

QC
807.5
.U6
A7
no.57
c.2

DEPARTMENT OF COMMERCE
UNITED STATES OF AMERICA

NOAA Technical Memorandum ERL ARL-57

U.S. DEPARTMENT OF COMMERCE
NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
Environmental Research Laboratories

AN EVALUATION OF PRECIPITATION pH DATA
FROM THE WASHINGTON, DC AREA
COLLECTED DURING 1975

John M. Miller
Gerald F. Cotton
Donald H. Pack
J. Murray Mitchell
Milton E. Smith

Air Resources Laboratory
Silver Springs, Maryland
August 1976

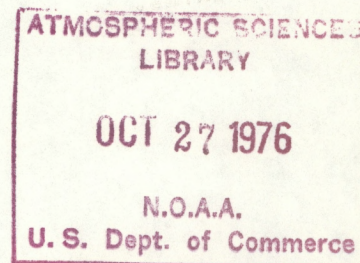
QC
807.5
46A7
no. 57

NOAA Technical Memorandum ERL ARL-57

AN EVALUATION OF PRECIPITATION pH DATA
FROM THE WASHINGTON, DC AREA
COLLECTED DURING 1975

John M. Miller
Gerald F. Cotton
Donald H. Pack
J. Murray Mitchell
Milton E. Smith

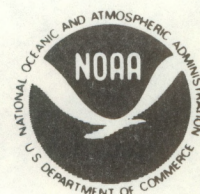
Air Resources Laboratory
Silver Springs, Maryland
August 1976



UNITED STATES
DEPARTMENT OF COMMERCE
Elliot L. Richardson, Secretary

NATIONAL OCEANIC AND
ATMOSPHERIC ADMINISTRATION
Robert M. White, Administrator

Environmental Research
Laboratories
Wilmot N. Hess, Director



LIBRARY
OCT 2 1976
U. S. Dept. of Commerce

CONTENTS

Abstract	iv
1. Introduction	1
2. Past Measurements	1
3. The Network, Method of Collection and pH Determination	2
4. Evaluation of the 1975 Data	3
5. Acknowledgement	5
6. References	6
Appendix	7
Tables and Figures	10

An Evaluation of Precipitation pH Data from the
Washington, DC Area Collected During 1975

John M. Miller, Gerald F. Cotton, Donald H. Pack,
J. Murray Mitchell and Milton E. Smith

An experimental volunteer program to collect precipitation for determination of pH (and pH only) was begun in April, 1974. The purpose was to gain practical experience in collection and analysis and some data on the acidity of precipitation in this area.

Rain or snow is collected in Taylor 4" diameter plastic rain gages by volunteers, transferred to washed plastic bottles, tightly capped, and brought to the ARL offices in Silver Spring.

pH measurements are made with a Fisher electrode and an Orion 401 pH meter following the manufacturer's instructions. pH determinations are usually made within 12-48 hours of collection.

The pH values compare well with pH values measured in the Northeastern U.S.

1. Introduction

The pH of precipitation samples can be viewed as a rough index of acid forming materials scavenged from the atmosphere. This report describes the modest program to collect precipitation in the District of Columbia and suburbs for pH determination. The data should supplement the information of the present and future networks planned for the North-eastern United States. In establishing the Washington network, it was hoped that some pattern of changing hydrogen ion deposition could be detected.

Originally the purpose of the network was to establish field test collection and analysis methods which could be eventually transferred to regional and baseline sites. These sites have limited chemistry facilities and preclude the use of sophisticated techniques. Active programs based on the experiences gained in the DC network have begun in Hawaii, Alaska and Samoa.

2. Past Measurements

Some of the earliest measurements of pH in the Washington area were made in 1949 by Landsberg⁽¹⁾. He measured the pH in individual rain drops during one storm. The values ranged from 3.91 to 4.84. See figure 3 for comparison with current rain event measurements in the area.

The next set of measurements was made by the Public Health Service at three sites. Data were collected at the National Airport (1959-1960) and Sterling, Virginia (1960-1964). The data are shown in Tables 1 and 2. A third set of measurements was taken at the CAMP station in Washington, DC from 1963 to 1965 (Table 3). All collections were monthly composites using the Wong open-close collector. The pH determinations were made at

the PHS laboratories in Cincinnati, Ohio⁽²⁾. Values from the three tables indicate that the yearly pH average in the early sixties was about 4.4.

After 1964, the PHS network was taken over by the National Center for Atmospheric Research (NCAR). Measurements made at the Sterling site have not been published.

3. The Network, Method of Collection and pH Determination

Between four and six sites located at the authors' residences have been active in the DC network since April 1974. The Gramax Building in Silver Spring was the sixth site. Figure 1 shows the full network plus Virginia Air Quality Stations.

The eleven inch, plastic rain gauge (Taylor Company) was used at all sites except the Gramax building location. A Misco open-close collector at the Gramax was used to provide a standard of comparison between the Taylor gauges and the more sophisticated Misco collector. A Hubbard Brook-type collector has been recently installed at the Pack residence in order to collect small precipitation amounts (Figure 2). The purpose and use of this collector is described in Appendix A.

As standard procedure for each location, rainwater was removed from the collector after every 24 hour period (usually 0700 LST). When sufficient amount of precipitation fell during this period, e.g. 0.25 inches or greater for the Taylor gauge, the sample was placed in a polyethylene bottle and the pH measured at the Gramax Building. When possible, the gauge was thoroughly rinsed with tap water and dried prior to the precipitation periods to remove any accumulated dry deposition. The determinations were made with a Fisher electrode and an Orion 401 pH

meter following the manufacturer's instructions. These determinations were made as soon as practical after collection.

4. Evaluation of the 1975 Data

The pH measurements for 1975 are presented in Table 4 and in a series of histograms. Figure 3 represents all 1975 data for all sites. The median value lies in the 4.0 to 4.1 pH range which is the same order of magnitude as the other pH measurements in the Northeast⁽³⁾. There seems to be a trimodal distribution of the data. One could speculate that this may be due to differing air mass regimes or precipitation type associated with the rainfall collection. Unfortunately, it is difficult to interpret the data in this manner and a rigorous evaluation awaits a larger data base.

The next three figures (4,5,6) present all the 1975 data for three different sites. The Pack residence is located west of the District. With typical west to east storm passage, the direct effects of the city air quality are less significant at this site than at others in the network. The figure shows a broad range of values with the median value one class interval higher than the combined data. Figure 5 shows the data taken at the Gramax building in downtown Silver Spring. One sees a distinct maximum at pH 3.91-4.0. The Gramax site is typical of the urban-suburban area of Washington. The Cotton residence is located approximately 20 km east of the metropolitan area. Here the distribution peaks broadly about a class interval greater than the composite data of 1975 (Figure 3). The indications of the trimodal distribution are evident in all three samples.

In Figure 7, all the data is plotted on a monthly basis for the entire year of 1975. From this plot an interesting and unexpected pattern

can be seen. One can postulate from these statistics an apparent annual cycle. Low pH values in May corroborate the findings of Meszaros in Hungary (4). Such a springtime maximum could be related to increased biological activities which produce organic acids. The high values in July were traced to a faulty electrode.

The most novel event of the year was the hail storm on July 10 from which the hailstones, each about $\frac{1}{2}$ " in diameter, were collected at a point north of the Smith residence just beyond the District line. The pH of the melt was determined to be 6.4 compared to the range 3.6 to 4.1 in the network from the same storm. The formation region of the hailstones as depicted in the National Weather Service freezing level facsimile maps was above the 5000 foot level. It is open to conjecture whether this pH difference is due to different formation regions or some additional factors.

The potential for comparison of pH values with other air quality measurements is enhanced by the location of Lewinsville, a monitoring station in the Fairfax County Air Pollution Control network and the Pack and Mitchell residences in the Washington pH network (see Figure 1). A monthly weighted average of the combined pH values at the two residences is exhibited in Figure 8 along with the monthly average ambient SO_2 and O_3 concentrations measured at Lewinsville. According to the theory of Penkett(5), ozone is important in the rapid oxidation of sulfur dioxide to sulfate, thus one might expect decreased SO_2 and increased ozone concentrations to be associated with decreased pH values. While there is some hint of this character over a portion of the period there are unexplained lag effects and contradictory behavior as well. The real situation,

which hopefully will become clearer as more data is accumulated, is undoubtedly much more complex than this.

Though much of what can be interpreted from the pH data is tentative the DC network in the coming years can provide useful information on the possible significant changes in the chemistry of precipitation in the DC area.

5. Acknowledgement

We wish to acknowledge Phillip D. Falconer for collecting the hail sample on July 10.

6. References

1. Landsberg, H.E., 1954: Some observations of the pH of precipitation elements. Arch. Meteorol. Geophys. Bioklimatal. Ser. A 7: 219-226.
2. Data from National Air Sampling Network (the Public Health Service).
3. Likens, G.E., F.H. Bormann and N.M. Johnson, 1972: Acid Rain. Environment 14: #2, 33-40.
4. Meszaros, E., 1974: On the spring increase of the concentration of trace constituents in atmospheric precipitation. Tellus 26: 402-407.
5. Penkett, S.A., 1972: Oxidation of SO_2 and Other Gases by O_3 in Aqueous Solution. Nature Physical Sciences 240: 105.

APPENDIX A

Precipitation pH-Washington, D.C.

Expanded Area Collector

Experience has shown that the volume of precipitation collected by the small diameter (10.16 cm) Taylor plastic rain gage is inadequate for accurate determination of pH by the method in use (Orion pH meter with a Fisher electrode) when the total precipitation amount is small.

Each mm of precipitation provides only slightly more than .8 cc of water. Our experience is that the 20 (approx.) cc of water obtained in a 0.25 cm (0.1 inch) precipitation event is marginal for determinations of pH. The program has been limiting determinations to precipitation collections of 0.64 cm (0.25 inch) or more to provide a minimum of about 50 cc of water.

This is an obviously undesirable practice from the standpoint of sampling statistics. It is even more undesirable in the present attempt to correlate surface air quality with precipitation pH as the smaller precipitation events are often correlated with prior high levels of air pollution than the expected need for large statistical samples suggests using every precipitation event possible.

On July 16, at 12:00 EDT a larger collector was installed at the Pack residence.

The collector system is shown in Figure 2. The open plastic funnel is 27.94 cm in diameter and provides a volume of water 7.56 times larger than the Taylor gage. Thus, this collector should provide 153 cc for a 0.25 cm (~0.1 inch) event. It will, however, require approximately 0.08 cm (0.03 inch) of precipitation to provide 50 cc of water for analysis.

Mounting:

The funnel is supported at a height of one meter above the ground by a plastic ring which is in turn attached by non-metallic fasteners to three metal supports. The ring was sized so that the upper edge of the funnel is approx. 5 cm above the level of the metal supports to avoid contamination.

The bottom of the funnel is connected to the 2 liter collector bottle by 15 cm of plastic tubing. This tubing enters the collector bottle via an air tight plastic insert in a large screw-on top. The collector bottle is mounted on a wooden support platform which holds the bottle and weight of the collected water and simultaneously provides rigidity to the supporting legs. This platform and tubing were designed so there are no barriers to gravity flow of the water. A short overflow tube is provided by a second plastic tube in the cap. This tube has its outside end opening downwards. This, together with the 180° bend in the tubing, prevents wind driven contamination from entering the collector bottle. A plastic restraining ring encircles the collector bottle and is attached to one of the legs to prevent displacement by the wind.

Operation:

1. All components of the system are thoroughly washed and rinsed before installation. After several days without precipitation this procedure is repeated to minimize collection of dry fallout.
2. After a precipitation collection the inlet tubing to the collector bottle is disconnected (by a sharp upward pull). The two-hole cap is replaced by a solid cap. This cap is kept stored in a sealed plastic

bag to avoid contamination of its surfaces. The collector bottle with the precipitation is returned to GMCC for analysis.

A new collector bottle is uncapped, the two-hole cap installed and inserted in the retaining ring. The tube from the collecting funnel is reinstalled firmly so that the flanged collar is tight against the top to prevent in-leakage.

The total precipitation amount is determined from the Taylor gage and its water (if sufficient) also collected for pH determination.

NOTE: It is anticipated that pre-rain cleaning of the large collector system may be crucial to the experiment.

Table 1. Measurement of the pH in Precipitation at National Airport, Washington, DC (taken from Public Health Service Statistics).

Month	1959	1960
Jan		4.1
Feb		4.0
Mar		5.0
Apr		4.0
May		5.5
Jun	4.3	4.4
Jul	4.3	6.2
Aug		4.1
Sep		
Oct	4.3	
Nov	4.5	
Dec		

Table 2. pH Measurements made on Monthly Samples at Sterling, Virginia

Month	1960	1961	1962	1963	1964
Jan		4.7	4.2	5.3	5.4
Feb		4.5	4.4	5.2	4.3
Mar		4.5	4.5	4.3	4.4
Apr		4.7	4.0	4.1	4.1
May		5.5	3.9	4.6	4.6
Jun		5.3	3.9	4.3	
Jul		4.7	6.9	4.2	
Aug		4.6	6.9	4.4	
Sep	4.5	4.2	6.2	4.8	
Oct	5.2	4.3	6.7	5.7	
Nov	5.4	4.2	5.3	4.7	
Dec	5.1	4.3	6.4	4.1	
Weighted Average	4.7	4.5	5.3	4.4	4.4

Table 3. pH Measurements Made on Monthly Samples at Washington, DC
CAMP Station

Month	1963	1964	1965
Jan	4.3	3.9	6.4
Feb	3.7	4.6	6.6
Mar	4.0	4.0	4.7
Apr	4.8	4.2	6.5
May	4.2	6.3	
Jun	4.1	5.6	
Jul	3.8	5.7	
Aug	3.9	4.6	
Sep	4.0		4.1
Oct	3.9		3.8
Nov	4.2		6.1
Dec	3.8		5.2
<hr/>			
Weighted Average*	4.0	4.4	4.6
<hr/>			

*Official rain gauge measurements not available.

Table 4. pH Values in the DC Area for 1975.

Date (1975)	MILLER		COTTON		MITCHELL		PACK		GRAMAX		SMITH	
	pH	in	pH	in	pH	in	pH	in	pH	in	pH	in
Jan 6	4.0	0.37	4.0	0.34	4.0	0.38			4.0			
Jan 9	4.2	0.36	3.9	0.45	4.0	0.25			4.0			
Jan 13			4.3	0.63	4.4	0.41			3.3/6.1			
Jan 18-19			4.2	0.44	4.3	0.49	3.9	0.95	4.0			
Jan 20			4.1	0.57	4.3	0.49						
Jan 25	4.1		4.3	0.40	4.2	0.41	4.4	0.23	3.7			
Jan 31	3.8	0.32	3.7	0.22	5.1	0.19	3.6	0.21	3.7			
Feb 2					4.2	0.10			4.5			
Feb 5	4.2	0.75	4.5	0.69	4.8	0.86	4.1	0.70	4.0			
Feb 12	3.7		3.7	0.37	3.8	0.44			3.7			
Feb 23-24	4.0		5.4	0.40			4.1	0.48	4.0			
Mar 12	4.0	0.60	4.3	0.47	3.9	0.42			4.0			
Mar 14-15	4.2	1.15	4.1	1.05	4.1	1.36			4.2			
Mar 16-17	4.2	0.47	4.2	0.44	4.0	0.46	3.8	0.49	3.9			
Mar 18	4.2	1.73	4.5	1.59	3.7	1.39	4.3	1.31	4.3			
Mar 23	3.7	0.64	3.6	1.08	3.6	0.57	3.8	0.49	3.6			
Mar 30	3.7	0.54	3.7	0.39	4.0	0.43			3.7			
Apr 3									4.3			
Apr 14	4.5	0.47	4.0	0.62	4.2	0.58	4.1	0.60	4.1		3.8	0.55
Apr 24	4.8	0.30			4.7 ⁽¹⁾	0.31	4.2	0.69				
Apr 25			4.1	0.71	3.7	0.74			3.7			
Apr 26			4.4	0.36							3.7	0.60
Apr 29			3.8	0.29	3.6	0.78	3.8	0.94			3.7	0.49
May 1					3.6	0.50						
May 3-5			4.0	1.00	3.7	1.15						
May 12			3.9	0.3	3.9 ⁽¹⁾	0.28			3.6			
May 13									3.8			
May 16	3.9	0.70	3.8	0.49	3.8	0.90	5.4 ⁽¹⁾	0.28	3.7			
May 22			3.3	0.46	3.8	0.90	3.5	2.15	3.6		3.6	2.03
May 24			3.3	0.21					3.6		3.7	0.60
May 25			3.7	0.31								
May 31							4.6	0.36			4.2	0.49

(1) Visible contamination in sample.

(2) Hubbard Brook (upper number)/Taylor gauge (lower number)

(3) Hailstones (~1/2" diameter) gave 6.4 pH.

Table 4. (Continued).

Date (1975)	MILLER		COTTON		MITCHELL		PACK		GRAMAX		SMITH	
	pH	in	pH	in	pH	in	pH	in	pH	in	pH	in
June 1			4.4	0.51	4.2	0.27			4.3			
June 5-6			4.0	0.60	3.8	0.35			4.2			
June 11-12	4.5	0.50	3.9	0.20	3.9	0.86	3.9	0.43	3.9		3.8	0.67
June 13	4.2	0.74			3.9	0.86	4.0	0.54	3.8			
June 20							4.1	0.10				
June 26	3.8	0.30	3.6	1.22			3.5	0.35	3.7			
June 27			4.8	0.20								
June 28	3.9										4.0	1.04
July 4					3.8	0.51	3.7	0.41				
July 8			4.5	0.35					3.8		4.1	2.65
July 9	4.6		3.7	0.15								
July 10 ⁽³⁾			4.0	1.22	4.1	2.14	3.6	1.06			3.9	1.15
July 13			4.7	2.94	4.7	2.57	4.3	0.33	4.6		4.6	4.70
July 14			4.6	1.63	4.6	1.08	4.5	3.42				
July 15	4.4		4.6	0.51					4.1			
July 16	4.0						4.7	0.34				
July 20			4.6	1.34	4.8	0.34			4.4		4.6	1.05
July 21							4.5 ⁽²⁾					
							4.5	1.61				
July 25							4.5 ⁽²⁾					
							4.4	0.38				
July 27							3.6	0.04				
July 29							3.5 ⁽²⁾					
							3.5	2.7				
Aug 5	3.9	0.56			4.5	0.77	4.3 ⁽²⁾		4.0		4.1	0.69
							4.3	0.41				
Aug 6	4.0						4.1	0.14	4.5			
Aug 7							3.7	0.08				
Aug 11					4.1	0.44	3.6	0.03				
Aug 14			4.1	0.69			4.1	1.24	3.8			
Aug 15							4.1	1.24	4.0			
Aug 16	4.0	1.25	3.9	0.27			4.1	1.24	4.0			
Aug 17			3.6	0.45			4.1	1.24	4.0		3.9	0.75
Aug 18							4.1 ⁽²⁾					
							4.1	0.28				
Aug 23							4.0	0.43				
Aug 25							3.4	0.04				
Aug 30	4.2	3.10							4.3			
Aug 31	4.2	2.25					4.1	3.10	4.3		4.1	3.22

Table 4. (Continued).

Date (1975)	MILLER		COTTON		MITCHELL		PACK		GRAMAX		SMITH	
	pH	in	pH	in	pH	in	pH	in	pH	in	pH	in
Sep 1							4.0	0.53			4.2	1.37
Spe 4							3.9	0.05				
Sep 6			3.8	0.20			4.7	0.29				
Sep 12	5.0	0.30			4.5	0.51	5.0	0.30				
Sep 13-14	5.1	0.51	4.5	0.28			5.0	0.32	4.2			
Sep 17	4.6	0.87			4.9	1.01						
Sep 19			4.5	0.95			4.7	1.07	4.8		4.7	0.9
Sep 23	4.3	1.52	4.1	1.27			4.5	1.44	4.4		4.3	1.50
Sep 24	4.3	1.32	4.2	1.60			4.4	1.11	4.6		4.3	1.60
Sep 25	4.6	1.42	4.1	1.37			4.4	1.29	4.3		4.2	1.42
Sep 26	4.6	6.00	4.1	2.51			4.7	4.10	4.7		4.6	6.32
Sep 27			5.3(1)	1.80			4.6	0.31	4.7			
Oct 9	4.7	1.22	4.5	1.40	4.4	1.13	4.4	1.04	4.2		4.7	1.19
Oct 10							3.6	0.09				
Oct 17	4.2	1.17			4.1	1.19			4.1			
Oct 18			4.1	0.80					4.0			
Oct 25							5.2	0.27				
Oct 30			3.6	0.24								
Nov 8			4.2	0.33			4.5	0.46				
Nov 10									4.1			
Nov 13	4.2	1.56	4.0	1.42	4.2	1.67			4.3		4.6	1.75
Nov 21									4.0			
Dec 1									4.0			
Dec 7			4.1	0.15					3.9			
Dec 9-10			4.0	0.33	3.9	0.62			3.9		4.1	0.52
Dec 26	4.4	1.33	4.4	1.03	4.3	1.27			4.0		4.5	1.22
Dec 31	4.2	2.39	4.3	2.25					4.0			

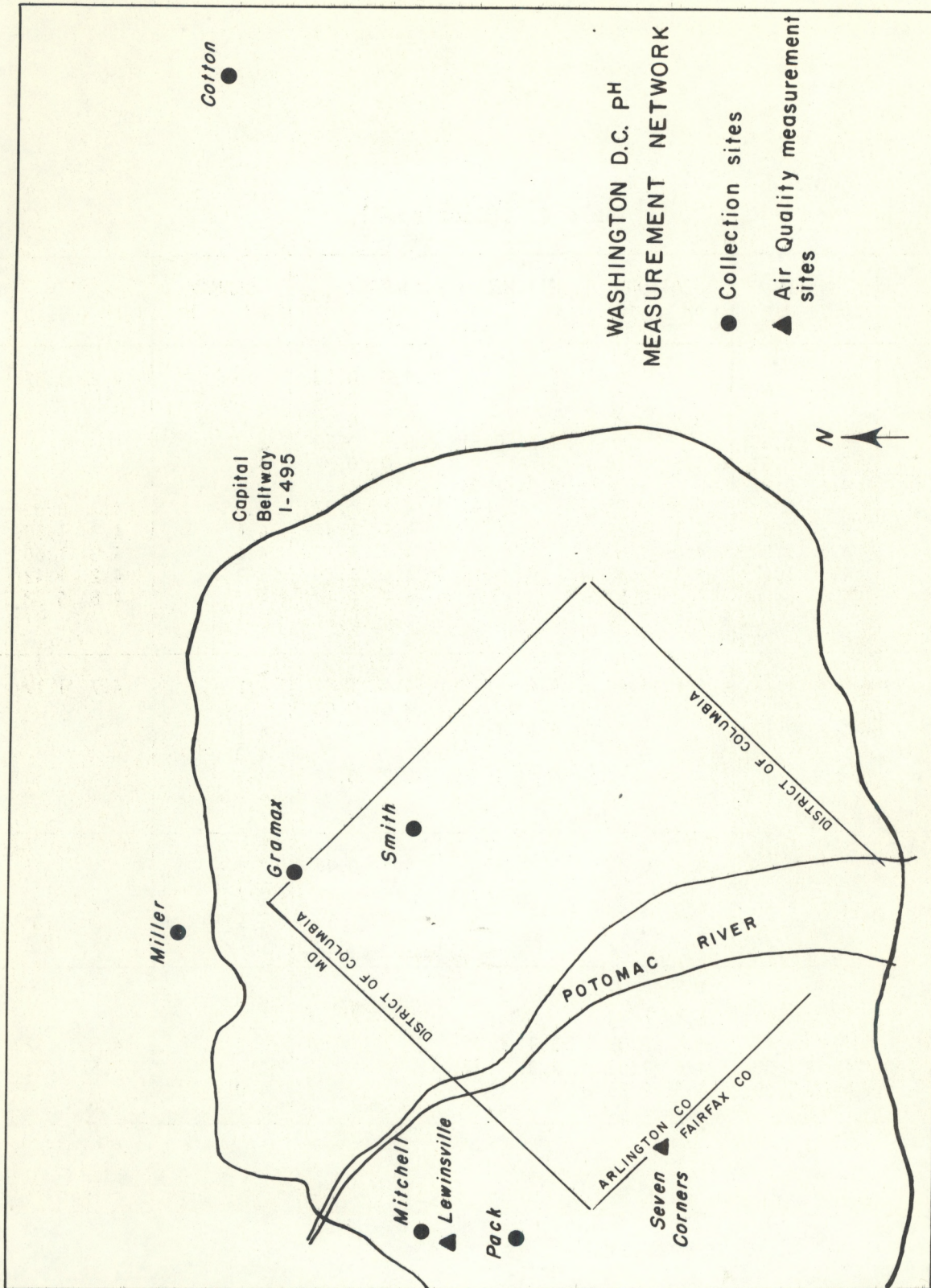


Figure 1. Site locations in the Washington, DC pH Measurement Network.

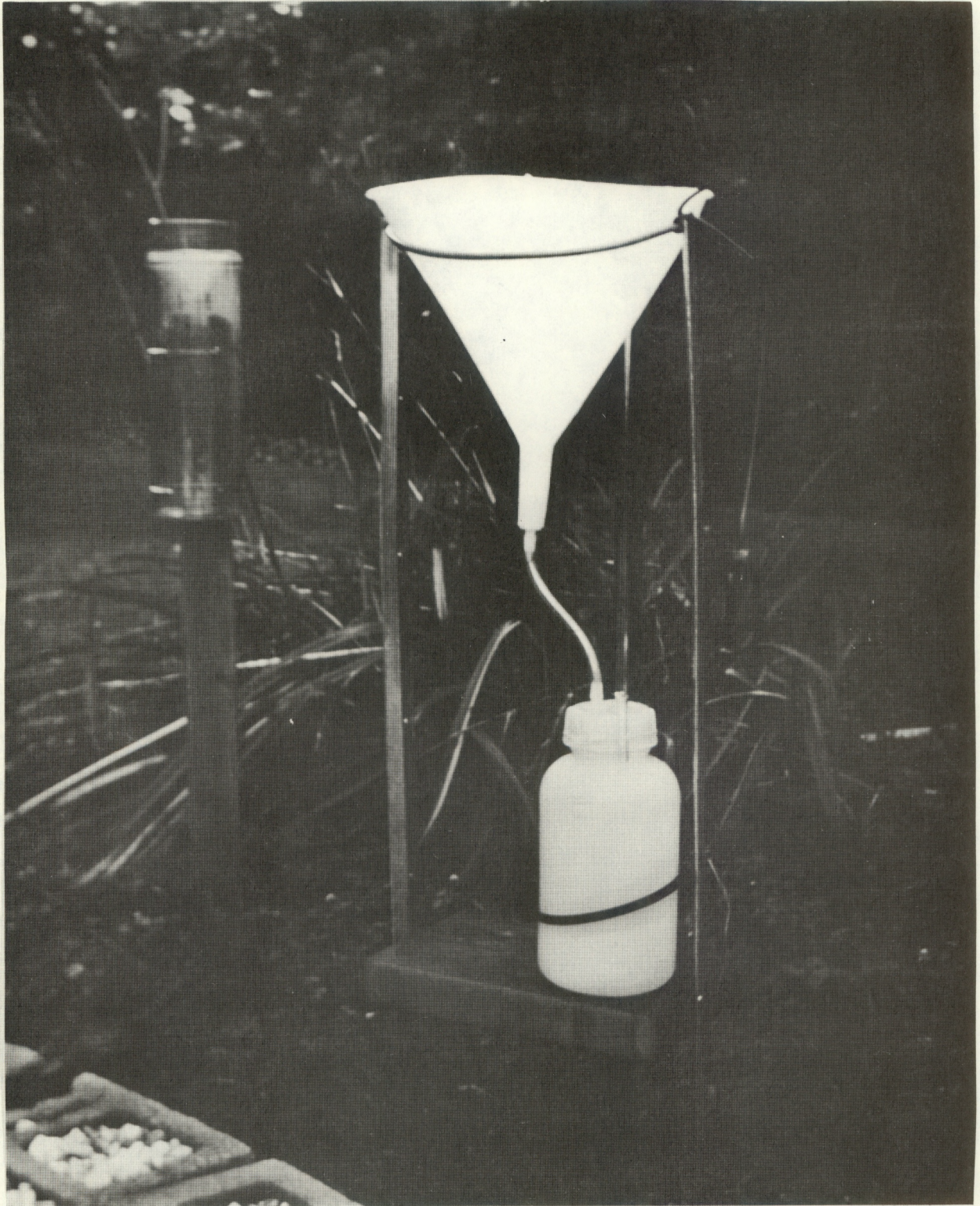


Figure 2. Hubbard-Brooke-type precipitation collector.

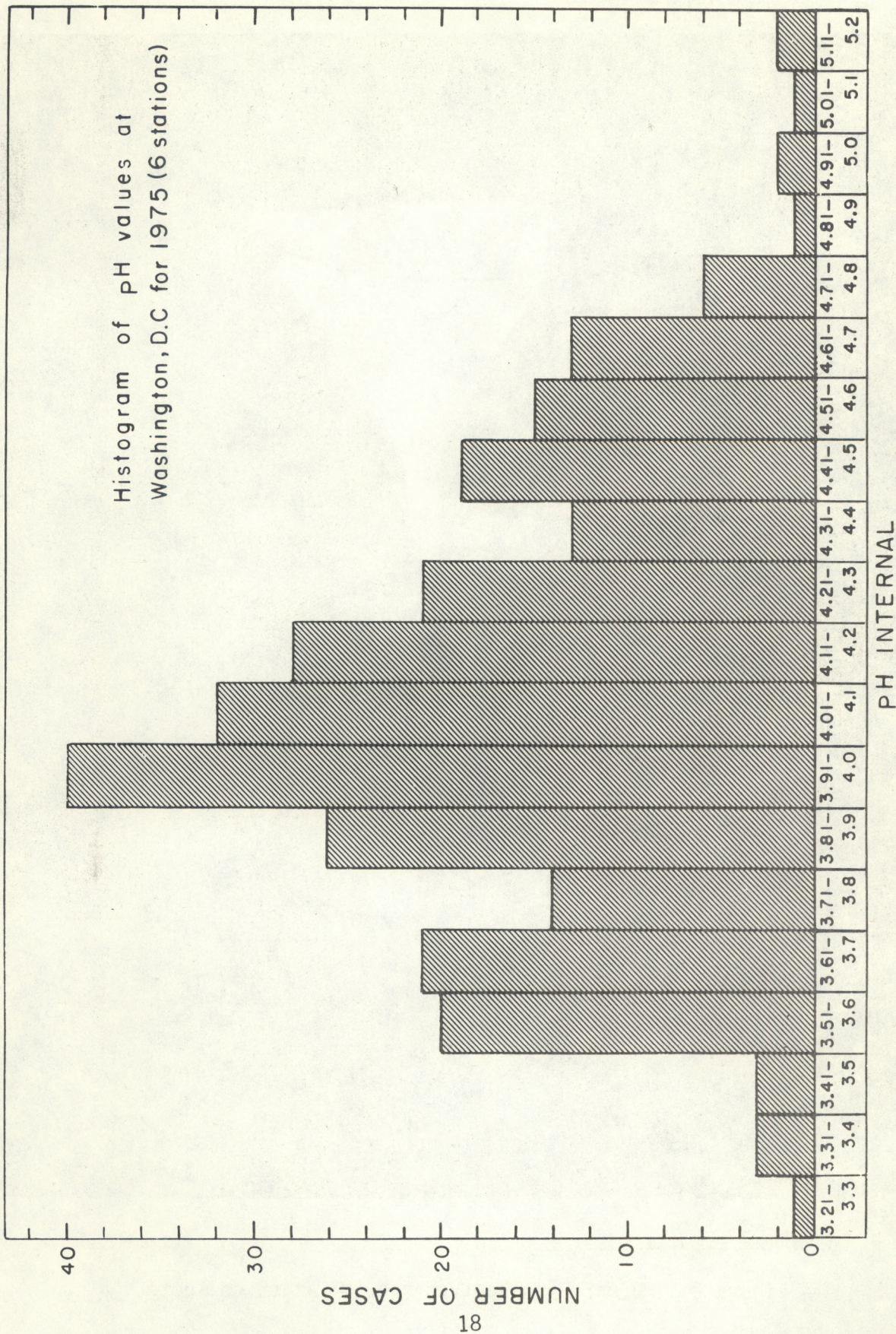


Figure 3. Histogram of pH values at Washington, DC for 1975 (6 stations).

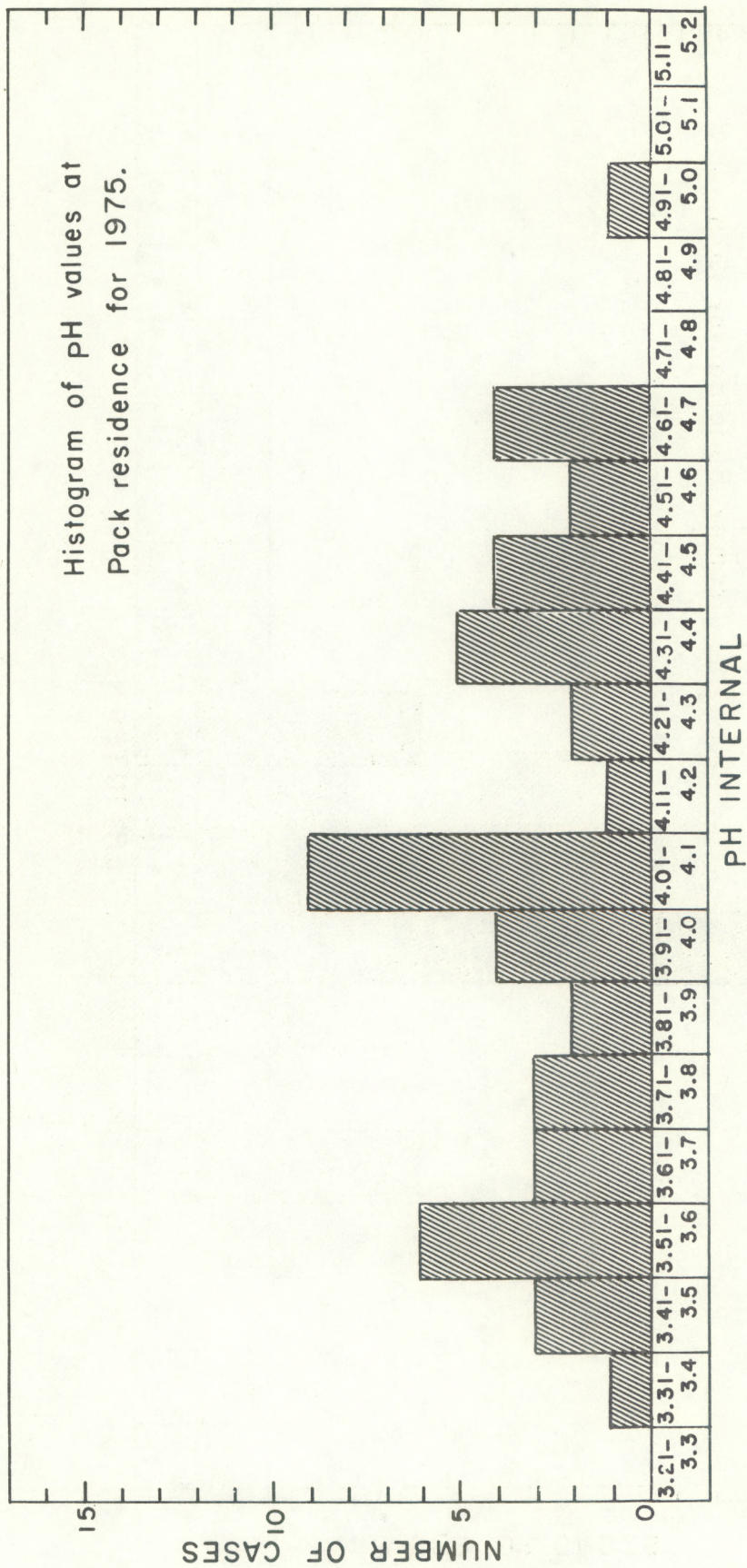


Figure 4. Histogram of pH values at Pack residence for 1975.

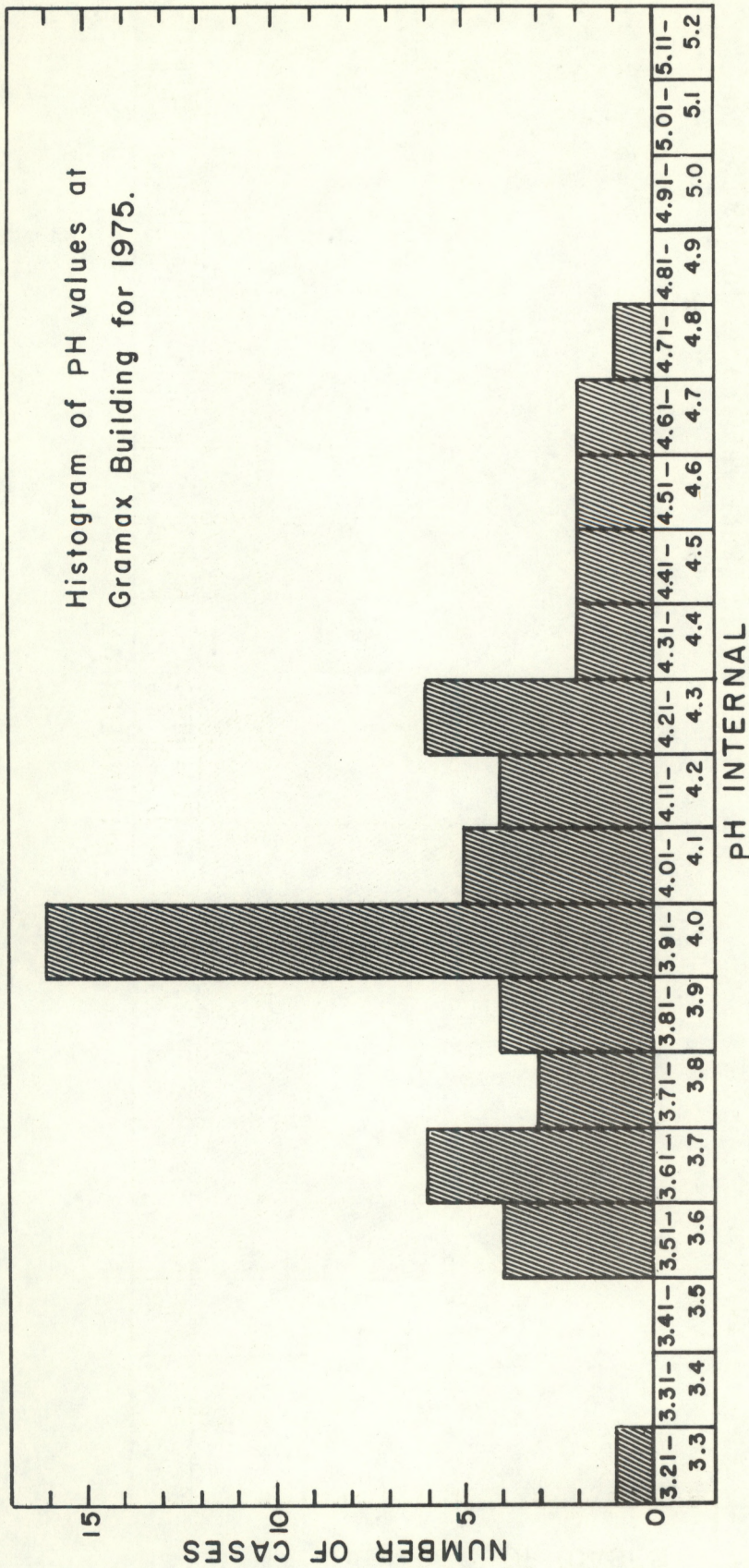


Figure 5. Histogram of pH values at Gramax Building for 1975.

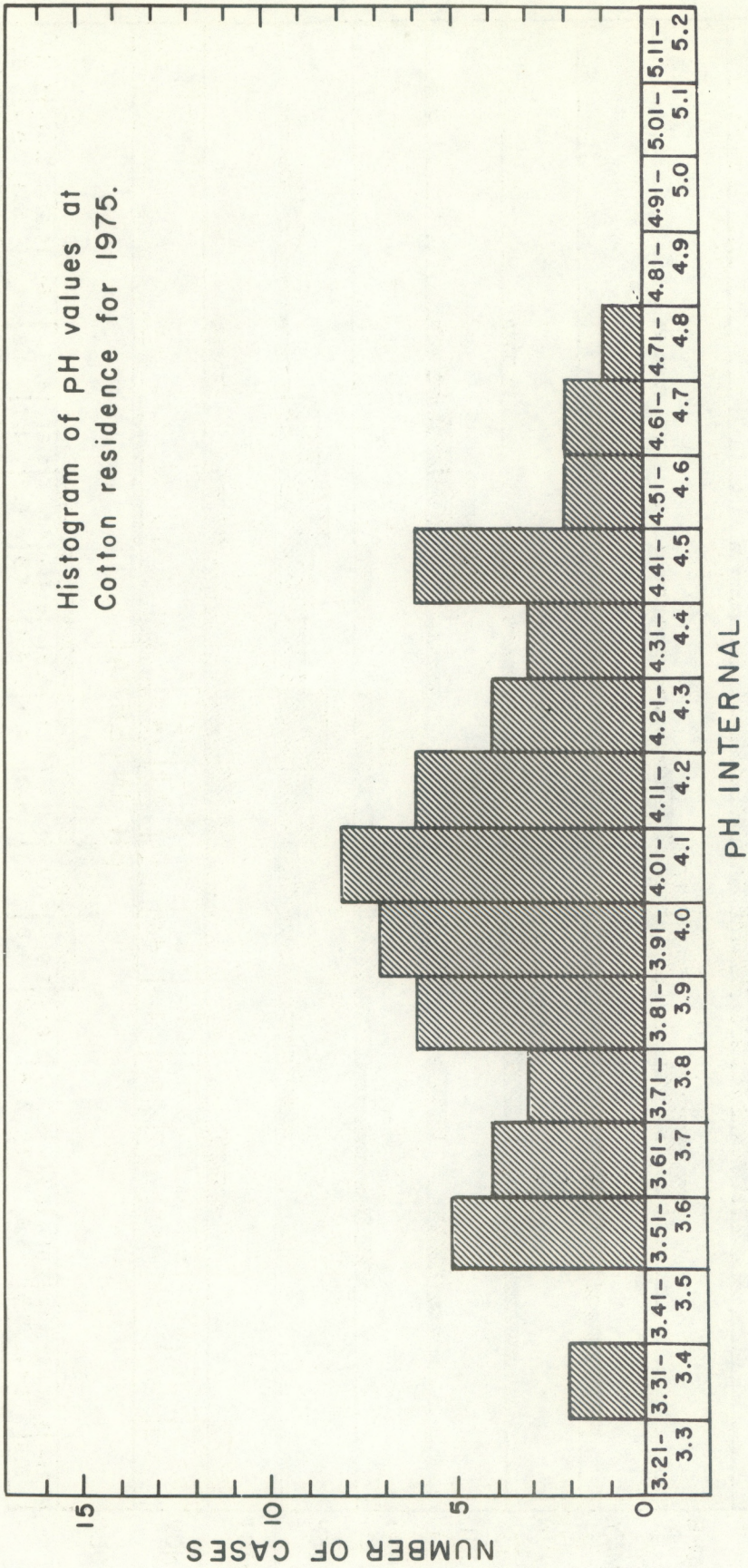
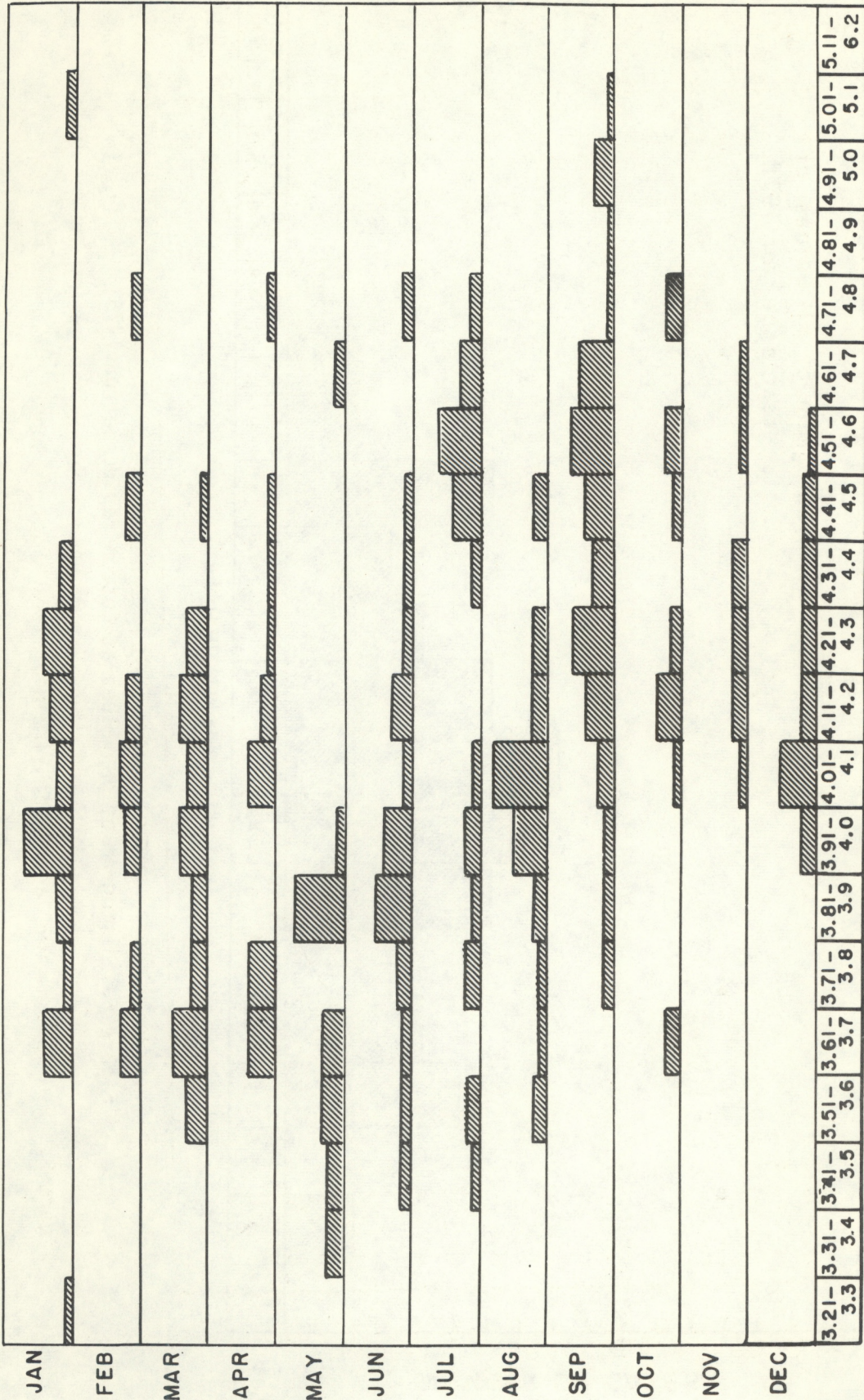


Figure 6. Histogram of pH values at Cotton residence for 1975.

ALL PH VALUES FOR 1975



PH INTERNAL

Figure 7. Histogram of monthly pH values for all Washington, DC stations in 1975.

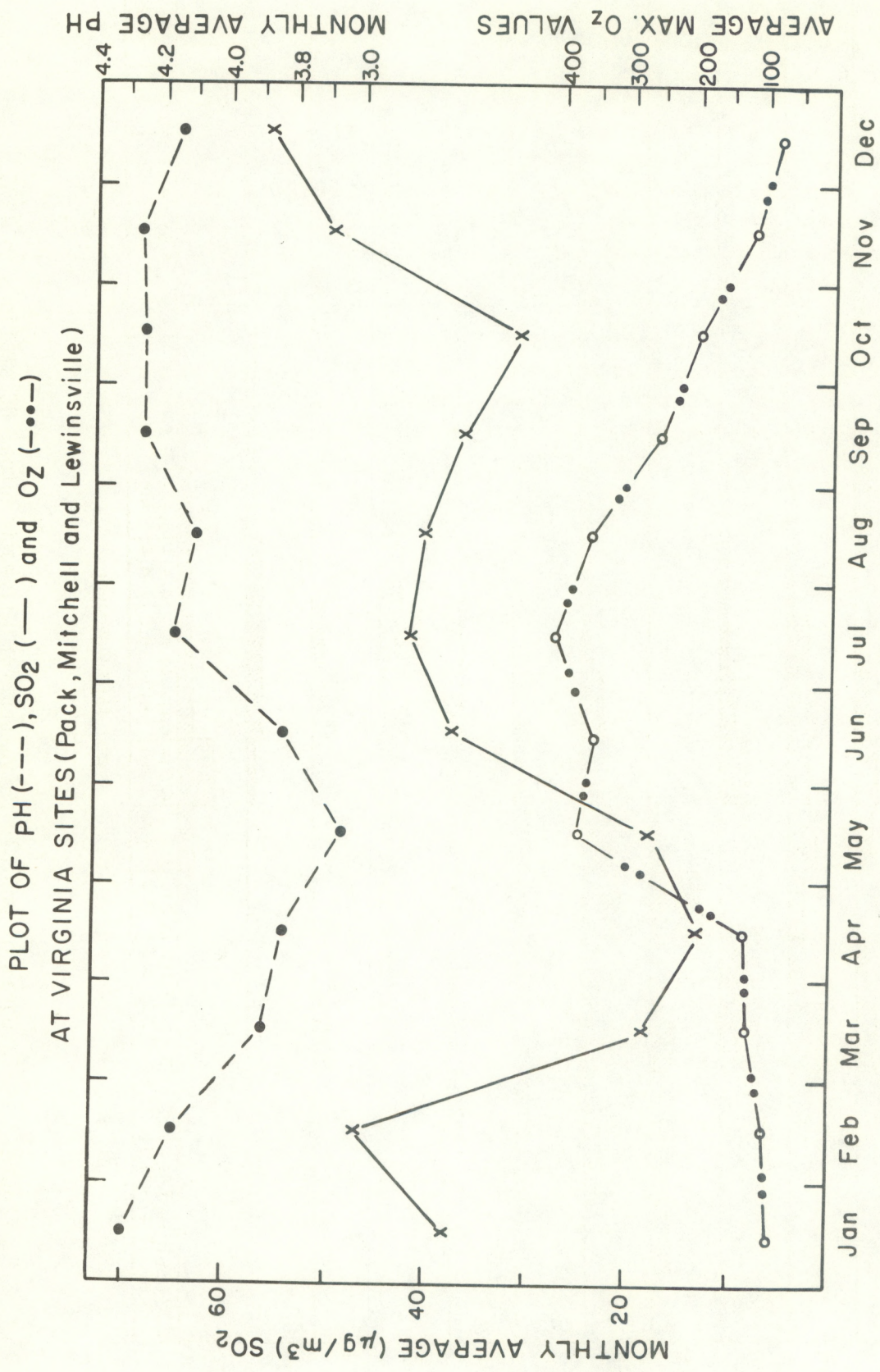


Figure 8. Plot of pH, SO₂, and O₂ at Virginia Sites (Pack, Mitchell and Lewinsville).