	5.40	5.50			N
8	4.8	32.0	5.40	5.65	0.14	0.58	T
9	5.2	37.2	4.98	5.70			A
10	2.8	40.0	9.26	5.80			M
11	2.9	42.9	8.94	5.75	0.14	0.57	I
12	3.8	46.7	6.82	5.80			N
13	4.2	50.9	6.17	5.85			A
14	4.5	55.4	5.76	5.75			T
15	7.9	63.3	3.28	5.80			I
16	8.9	72.2	2.91	5.85	0.17	0.66	O
17	5.4	77.6	4.80	5.85			N
18	5.5	83.1	4.71	5.70			
19	6.2	89.3	4.18	5.60			
20	5.0	94.3	5.18	5.60			
21	6.6	100.9	3.93	5.55	0.26	0.70	
22	7.1	108.0	3.65	5.60			
23	6.5	114.5	3.99	5.50			
24	6.5	121.0	3.99	5.55			
25	8.3	129.3	3.12	5.70			
26	8.9	138.2	2.91	5.70	0.32	0.90	
27	10.5	148.7	2.47	5.60			
28	12.9	161.6	2.01	5.60			
29	14.7	176.3	1.76	5.70			
30	13.6	189.9	1.91	5.65			
31	12.3	202.2	2.11	5.50	0.28	1.05	
32	11.9	214.1	2.18	5.40			
33	14.2	228.3	1.83	5.50			
34		228.3		5.30	0.44	1.22	

TABLE 18. INTENSITY, pH, AND CHEMISTRY OF SELECTED SAMPLES
RAINSTORM, 19 OCT 1977

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	IONS (mg/l)		REMARKS
					NO ₃ ⁻	SO ₄ ⁻²	
1		0.0					
2	0.8	0.8	32.40	4.30	2.51	4.92	N
3	0.8	1.6	32.40	4.10			O
4	0.9	2.5	28.80	4.10			
5	1.5	4.0	17.28	4.10			C
6	5.8	9.8	4.47	4.20	1.38	2.94	O
7	1.9	11.7	13.64	4.20			N
8	2.1	13.8	12.34	4.10			T
9	2.4	16.2	10.80	4.00			A
10	3.6	19.8	7.20	3.85			M
11	3.5	23.3	7.41	3.80	2.32	5.83	I
12	3.3	26.6	7.85	4.00			N
13	3.0	29.6	8.64	3.95			A
14	2.8	32.4	9.26	3.95			T
15	6.1	38.5	4.25	3.90			I
16	7.1	45.6	3.65	4.00	2.01	3.48	O
17	4.2	49.8	6.17	3.95			N
18	3.7	53.5	7.01	3.95			
19	2.6	56.1	9.97	3.95			
20	3.2	59.3	8.10	3.95			
21	3.1	62.4	8.36	4.10	1.91	2.80	
22	2.5	64.9	10.37	4.10			
23	2.1	67.0	12.34	4.20			
24	2.1	69.1	12.34	4.30			
25	1.6	70.7	16.20	4.40			
26	1.8	72.5	14.40	4.40	1.13	1.38	
27	3.0	75.5	8.64	4.45			
28	2.8	78.3	9.26	4.35			
29	1.8	80.1	14.40	4.35			
30	2.1	82.2	12.34	4.35			
31	2.0	84.2	12.96	4.40	1.17	1.81	
32	2.2	86.4	11.78	4.40			
33	2.9	89.3	8.94	4.50			
34	3.0	92.3	8.64	4.45			
35	1.9	94.2	13.64	4.65			
36	2.1	96.3	12.34	4.65	0.84	1.31	
37	2.9	99.2	8.94	4.60			
38	3.0	102.2	8.64	4.70	0.88	1.49	
39	3.2	105.4	8.10	4.60			
40	7.8	113.2	3.32	4.70	1.18	1.38	
41	16.6	129.8	1.56	4.70			

TABLE 19. INTENSITY, pH, AND CHEMISTRY OF SELECTED SAMPLES
RAINSTORM, 24-26 JAN 1978

SAMPLE NUMBER	TIME BETWEEN (min)	TIME ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	Cl ⁻	NO ₃ ⁻	SO ₄ ⁻²	IONS (mg/l)		K ⁺	Ca ⁺²	Mg ⁺²	RMKS
								Na ⁺	NH ₄ ⁺				
1		0.0											
2	804.0	804.0	0.04	3.74	2.30	7.06	13.54						X
3	16.5	820.5	1.81	3.76				0.44	0.55	0.14	1.26	BDL	C1
4	19.8	840.3	1.51	3.79				0.44	0.55	0.14	1.26	BDL	C1
5	95.9	936.2	0.31	3.79	0.44	4.23	2.80						X
6	52.7	988.9	0.57	3.81									X
7	75.0	1063.9	0.40	3.94	0.48	1.89	2.28						X
8	27.9	1091.8	1.07	3.91	1.69	3.65	4.35						C1
9	16.7	1108.5	1.79	3.88				0.40	0.30	0.16			C1
10	13.4	1121.9	2.23	3.90				0.40	0.30	0.16			C1
11	12.4	1134.3	2.41	3.93									C1
12	15.8	1150.1	1.89	3.91	0.35	1.07	2.54						C1
13	17.0	1167.1	1.76	3.95									C1
14	17.9	1185.0	1.67	3.98									
15	21.3	1206.3	1.41	3.93				0.26	0.14	0.09			
16	15.7	1222.0	1.91	3.90	0.33	1.07	2.99	0.26	0.14	0.09			
17	15.1	1237.1	1.98	3.90									
18	11.9	1249.0	2.52	3.87									
19	12.8	1261.8	2.34	3.94									
20	12.9	1274.7	2.32	4.02									
21	9.7	1284.4	3.09	3.99									
22	9.2	1293.6	3.25	3.94	0.33	2.37	1.98						
23	9.3	1302.9	3.22	4.03									
24	6.5	1309.4	4.61	4.14				0.24	0.03	0.09			
25	8.1	1317.5	3.70	4.18				0.24	0.03	0.09			
26	3.8	1321.3	7.88	4.20	0.33	0.88	1.30						
27	10.6	1331.9	2.82	4.13				0.24	0.04	BDL			
28	13.0	1344.9	2.30	4.17				0.24	0.04	BDL			
29	16.8	1361.7	1.78	4.09									
30	16.3	1378.0	1.84	4.00	0.35	1.78	2.11						

Continued

TABLE 19 Continued

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	Cl ⁻	NO ₃ ⁻	SO ₄ ⁻²	IONS Na ⁺	(mg/l) NH ₄ ⁺	K ⁺	Ca ⁺²	Mg ⁺²	RMKS
31	7.4	1385.4	4.05	4.13									
32	5.4	1390.8	5.54	3.95									
33	6.4	1397.2	4.68	4.20									
34	5.3	1402.5	5.65	4.06				0.28	0.04	BDL	0.88	BDL	
35	5.6	1408.1	5.35	4.10				0.28	0.04	BDL	0.88	BDL	
36	9.3	1417.4	3.22	4.15									
37	8.2	1425.6	3.65	3.93	0.34	0.65	5.84						
38	6.6	1432.2	4.54	4.10									
39	6.3	1438.5	4.75	4.22									
40	6.1	1444.6	4.91	4.14									
41	5.7	1450.3	5.25	4.27									
42	5.6	1455.9	5.35	4.33	0.34	0.89	1.11						
43	6.9	1462.8	4.34	4.26				0.27	0.03	0.04	BDL	0.05	
44	8.5	1471.3	3.52	4.27				0.27	0.03	0.04	BDL	0.05	
45	12.0	1483.3	2.50	4.17									
46	20.6	1503.9	1.45	4.12									
47	15.9	1519.8	1.88	3.95									
48	36.3	1556.1	0.82	3.92	0.35	2.53	3.27						X
49	23.4	1579.5	1.28	3.94									Cl
50	99.0	1678.5	0.30	3.70									X
51	102.0	1780.5	0.29	3.69	0.47	4.73	6.19						X
52	52.7	1833.2	0.57	3.83									X
53	15.8	1849.0	1.89	3.92									Cl
54	16.4	1865.4	1.83	4.06				0.24	0.04	BDL			Cl
55	13.3	1878.7	2.25	4.09				0.24	0.04	BDL			Cl
56	14.2	1892.9	2.11	4.15									Cl
57	12.1	1905.0	2.47	4.10									Cl
58	5.8	1910.8	5.16	4.15									Cl
59	6.5	1917.3	4.61	4.18				0.24	BDL	BDL			
60	6.8	1924.1	4.40	4.19				0.24	BDL	BDL			

Continued

TABLE 19 Continued

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	Cl ⁻	NO ₃ ⁻	SO ₄ ⁻²	IONS Na ⁺	(mg/l) NH ₄ ⁺	K ⁺	Ca ⁺²	Mg ⁺²	RMKS
61	4.6	1928.7	6.51	4.28									
62	4.9	1933.6	6.11	4.32	BDL	0.43	1.09						
63	8.0	1941.6	3.74	4.26									
64	29.0	1970.6	1.03	4.02									
65	17.2	1987.8	1.74	3.82				0.69	0.39	0.04	0.49	0.06	
66	79.2	2067.0	0.38	3.82				0.69	0.39	0.04	0.49	0.06	X
67	39.6	2106.6	0.76	3.62	1.97	2.58	5.10						X
68	2.8	2109.4	10.69	3.75									Cl
69	1.6	2111.0	18.71	3.99	0.59	0.74	1.41						Cl
70	1.1	2112.1	27.22	4.27				0.40	0.04	0.01	0.38	0.31	Cl
71	1.0	2113.1	29.94	4.39	0.36	0.36	1.09						
72	0.7	2113.8	42.77	4.43				0.31	0.03	0.03	0.46	0.03	
73	1.1	2114.9	27.22	4.59	0.33	0.28	0.94						
74	11.8	2126.7	2.54	4.57									
75	67.3	2194.0	0.44	4.24									X
76	30.5	2224.5	0.98	4.10	1.37	1.10	4.61						X
77	6.1	2230.6	4.91	4.74				5.04	0.11	0.21	5.56	1.24	Cl
78	7.2	2237.8	4.16	5.01	4.62	0.51	3.00						Cl
79	17.9	2255.7	1.67	4.56									Cl
80	6.2	2261.9	4.83	4.87				0.09	0.04	0.04	5.44	0.25	Cl
81	6.7	2268.6	4.47	4.72	0.40	0.59	2.12						Cl
82	21.0	2289.6	1.43	4.61									Cl

TABLE 20. INTENSITY, pH, AND CHEMISTRY OF SELECTED SAMPLES
SNOWSTORM, 6-7 FEB 1978

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	Cl ⁻	NO ₃ ⁻	SO ₄ ⁻²	IONS (mg/l)		K ⁺	Ca ⁺²	Mg ⁺²	RMKS
								Na ⁺	NH ₄ ⁺				
1		0.0											
2	823.0	823.0	0.04	4.75	1.65	3.72	3.58	3.20	1.46	1.15	6.04	BDL	X
3	48.5	871.5	0.62	4.67				1.17	0.38	0.44			C1
4	39.2	910.7	0.76	4.67				1.05	0.31	0.38	1.32	0.12	C1
5	10.2	920.9	2.94	4.67	1.64	2.84	3.44	1.09	0.18	0.46			C1
6	17.7	938.6	1.69	4.77				0.96	0.26	0.35	1.73	0.12	C1
7	25.5	964.1	1.17	5.07	0.85	1.62	3.26	0.67	0.16	0.22			C1
8	67.8	1031.9	0.44	5.58	BDL	0.63	3.14	0.58	0.26	0.17			
9	87.0	1118.9	0.34	5.67				1.02	0.32	0.42	2.26	0.08	
10	13.4	1132.3	2.23	5.35	1.65	1.07	3.41	1.36	0.25	0.61			
11	13.2	1145.5	2.27	5.30				1.39	0.28	0.65	1.10	0.05	
12	28.5	1174.0	1.05	5.51	1.19	0.62	3.23	1.04	0.27	0.44			
13	62.0	1236.0	0.48	5.65				1.73	0.53	0.80	1.48	0.09	
14	142.0	1378.0	0.21	5.98	0.95	0.88	3.99	0.87	0.58	0.34			X
15	41.0	1419.0	0.73	5.93	BDL	0.55	3.34	0.61	0.15	0.20			C1
16	86.0	1505.0	0.35	6.08				0.71	0.45	0.21	2.79	0.07	C1
17	184.0	1689.0	0.16	6.36	1.17	2.06	5.53	1.02	0.70	0.22			X
18	493.0	2162.0	0.06	6.54				2.11	1.10	0.71	10.72	0.30	X
19	0.0	2162.0		6.54	6.81	4.09	18.23	4.61	2.09	2.56			C1

TABLE 21. INTENSITY, pH, AND CHEMISTRY OF SELECTED SAMPLES
SNOWSTORM, 3 MARCH 1978

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	Cl ⁻	NO ₃ ⁻	SO ₄ ⁻²	IONS (mg/l)		K ⁺	PO ₄ ⁻³	RMKS
								Na ⁺	NH ₄ ⁺			
1			0.0									
2	227.0	227.0	0.13	5.70	1.57	12.36	12.97				0.16	X
3	33.0	260.0	0.91	5.55	0.05	6.06	4.63	3.09	0.40	1.50	0.12	Cl
4	16.8	276.8	1.78	5.26	1.24	2.67	2.55				0.13	Cl
5	22.0	298.8	1.36	5.10	0.17	2.22	2.32	0.73	0.43	0.31	0.11	Cl
6	34.5	333.3	0.87	4.77	BDL	2.39	2.71	0.60	0.40	0.31	0.12	Cl
7	48.5	381.8	0.62	4.85	BDL	2.75	2.54	0.46	0.47	0.15	0.10	Cl
8	41.5	423.3	0.72	4.77	BDL	1.45	1.71	0.15	0.33	BDL	0.10	
9	33.2	456.5	0.90	4.80	BDL	1.16	1.46	0.08	0.17	BDL	0.10	
10	42.2	498.7	0.71	4.66	BDL	1.10	1.54	0.08	0.31	0.91	BDL	
11	27.4	526.1	1.09	4.76	BDL	0.89	1.12	0.05	0.24	BDL	BDL	
12	21.4	547.5	1.40	4.72	BDL	1.01	1.15	0.05	0.29	BDL	BDL	
13	49.2	596.7	0.61	4.77	BDL	1.46	1.11	0.05	0.33	BDL	BDL	

TABLE 22. INTENSITY, pH, AND CHEMISTRY OF SELECTED SAMPLES
RAINSTORM, 14-15 MARCH 1978

SAMPLE NUMBER	TIME BETWEEN (min)	TIME ELAPSED (min)	INTENSITY (mm/hr)	pH	IONS (mg/l)		K ⁺	Ca ⁺²	Mg ⁺²	REMARKS
					Na ⁺	NH ₄ ⁺				
1		0.0		3.60	12.01	3.964	0.87	5.68	1.51	
2	199.5	199.5	0.15	3.49	4.88	1.453	0.24	2.16	0.71	X
3	7.5	207.0	3.99	3.55	4.50	1.196	0.25	1.51	0.67	C1
4	8.9	215.9	3.36	3.50	3.56	1.128	0.19	1.35	0.52	C1
5	7.4	223.3	4.05	3.54	3.53	1.099	0.15	3.94	0.59	C1
6	9.8	233.1	3.06	3.61	2.56	0.982	0.18	BDL	0.45	C1
7	6.9	240.0	4.34	3.69	1.81	0.801	0.10	1.19	0.42	C1
8	6.0	246.0	4.99	3.74	1.21	0.612	0.08	0.77	0.37	C1
9	9.4	255.4	3.19	3.73	1.42	0.707	0.05	0.95	0.41	
10	9.7	265.1	3.09	3.56	2.80	1.022	0.09	1.04	0.53	
11	8.0	273.1	3.74	3.55	3.72	1.043	0.13	1.27	0.60	
12	24.7	297.8	1.21	3.51	7.32	1.438	0.30	1.39	0.96	
13	6.6	304.4	4.54	3.54	7.57	1.210	0.32	1.14	0.94	
14	16.7	321.1	1.79	3.51	8.12	1.261	0.34			
15	16.8	337.9	1.78	3.58	7.18	1.186	0.24	0.65	0.62	
16	18.8	356.7	1.59	3.60	6.00	1.104	0.19	0.95	0.19	
17	16.2	372.9	1.85	3.57	4.00	1.219	0.14			
18	47.6	420.5	0.63	3.50	5.06	1.467	0.21			X
19	16.6	437.1	1.80	3.60	3.88	1.033	0.15			C1
20	9.0	446.1	3.33	3.77	2.23	0.657	0.12			C1
21	6.9	453.0	4.34	3.98	1.17	0.381	0.05			C1
22	5.8	458.8	5.16	4.05	0.75	0.322	0.05			C1
23	6.9	465.7	4.34	3.96	0.39	0.394	0.05			C1
24	3.8	469.5	7.88	4.26	0.44	0.439	0.07	0.86	0.32	C1
25	1.9	471.4	15.76	4.10	0.35	0.348	0.03			

Continued

TABLE 22 Continued									
SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	IONS (mg/l)		K ⁺	Ca ⁺²	Mg ⁺²
					Na ⁺	NH ₄ ⁺			
26	0.6	472.0	49.90	4.25	0.25	0.248	BDL	0.56	0.29
27	0.7	472.7	42.77	4.45	0.10	0.104	BDL		
28	0.8	473.5	37.43	3.95	0.08	0.078	BDL	0.41	BDL
29	0.8	474.3	37.43	4.01	0.05	0.048	BDL	0.38	0.26
30	3.1	477.4	9.66	4.19	0.06	0.056	BDL	0.24	0.24
31	6.2	483.6	4.83	4.33	0.05	0.046	BDL		
32	8.7	492.3	3.44	4.24	0.05	0.052	BDL		

TABLE 23. INTENSITY, pH, AND CHEMISTRY OF SELECTED SAMPLES
SNOWSTORM, 16-17 MARCH 1978

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED (min)	TIME (mm/hr)	INTENSITY pH	Cl ⁻ (mg/l)	NO ₃ ⁻ (mg/l)	IONS SO ₄ ⁻² (mg/l)	Fe (μg/l)	REMARKS
1		0.0							
2	39.7	39.7	0.75	3.73	0.16	9.41	6.36	145	
3	19.8	59.5	1.51	3.75	BDL	5.31	5.10	110	
4	21.4	80.9	1.40	3.85	BDL	4.09	3.31	82	
5	31.0	111.9	0.97	3.85	BDL	4.41	2.11	55	
6	22.0	133.9	1.36	3.86	BDL	3.14	1.69	63	
7	16.3	150.2	1.84	3.95	BDL	2.95	1.43	33	
8	11.4	161.6	2.63	3.97	BDL	2.81	1.27	30	
9	11.5	173.1	2.60	3.97	BDL	2.57	1.27	20	
10	8.4	181.5	3.56	4.06	BDL	1.93	1.10	24	
11	12.9	194.4	2.32	4.16	BDL	1.04	1.23	11	
12	8.1	202.5	3.70	4.23	BDL	0.92	1.25	15	
13	11.9	214.4	2.52	4.07	BDL	1.38	1.71	21	
14	11.1	225.5	2.70	4.03	BDL	1.00	1.95	16	
15	12.7	238.2	2.36	4.08	BDL	0.94	1.97	21	
16	21.7	259.9	1.38	4.17	BDL	1.06	1.80	22	
17	115.8	375.7	0.26	4.03	8.47	2.39	5.28	35	X
18	43.8	419.5	0.68	4.03	0.78	2.33	2.86	340	X

TABLE 24. INTENSITY, pH, AND CHEMISTRY OF SELECTED SAMPLES
RAINSTORM, 18-20 APRIL 1978

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	IONS (mg/l)			Na ⁺	NH ₄ ⁺	K ⁺	REMARKS
					Cl ⁻	NO ₃ ⁻	SO ₄ ⁻²				
1		0.0									
2	687.0	687.0	0.04	3.61				1.14	1.93	0.40	X
3	22.2	709.2	1.35	3.83				0.62	0.67	0.19	C1
4	13.5	722.7	2.22	3.82				0.40	0.37	BDL	C1
5	14.8	737.5	2.02	3.93				0.60	0.29	BDL	C1
6	11.4	748.9	2.63	3.99	0.29	2.50	4.82				C1
7	11.6	760.5	2.58	3.92	0.26	2.28	4.82				C1
8	23.2	783.7	1.29	4.06	0.25	2.24	4.82				C1
9	10.0	793.7	2.99	3.87	0.76	1.15	6.96				
10	6.6	800.3	4.54	3.97							
11	9.8	810.1	3.06	3.94							
12	9.6	819.7	3.12	4.04							
13	7.5	827.2	3.99	4.17							
14	8.6	835.8	3.48	4.12							
15	6.1	841.9	4.91	4.10	BDL	1.14	3.57				
16	4.0	845.9	7.49	4.10							
17	3.2	849.1	9.36	4.08				0.28	0.09	BDL	
18	3.2	852.3	9.36	3.85	BDL	2.10	3.75				
19	2.9	855.2	10.32	3.90				0.13	0.17	BDL	
20	2.9	858.1	10.32	3.92							
21	4.8	862.9	6.24	4.01							
22	5.0	867.9	5.99	4.13	BDL	0.65	1.61				
23	6.7	874.6	4.47	4.05				0.08	0.12	BDL	
24	3.6	878.2	8.32	4.03				0.11	0.14	BDL	
25	4.4	882.6	6.80	3.93				0.25	0.11	BDL	
26	20.3	902.9	1.47	3.82	BDL	3.09	2.50				
27	11.4	914.3	2.63	3.96	BDL	1.74	2.68				
28	10.6	924.9	2.82	3.91				0.10	0.32	BDL	
29	10.8	935.7	2.77	3.90				0.17	BDL	BDL	
30	12.7	948.4	2.36	3.91				0.12	0.18	BDL	

Continued

TABLE 24 Continued

SAMPLE NUMBER	TIME BETWEEN (min)	ELAPSED TIME (min)	INTENSITY (mm/hr)	pH	IONS (mg/l)			Na ⁺	NH ₄ ⁺	K ⁺	REMARKS
					Cl ⁻	NO ₃ ⁻	SO ₄ ⁻²				
31	10.5	958.9	2.85	3.87	BDL	1.95	3.21				
32	9.4	968.3	3.19	3.84				0.19	0.09	BDL	
33	8.2	976.5	3.65	3.89				0.11	0.09	BDL	
34	10.2	986.7	2.94	3.87							
35	11.0	997.7	2.72	3.87	BDL	1.62	3.04				
36	9.1	1006.8	3.29	4.00	BDL	0.69	2.85				
37	12.2	1019.0	2.45	3.97							
38	26.9	1045.9	1.11	4.13	BDL	1.30	1.61				
39	45.9	1091.8	0.65	4.13				0.41	0.17	BDL	X
40	82.0	1173.8	0.37	4.13				0.27	0.17	BDL	X
41	34.2	1208.0	0.88	4.04				0.28	0.17	BDL	X
42	60.5	1268.5	0.49	4.02	BDL	1.18	3.93				X
43	7.3	1275.8	4.10	4.07	0.18	1.70	3.04				C1
44	50.1	1325.9	0.60	4.23							X
45	6.6	1332.5	4.54	4.38							C1
46	5.2	1337.7	5.76	4.40	BDL	0.91	1.38				C1
47	8.7	1346.4	3.44	4.65	BDL	0.37	0.75				C1
48	7.6	1354.0	3.94	4.72							C1
49	376.4	1730.4	0.08	4.62							X
50	16.1	1746.5	1.86	4.61	BDL	1.43	1.34				C1
51	4.5	1751.0	6.65	3.82	0.46	4.91	4.64				C1
52	30.3	1781.3	0.99	3.85							X
53	8.6	1789.9	3.48	3.88				0.45	0.35	0.04	C1
54	42.7	1832.6	0.70	3.82	0.34	2.83	3.48				X
55	33.1	1865.7	0.90	3.95							X
56	16.8	1882.5	1.78	3.92							C1
57	102.0	1984.5	0.29	3.90	0.21	2.38	2.86				X

Heavy metal ions analyzed in samples 10-14, 16, 20 and 21.
Continued

TABLE 24 Continued
HEAVY METAL ANALYSES
IONS (μ g/l)

SAMPLE NUMBER	Fe	Al	Ni	Mn	Cu	Pb	REMARKS
10	14.6	35.1	33.3	4.5	3.5	244.0	
11	0.5	44.1	119.2		7.7	64.5	
12	8.0	26.8	200.2		12.8	28.1	
13	8.6	40.1	133.6		33.4	25.1	
14		55.8	158.0		4.5	39.8	
15							
16	7.4	67.4	28.5		9.7	5.5	
17							
18							
19							
20	0.1	101.1	17.4		7.2		
21		52.1	66.5		2.4	45.4	

APPENDIX B
TABULATION OF STORM INFORMATION

	STORM TYPE	DIRECTION OF APPROACH	MEAN TEMPERATURE
20 Oct 76	Cold Front	From Midwest	55
7 Dec 76	Cold Front	From Midwest	
17-18 Mar 77	Warm Front	From Midwest	
22 Mar 77	Low Pressure	From Midwest	
28 Mar 77	Warm Front	Undetermined	47
4-6 Apr 77	Low Pressure	From Midwest	44
23-24 Apr 77	Cold Front	From Canada	45
2 June 77	Cold Front	From Midwest	
7 June 77	Convective	Undetermined	
18 Aug 77	Cold Front	Undetermined	74
16-17 Sep 77	Warm Front	From Midwest	
18 Sep 77	Convective	Undetermined	
24-26 Sep 77	Low Pressure	From Midwest	57
26 Sep 77	Low Pressure	From Midwest	66
17 Oct 77	Low Pressure	Up Atlantic Coast	47
19 Oct 77	Low Pressure	Undetermined	55
24-26 Jan 78	Low Pressure	From Midwest	42
6-7 Feb 78	Low Pressure	Undetermined	28
3 Mar 78	Low pressure	Up Atlantic Coast	
		From the Gulf	
14-15 Mar 78	Low Pressure	Midwest	45
16-17 Mar 78	Low Pressure	From Great Lakes	
18-20 Apr 78	Low Pressure	Midwest	

APPENDIX C

INTERPRETATION OF PERIODS OF CONTAMINATION FOR THE TWENTY-TWO STORMS

The following criteria were used in interpreting the storm data:
Dry Deposition Contamination Periods -

Rainstorm - all periods with intensity less than 1.0 mm/hr.

Snowstorm - all periods with intensity less than 0.25 mm/hr.

Cleansing: Chemical data has been used when available or an arbitrary 3-8 samples following the suspected dry deposition depending upon the intensity of rain. The deletion of these samples is to account for the cleansing of dry deposition from the funnel.

- 1 - Rainstorm - 20 October 1976 (TABLE 3 AND FIGURE 10)
Contamination at sample 40 and 47. Samples 41-46 represent the cleansing period. Samples 1-39 are contamination free.
- 2 - Rainstorm - 7 December 1976 (TABLE 4 AND FIGURE 11)
Contamination of samples 45 and 46. No cleansing period as the storm ends. Samples 1 to 44 are contamination free.
- 3 - Snow Changing to Rain - 17-18 March 1977 (TABLE 5 AND FIGURE 12)
Contamination at sample 38, cleansing samples 39 to 42. Contamination at sample 47, cleansing at 48 through the end of the storm. Samples 1 to 37 and 43 to 46 are contamination free.
- 4 - Rainstorm - 22 March 1977 (TABLE 6 AND FIGURE 13)
Contamination at sample 2; cleansing from sample 3 to 10. Contamination at sample 110 with cleansing through sample 118. Contamination of samples 138 to 146. No cleansing as the storm ends. Samples 11 to 109 and 119 to 137 are contamination free.
- 5 - Rainstorm - 28 March 1977 (TABLE 7 AND FIGURE 14)
Contamination at samples 12, 13, 19, 21, and 22. No opportunity for cleansing. Samples 1 to 11 are contamination free.
- 6 - Rainstorm - 4-6 April 1977 (TABLE 8 AND FIGURE 15)
Contamination at sample 2; cleansing period samples 3 to 10.

Contamination at samples 57, 59, 63 to 67. These are sufficiently close together so that cleansing doesn't become effective until 68. Contamination at samples 73, 74, 79, 82, and 83, again close enough together so that good data is not produced through the end of the storm. Samples 11 through 56 are contamination free.

- 7 - Rainstorm - 23-24 April 1977 (TABLE 9 AND FIGURE 16)
Contamination at samples 4 to 6 and again at 11. Cleansing is effective at samples 12 to 15. Contamination at sample 30; cleansing 31 to 33. Contamination at samples 42 and 43. Contamination free samples at samples 1 to 3, 16 to 29, and 34 to 41.
- 8 - Rainstorm - 2 June 1977 (TABLE 10 AND FIGURE 8)
Contamination at sample 16 and 22; cleansing in effect at samples 17-19 and 23-26. Contamination at 30 and 32 with cleansing in effect from 33 to 39. Contamination free samples at samples 1 to 15, 20 and 21, 27 to 29, and 40 to 43.
- 9 - Rainstorm - 7 June 1977 (TABLE 11 AND FIGURE 17) Samples 2 and 3 are contamination free, all the rest are contaminated.
- 10 - Rainstorm - 18 August 1977 (TABLE 12 AND FIGURE 18)
Contamination at samples 8 and 11. Cleansing effective samples 12 to 14. Samples 1 to 7 and 15 through 34 are contamination free.
- 11 - Rainstorm - 16-17 September 1977 (TABLE 13 AND FIGURE 19)
Samples 1 through 11 are contaminated. Cleansing in effect samples 12 through 17. Contamination at sample 48, cleansing through the end of the storm. Samples 18 to 47 are contamination free.
- 12 - Rainstorm - 18 September 1977 (TABLE 14 AND FIGURE 20)
Contamination at samples 2 and 3, cleansing in effect samples 4 to 6. Samples 7 to 14 are contamination free.
- 13 - Rainstorm - 24-26 September 1977 (TABLE 15 AND FIGURE 21)
Contamination at sample 7, cleansing at 8 to 13. More contamination at sample 21, cleansing at 22 to 28. Contamination in linked periods, samples 41, 42, 46, 48, 49, and 56; cleansing through to sample 62. Contamination at 87, with cleansing 88 to 93. Contamination again at 135, 136, and 137 with cleansing up to 143. Another episode at 189 with cleansing up to 195. Contamination from 202 through the end of the storm. Samples 1 to 6, 14 to 20, 29 to 40, 94 to 134, 144 to 188, and 196 to 201 are contamination free. Samples 63 to 86 not considered because lack of intensity data.

- 14 - Rainstorm - 26 September 1977 (TABLE 16 AND FIGURE 22)
Contamination at sample 48 with cleansing to 51.
Contamination at 57 and 59; cleansing to 63. Once again at
sample 92 with cleansing to 95. Samples 1 to 47, 52 to 56,
64 to 91, and 96 to 99 are contamination free.
- 15 - Rainstorm - 17 October 1977 (TABLE 17 AND FIGURE 23) No
periods of contamination.
- 16 - Rainstorm - 19 October 1977 (TABLE 18 AND FIGURE 9) No
periods of contamination.
- 17 - Rainstorm - 24-26 January 1978 (TABLE 19 AND FIGURE 24)
Contamination samples 1 through 7; cleansing 8 to 13.
Contamination samples 48 through 52 with cleansing in effect
through sample 58. Contamination at samples 66 and 67,
cleansing 68 to 70. Contamination at 75 and 76; cleansing in
action as the storms end. Samples 14 to 47, 59 to 65, and 71
to 74 are contamination free.
- 18 - Snowstorm - 6-7 February 1978 (TABLE 20 AND FIGURE 25) An
intensity discriminator of 0.25 mm/hr was chosen as each of
the four time periods below showed jumps in the dissolved
constituent levels. Contamination at sample 2, cleansing in
effect 3 to 7. Contamination again at 14, 17, and 18 with no
opportunity for cleansing through the end of the storm.
Samples 8 to 13 are contamination free.
- 19 - Snowstorm - 3 March 1978 (TABLE 21 AND FIGURE 26)
Contamination at sample 2, cleansing in effect 3 to 7.
Samples 8 to 13 are contamination free.
- 20 - Rainstorm - 14-15 March 1978 (TABLE 22 AND FIGURE 27)
Contamination at sample 2, with cleansing in effect through
sample 8. Contamination at sample 18 and cleansing 19 to 24.
Samples 9 to 17 and 25 to 32 are contamination free.
- 21 - Snowstorm - 16-17 March 1978 (TABLE 23 AND FIGURE 28)
Contamination at sample 17 through the end of the storm.
Samples 1 to 16 are contamination free.
- 22 - Rainstorm - 18-20 April 1978 (TABLE 24 AND FIGURE 29)
Contamination at sample 2, cleansing 3 to 8. Contamination
at samples 39-42, 44, 49, 52, 54, 55, and 57. No period
sufficient for cleansing between these episodes. Samples 9
to 38 are contamination free.

APPENDIX D

REAGENTS USED FOR STANDARDS

<u>ION</u>		<u>REAGENT</u>
Chloride	Cl^-	NaCl
Nitrate	NO_3^-	NH_4NO_3
Phosphate	PO_4^{3-}	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$
Sulfate	SO_4^{2-}	K_2SO_4
Floride	F^-	NaF
Sodium	Na^+	NaCl
Ammonium	NH_4^+	NH_4NO_3
Potassium	K^+	KCl
Magnesium	Mg^{+2}	$\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)$
Calcium	Ca^{+2}	CaCl_2

TECHNICAL REPORT DATA
(Please read instructions on the reverse before completing)

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16. ABSTRACT Sequential sampling techniques and applications to collect precipitation are reviewed. Chemical data for samples collected by an intensity-weighted sequential sampling device in operation at the U.S. Military Academy, West Point, New York from October 1976 to April 1978 are presented and discussed. The problem of dry deposition is explored. A newly designed intensity-weighted sequential sampler that excludes dry deposition is presented. The experiments have shown that intensity-weighted sequential sampling is a viable technique for monitoring the rapid changes in precipitation chemistry within a storm. Complete chemical data are needed from individual storms to evaluate intensity related scavenging.					
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