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WET DEPOSITION IN THE NORTHEASTERN UNITED STATES

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WET DEPOSITION IN THE NORTHEASTERN UNITED STATES

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December 1980

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Abstract

Attempts are made to examine concentration and wet deposition of pollutant material at selected stations within the northeastern United States and to characterize as many events as possible with respect to air mass origin. Further attempts are made to develop a regional pattern for the deposition of dominant ion species.

MAP3S data for 1977-1979 are used to determine concentration and deposition on an event basis from which monthly, seasonal, annual, and cumulative averages are developed.

The ARL-ATAD trajectory model is used to characterize individual events as to air mass origin. Case studies are examined to illustrate variability in the chemical composition of precipitation originating from distinctly different air mass trajectories. A difference in concentration of pollution-related ions in precipitation is noted between "Midwest/Ohio Valley" and "Great Lakes/Canadian" air mass origins for carefully selected cases.

Total deposition of the major ions is examined in an effort to develop a regional pattern for deposition over a period of at least one year. For that purpose, total deposition is normalized to remove the variability in precipitation amounts for inter-station comparison. No marked gradient is noted in the normalized deposition totals within the northeast of the United States. The Adirondack region exhibited the lowest normalized ion deposition value, while the Illinois station showed the highest of the MAP3S network.

The data analysis suggest that the acid rain phenomena covers the entire northeast. The concept of large scale mixing or a "regional superbowl" emerges to account for the lack of a significant gradient in the normalized deposition.

CHAPTER 1

HISTORICAL REVIEW OF ACID PRECIPITATION

In recent years precipitation chemistry, and acid precipitation in particular, has attracted attention in the scientific community as well as the general public. Acid precipitation is generally accepted as an international phenomena, thus stimulating cooperation between various countries and organizations.

The most accepted definition of acid precipitation is that which has a pH below 5.6, or the lowest pH that could be produced by carbonic acid if pure water were in equilibrium with atmospheric carbon dioxide at 25°C (Barrett and Brodin, 1955). This equilibrium is expressed by:

$$CO_{2(gas)} + H_2O_{(liquid)} \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^-$$

However, generally and particularly in cases of "rain with high acidity" a significant amount of H^+ present is attributable to other components including sulfuric and nitric acids (Cooper et al., 1976).

The European community was the first to recognize the need for chemical analysis of the air and precipitation. John Evelyn (1661) was one of the first researchers to address atmospheric pollution and proposed solutions to the problem which included taller chimneys, increased distance between source and receptor, consideration of prevailing winds, and topographic obstacles. Miller (1905) credits Marggraf with conducting the earliest precipitation chemistry measurements of rain and snow in Berlin, 1761-1767, in which he measured nitric acid, chlorine, and lime.

However, it wasn't until the middle of the 19th century until a concerted effort was undertaken to establish monitoring networks and seriously study air quality. Marchand (1852) recognized the need to include both rain and snow to provide the complete annual description of precipitation chemistry. Chatin (1852) noted an increased chlorine content in the rain with maritime trajectories as origin and also proposed dew and mist as deposition mechanisms.

Robert Angus Smith (1872) published an extraordinary work entitled Air and Rain: The Beginnings of a Chemical Climatology in which he first used the terminology "acid rain." This comprehensive text examines precipitation chemistry at various global locations, air quality at various locations and environs, and the effect of both air and water pollution. The work of Smith is especially noteworthy not only because it provides an early history of spatial variability in precipitation chemistry, but it is also extremely comprehensive in that the analysis includes sulphates, ammonia, nitric acid, free acid, and chlorides as illustrated in Table 1.

One of the main thrusts of the work of Smith was to show the variability of air and water quality, particularly between rural and city environments as shown in Table 2.

Unfortunately, the work of Smith went essentially unnoticed until recently when he received the credit he so rightly deserves.

Around 1850 a monitoring network was established at Rothamsted, England, which provided a continuous source of precipitation chemistry measurements for the next 50 years. Lawes et al. (1881, 1883) were the first to present a detailed report of these collections by studying daily and monthly concentrations of nitrogen, ammonia, and sulfuric acid. Although they noted the direction of the wind at the time of collection, correlations between daily concentrations and direction was inconclusive. Sulfuric acid deposition was found to be equally distributed between winter and summer while two-thirds of

TABLE 1

Manchester Rain-Water Collected during 1869
Acids (Combined and Free) and Acidity

		Hydrochloric Acid		Sulphuric Acid (Anhydrous)			Acidity Calculated as Sulphuric Acid (Anhydrous)	
Date		Grains per Gallon	Parts per Million	Grains per Gallon	Parts per Million	Proportion-Hydrochloric to Sulphuric Acid	Grains per Gallon	Parts per Million
January	(a)	.5110	7.30	5.6000	80	1 to 10.96	2.3087	32.98
February	"	.6387	9.12	2.9400	42	1 " 4.60	1.6930	24.20
March	"	.7300	10.43	7.3500	105	1 " 10.07	1.3664	19.52
April	"	.3006	4.29	3.6750	52.50	1 " 12.22	.5465	7.81
May	"	.3193	4.56	2.9400	42	1 " 9.20	1.4347	20.49
June	"	.5677	8.11	3.2666	46.67	1 " 5.75	.9565	13.66
July	"	.3931	5.62	3.2666	46.67	1 " 8.31	.4782	6.83
August	"	.3006	4.29	2.9400	42	1 " 9.78	.7857	11.22
"	(b)	.1460	2.08	2.9400	42	1 " 20.14	None	None
"	(c)	.2044	2.92	1.7294	24.71	1 " 8.46	-	-
September	(a)	.3407	4.87	3.2667	46.67	1 " 9.59	.4441	6.34
"	(b)	.2555	3.65	1.9600	28	1 " 7.67	None	None
"	(c)	.2044	2.92	.9800	14	1 " 4.79	.0683	.98
October	(a)	.4258	6.08	3.7800	54	1 " 8.88	1.1273	16.10
"	(b)	.3931	5.61	1.5474	22.11	1 " 3.94	.1366	1.95
"	(c)	.5678	8.11	1.5474	22.11	1 " 2.72	.1366	1.95
November	(a)	.7862	11.23	2.9400	42	1 " 3.74	.3074	4.39
"	(b)	.7300	10.43	4.2000	60	1 " 5.73	.0842	.49
"	(c)	.6012	8.60	1.4700	21	1 " 2.44	.1025	1.46
December	(a)	.1022	1.46	.9187	13.12	1 " 8.99	.1879	2.68
"	(b)	.3194	4.56	2.9400	42	1 " 9.20	.3416	4.88
"	(c)	.2222	3.17	1.9600	28	1 " 8.82	.3758	5.37
Mean		.4118	5.88	2.9163	41.66	1 to 7.08	.5833	8.33
Mean of (a)		.4513	6.45	3.5736	51.05	1 " 7.91	.9697	13.85
Mean of (a) from August		.3911	5.59	2.7691	39.56	1 " 7.08	.5705	8.15
Mean of (b)		.3688	5.27	2.7175	38.82	1 " 7.37	.1025	1.46
Mean of (c)		.3600	5.14	1.5373	21.96	1 " 4.27	.1708	2.44

(a) Behind the laboratory, 12 ft. above the ground
(b) Same place, 30 ft. above the ground
(c) Behind the Literary and Philosophical Society, George Street, 2 ft. above the ground

TABLE 2

Averages. Hydrochloric Acid (Chlorides)

Rain Obtained from	Grains per Gallon	Parts per Million
Darmstadt	.0681	.97
London, specimens for 1869	.0872	1.25
German specimens	.0919	1.31
Birkenhead, Liverpool	.2217	3.17
Scotland - Inland country places	.2357	3.37
Near an Alkali Works	.2380	3.40
England - Inland country places	.2795	3.99
Manchester, 1870	.4055	5.79
Manchester, average of 1869 and 1870	.4086	5.83
Scotland - towns (Glasgow not included)	.4102	5.86
Manchester, 1869	.4118	5.88
Newcastle-on-Tyne	.5678	8.11
England - towns	.6093	8.70
Glasgow	.6282	8.97
St. Helen's	.6670	9.53
Liverpool	.7110	10.16
Scotland - Seacoast country places, west	.8600	12.28
Scotland - Seacoast country places, average of east and west	.8819	12.59
Scotland - Seacoast country places, east	.9039	12.91
Runcorn	1.8022	25.74
Waterloo, near Liverpool	2.5550	36.50
Ireland - Valentia	3.4067	48.67
England - Seacoast country place, west (only one)	3.9308	56.15

TABLE 2 (Continued)

Averages. Sulphuric Acid (Sulphates)

Rain Obtained from	Grains per Gallon	Parts per Million
Scotland - Inland country places	.1444	2.06
Ireland - Valentia	.1911	2.73
Scotland - Seacoast country places, west	.2529	3.61
England - Inland country places	.3865	5.52
Scotland - Seacoast country, avg. of E and W	.3947	5.64
England - Seacoast (west) country	.4116	5.88
Scotland - Seacoast country places, east	.5366	7.66
Waterloo, Liverpool	.8004	11.43
German specimens	1.1481	16.40
Scotland - towns (Glasgow not included)	1.1553	16.50
London, 1869	1.4345	20.49
Birkenhead, near Liverpool	1.6210	23.16
Runcorn	1.6537	23.62
Darmstadt - Germany	2.0417	29.17
St. Helen's	2.3232	33.19
England - towns	2.3988	34.27
Liverpool	2.7714	39.59
Manchester, 1869	2.9163	41.66
Newcastle-on-Tyne	3.1111	44.44
Manchester, average of 1869 and 1870	3.1378	44.82
Manchester, 1870	3.3593	47.99
Glasgow	4.9139	70.19
Near an Alkali Works	5.1310	73.30

the chlorine was deposited during the winter months. The average value for SO_3 averaged over two years was 2.41 ppm amounting to 18.5 lbs. deposited per acre per year. The winter chlorine deposition maxima was later verified by Kirch (1887, 1900) with the winter/summer ratio being approximately 1.5 averaged over 26 years.

Miller (1905) continued the work at Rothamsted, as well as comparing nitrogen, chlorine, and sulfuric acid for various locations and demonstrated large global variations in concentration and deposition as shown in Tables 3-5.

Crowther and Ruston (1911) showed that "smoke-infested localities" such such as Garforth, England, exhibit considerably higher average deposition values than do the relatively clear rural environments such as Rothamsted, with sulfur deposited being five times higher. Coal combustion was proposed as the mechanism for the increased level of impurities. Free acid was also examined producing evidence that winter rainfall was twice as acidic as summer for that locale due to the highly acidic fogs that linger in the winter months. The increased level of free acid in the atmosphere was also found to have a detrimental effect on plants by direct action and indirectly reducing ammoniacal fermentation of the soil humus.

Masson et al. (1917) found that the amount of rainfall in Australia varied inversely with the concentration of oxidized nitrogen while there was no correlation between the total amount of nitrogen and total rainfall.

North American researchers also recognized the need to study precipitation chemistry. Shutt et al. (1917) found a maximum nitrogen deposition in April and May in Ottawa, Canada, and surmized this was beneficial since crops were normally fertilized at this time. However, no consideration was given to the fact that the high levels of nitrogen might be a result of the fertilization. MacIntire and Young (1923) found no evidence that precipitation

TABLE 3

Nitrogen as Ammonia and Nitric Acid in Rain

			Nitrogen						
			Per Million		Per Acre Per Annum			% of Total	
	Date	Rainfall (inches)	as NH_3	as N_2O_5	as NH_3 (lb.)	as N_2O_5 (lb.)	Total (lb.)	as NH_3	as N_2O_5
Rothamsted	1888-9 1900-1	27.25	0.440	0.183	2.71	1.13	3.84	70.6	29.4
Copenhagen (114)	1880-5	21.95	1.97	0.473	9.27	2.21	11.48	80.8	19.2
Gembloux (93)	1889-91	27.23	1.143	0.345	7.07	2.14	9.21	76.8	23.2
Montsonris (67)	1876-1900	21.52	2.13	0.66	10.37	3.22	13.59	76.3	23.7
Mettray (66)	1877	29.90	0.409	-	2.77	-	-	-	-
Dahme (39)	1865	17.09	1.42	0.30	5.50	1.16	6.66	82.6	17.4
Ida-Marienhutte (25)	1865-70	22.65	-	-	-	-	9.92	-	-
Insterburg (39)	1864-6	25.67	0.65	0.38	3.90	2.25	6.15	63.1	36.9
Kuschen (39)	1864-6	14.78	0.48	0.16	1.63	0.55	2.18	75.0	25.0
Proskan (39)	1864-5	17.81	3.21	1.73	12.94	6.97	19.91	65.0	35.0
Regenwalde (39)	1864-7	22.72	2.08	0.62	10.69	3.28	13.97	77.0	23.0
Rostock (53)	1880-1	33.27	0.892	-	6.73	-	-	-	-
Florence (11)	1869-75	38.31	1.004	0.57	8.70	3.09	11.79	73.8	26.2
Vallembrosa (11)	1872-5	59.89	0.617	0.253	8.36	3.46	11.82	70.7	29.3
Scandicci (90)	1888-90	29.18	0.614	0.266	4.06	1.76	5.82	69.8	30.2
Catania (10)	1888-9	18.36	0.327	0.161	1.36	0.67	2.03	66.9	33.1
St. Michele, Tirol (69)	1885-6	43.93	1.188	0.579	11.83	5.76	17.59	67.3	32.7
Libwerd, Bohemia	1877-8	24.41	1.3	0.61	7.18	3.37	10.55	68.1	31.9
Pecek	1883-4 to 1885-6	19.34	1.26	0.50	5.53	2.19	7.72	71.6	28.4
Ploty (122)	1900-3	17.49	0.854	0.061	3.38	0.24	3.62	93.3	6.7
Pretoria (113)	1904*	-	0.68	0.12	-	-	-	85.1	14.9
Tokyo (59)	1883-4	52.67	-	0.093	-	1.11}	2.88	61.6	38.4
"	1885	62.28	0.126	-	1.77	-			
New Zealand (51)	1884-8	29.70	0.076	0.169	0.50	1.13	1.63	30.7	69.3
Kansas (42)	1887-9	29.41	0.393	0.154	2.62	1.03	3.64	71.8	28.2
Mississippi (112)	1894-5	44.11	0.235	0.074	2.35	0.74	3.09	76.0	24.0

TABLE 3 (Continued)

Tropical Rain

			Nitrogen							
			Per Million		Per Acre Per Annum			% of Total	
	Date	Rainfall (inches)	as NH_3	as N_2O_5	as NH_3 (lb.)	as N_2O_5 (lb.)	Total (lb.)	as NH_3	as N_2O_5
Calcutta	1891	46.01	0.172	0.115	1.79	1.20	2.99	59.7	40.3
Madras	1888-93	39.21	-	-	-	-	1.91	-	-
Ceylon (4)	1898-9	82.13	0.196	0.069	3.65	1.28	4.93	72.0	28.0
East Java (75)	1891	(47)	0.11	0.06	1.13	0.71	1.84	61.5	38.5
Mauritius (21)	1895	(70)	0.43	0.40	6.81	6.34	13.15	51.8	48.2
Reunion (88)	1886-7	(40)	-	0.69	-	6.24	-	-	-
Barbados (5)	1885-97	63.95	0.084	0.268	1.22	3.88	5.10	23.9	76.1
Venezuela (71 and 88)	1883-5	(40)	1.55	0.58	14.03	5.20	19.23	72.8	27.2
British Guiana† (52)	1890-1900	102.41	0.055	0.078	1.17	1.82	2.99	39.1	60.9
Campinas (30)	1890	-	0.99	-	-	-	-	-	-

*February to June only

†In part unpublished

TABLE 4

Nitrogen as Nitrous and Nitric Acids in Rain and Snow

		Nitrogen							
		Per Million						Per Acre	
	Rainfall (inches)	as Nitrites			as Nitrates			as Nitrites (lb.)	as Nitrates (lb.)
		Min.	Max.	Mean	Min.	Max.	Mean		
St. Chamas (31)	(20)	0.0	0.316	0.133	0.001	0.716	0.162	(0.60)	(0.73)
St. Chamas (snow)	-	-	-	0.250	-	-	-	-	-
Langres (31)	-	-	-	0.270	-	-	0.881	-	-
Scandicci (90)	27.28	0.0	0.0168	0.0045	0.033	0.729	0.255	0.028	1.687
Catania (10)	18.36	0.0001	0.0027	0.0006	0.035	0.244	0.161	0.003	0.671
Ploty (122)	17.49	0.0	0.025	0.011	0.002	0.178	0.050	0.043	0.197

TABLE 5

Chlorine and Sulphuric Acid in Rain

			Per Million				Per Acre		
	Date	Rainfall (inches)	Chlorine Min.	Chlorine Max.	Chlorine Mean	Sulfuric Acid	Chlorine (lb.)	Sulphuric Acid (lb.)	SO_3 to 1 Cl
Rothamsted	1877-8 1900-1	28.78	0.40	20.10	2.28	2.57*	14.87	17.41*	1.19
Cirencester (60)	1874-1900	30.61	1.15	10.38	3.17	-	21.90	-	-
Scandicci (91)	1889-91	27.67	0.17	31.95	5.63	-	35.35	-	-
Perugia (14)	1886-7	33.96	1.38	40.28	3.15	-	24.22	-	-
Catania (10)	1888-9	18.36	1.47	7.36	5.48	5.02	22.79	20.89	0.92
LaGuardia (79)	1892-3	56.42	7.1	71.9	31.2	-	399.5	-	-
New Zealand (51)	1884-8	29.70	2.6	36.4	8.83	2.22	59.44	14.94	0.25
Barbados (5)	1885-97	63.95	3.55	33.97	8.14	-	127.8	-	-
British Guiana (52)	1890-1900	102.41	(1.68)	(17.68)	5.04	-	116.88	-	-
Ceylon (4)	1898-9	82.13	-	-	9.72	-	180.63	-	-
Calcutta	1894	46.01	1.82	5.44	3.16	-	32.87	-	-
Madras	1888-93	39.21	-	-	4.08	-	36.27	-	-

*1881-87

depleted the soil of bases in Tennessee and also suggested it might even be beneficial. Potter (1930) was one of the first researchers to present his results in terms of pH when reporting his measurements of rain, potable water, and water collected from plants in New England. His values ranged from 5.0 to 7.6 with the lowest values being from potable water.

It became apparent that individual efforts would not be able to provide the complete picture of precipitation chemistry from source to receptor. Scandinavian researchers were the first to recognize the potential environmental impact of acid precipitation, formulate a comprehensive monitoring network, and carefully analyze data. The first organized Scandinavian network was established by Torstensson, Egner, and Angstrom (Emanuelson, Eriksson, and Egner, 1954) and consisted of 28 stations located primarily in southeastern Sweden. This network collected monthly samples during the period October 1, 1947 to September 30, 1950. Eriksson (1952a, 1952b) used this network to develop a relationship between natural and anthropogenic sources of gases and aerosols. Barrett and Brodin (1955) used the data of this rural Scandinavian network to obtain spatial and temporal variations of the acid-alkaline balance of precipitation. Southern Scandinavia was found to be more acidic, particularly during winter months at the time of maximum combustion of fossil fuels and southerly flow from the European continent. This was one of the first proposals of long range transport of pollutants across international boundaries and thereby firmly established acid precipitation as a regional or synoptic problem.

In 1954 the rural Scandinavian network was expanded to include the British Isles as well as all of Scandinavia (Egner and Eriksson, 1955). This marked the first international cooperation on acid precipitation monitoring. This network was later expanded to include stations in France, Germany, and the Soviet Union. This network showed an increased concentration of both sulfate and nitrate. Based on these data Granat (1972) developed a model based on a stoichiometric relation between acids and bases to interpret the amount of acid found in precipitation and predict future depositions of acid by precipitation. Marr and Radke (1971) used the data of two of the Scandinavian stations to study the influence of synoptic weather patterns on the chemical composition of monthly precipitation samples. They found a definite correlation between chloride deposition and frequency of rain-bearing flows in the SSW-NW sector and between sulfur deposition and rain-bearing flows in the SE-SW-NW sector implicating the heavily industrialized regions of England and northern Germany.

Selezneva (1972) used a Russian network similar to that of the Scandinavian system to estimate the background concentrations for different geographical regions of the USSR. He estimated that the background levels account for 30-40% of the total contamination and local sources contribute the remaining 60-70% of which 20-30% are natural sources and the remainder being of anthropogenic origin.

European results regenerated research interest in the United States with Houghton measuring the pH of rain at Brookline, Maine, in 1939 (Likens, 1975). He obtained a value of 5.9 for a single rainstorm. In 1949 Landsberg (1954) measured precipitation pH and obtained for individual raindrops a mean value of 4.2. In 1952-53 Landsberg measured a mean value of 4 for a large number of storms near Boston, Massachusetts. Herman and Gorham (1957) analyzed precipitation at Kentville, Nova Scotia, during the period 1952-54 and found an average value of a pH of 5.7 for all types of precipitation sampled.

Prior to 1955 all precipitation chemistry measurements, both American and European, were ground based well within the boundary layer. Houghton (1955) was the first to recognize that the pH could change between cloud water and that of the precipitation collected at the ground. He made fog and cloud water measurements at four northeastern sites within the boundary layer and one above the boundary layer located at Mount Washington, New Hampshire. His cloud water pH measurements varied from 3.0 to 5.9 with a mean of 4.5 while his mean value of 7.2 for Kent Island was considerably more than that of Herman and Gorham (1957).

The first comprehensive United States network consisting of 67 stations was organized by Junge and operated from July 1955 through July 1956. Junge (1958) and Junge and Gustafson (1956) utilized this network to compute the distribution of ammonia, nitrate, and chloride over the United States during this period. Junge and Werby (1958) later presented concentrations of sodium, potassium, calcium, and sulfate and estimated the average global residence time of SO_4 to be 40 days. Although the Junge network presented data on the majority of the constituents normally considered in precipitation chemistry studies, it failed to record hydrogen and magnesium ions. Cogbill and Likens (1974) attempted to fill this data void by using chemical mass balancing techniques to calculate the pH of the northeastern United States based on the data of the Junge network. Their work established the presence of acid precipitation prior to 1955.

The establishment of the Hubbard Brook Experimental Forest in New Hampshire in 1963 provided an excellent opportunity to study the effect of industrialized centers on the rural environment. Since Hubbard Brook operated for over 10 years, it provided the most comprehensive record of precipitation chemistry in the United States. All measurements were of precipitating clouds with instruments based well within the planetary boundary layer. Based on these measurements Likens et al. (1976) found that sulfate and hydrogen dominated the Hubbard Brook region, with $SO_4^=$ being 2.5 times more prevalent than the next most abundant anion and the hydrogen 5.9 times more common than the next most abundant cation. He characterized the precipitation at Hubbard Brook as a contaminated solution of sulfuric and nitric acid with a pH of about 4.1.

The composition of rainfall from the work of Likens et al. averaged over an 11 year period at the Hubbard Brook Experimental Forest, New Hampshire, is presented in Table 6.

TABLE 6

Composition of Rainfall

(The units are microequivalents per liter of liquid precipitation)

Species	Quantity μeq/liter
$SO_4^=$	59.7
NO_3^-	23.1
Cl^-	14.4
$PO_4^\equiv$	0.25
H^+	73.9
NH_4^+	12.1
Ca^{++}	8.6
Na^+	5.4
Mg^{++}	3.7
K^+	1.9

$$\text{ratio} \frac{H^+ + NH_4^+}{SO_4^= + NO_3^-} = 1.04$$

$$Ca^{++} + Mg^{++} = 12.3$$

The sum of the concentrations of the anions (97.5 μeq/liter) is nearly equal to the sum of the concentrations of cations (105.6 μeq/liter). The standard deviations of the sums (±3.5 μeq/liter) are small enough so that the difference between them is significant at the one sigma level of confidence. It is therefore possible that other unidentified anions with total concentrations on the order of 1.5-16.0 μeq/liter might be present. Likens et al. was one of the first investigators in the United States to maintain a carefully supervised and quality controlled precipitation chemistry network dedicated to determine the flow of material from the atmosphere into a calibrated watershed. Likens et al. observed that there has been a slight upward trend in concentration of hydrogen ion between 1964-1965 and 1970-1971, followed by a downward trend until 1973-1974; overall (1964-1974), however, no trend in concentration is statistically significant (see Figure 1).

A different result was obtained by Dovland et al. (1976) from pH measurements at three Norwegian stations, shown in Figure 2. The decrease, especially in the beginning of the sixties, is quite evident. However, as pointed out by Perhac (1980), British statisticians from the Central Electricity Generating Board have examined the pH data in Figure 2, and found no trend from 1955 to 1964 and none from 1965 to 1977. The cause of the sudden change of pH in 1964-1965 is not known. Changes in method of sample collection (which did happen), the use of different analytical techniques, or changes in natural or anthropogenic emissions are factors to be considered. The average concentration of major ions in the precipitation at two Norwegian sites are presented in Table 7 (Johannessen and Joranger, 1976). It is argued in the OECD (1977) report that a major part of the sulfur compounds deposited in Norway may be traced back to fossil fuel combustion in other European countries.

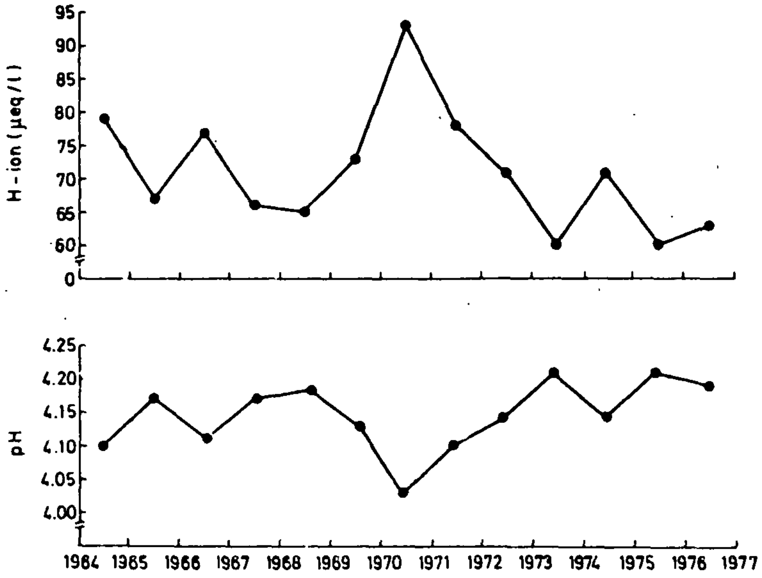

Figure 1. Annual hydrogen ion concentration and pH of precipitation (weighted for volume) at the Hubbard Brook Experimental Forest from 1964 to 1977. (from Likens, 1980)

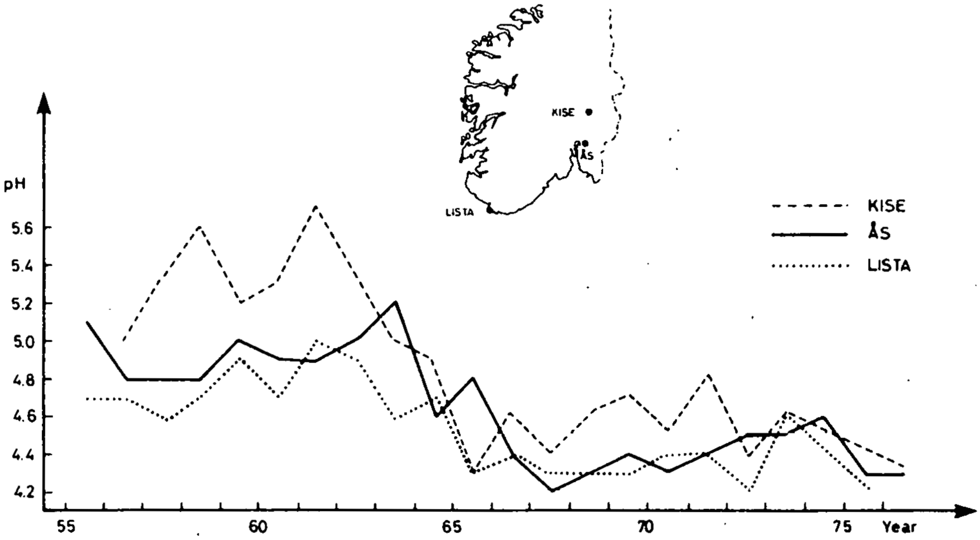

Figure 2. Time variation of annual mean pH of precipitation at three Norwegian stations. The annual mean pH is determined from the total deposition of H^+ divided by the amount of precipitation. (from Seip and Tollan, 1978)

TABLE 7

Average Concentrations (μeq/liter) of Major Ions in the Precipitation at Birkenes in Aust-Agder County (June 1972 to June 1977) and Treungen in Telemark County (September 1973 to June 1975)

	Birkenes*	Treungen
H^+	65	52
Ca	15	7
Mg	17	6
Na	79	26[a]
K	7	2
NH_4	41	26
SO_4	88	59
Cl	61	22
NO_3	44	27

[a] Calculated from the Mg concentration using the Na/Mg ratio in seawater

	Birkenes*	Treungen
$\frac{H^+ + NH_4^+}{SO_4^= + NO_3^-} =$	0.8	0.9
$Ca^{++} + Mg^{++} =$	32	13

*Birkenes is located close to the coast.

The knowledge of pH in precipitation is one important atmospheric chemistry parameter, but certainly not the only one. More important to know, however, is the total composition of the precipitation as was pointed out earlier. Knowledge of ion composition allowed Cogbill and Likens (1974) to calculate the pH for the 24 sites in the eastern United States where Junge collected precipitation with wet-only collectors in 1955-56. The resulting pH isolines are shown in Figure 3.

A large area of the northeastern United States was subjected to acid precipitation by the mid-1950s.

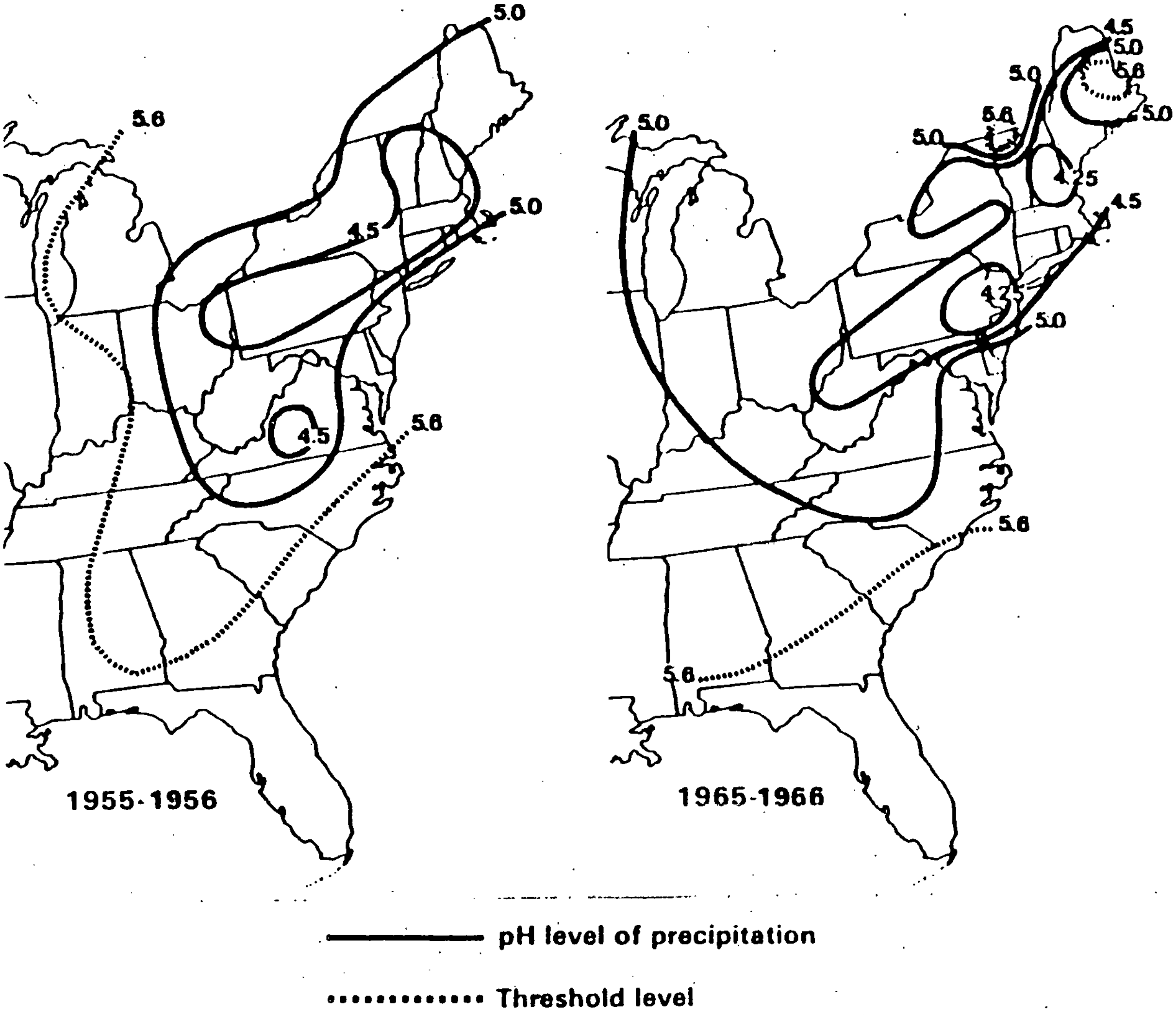

Figure 3. pH comparisons for 1955-1956 and 1965-1966. (Cogbill, 1975b)

The National Center for Atmospheric Research organized the National Precipitation Sampling Network and collected data on a monthly basis from 33 locations across the United States from 1960 to 1966 (Lodge et al., 1968) using wet-only, automatic collectors. The pH values were not included in the final report, but Cogbill and Likens (1974) again used chemical balancing techniques with the combined data of Lodge et al. (1968), Gambell and Fisher (1966), and Pearson and Fisher (1971) to calculate pH for the eastern United States for 1965-66. The vast majority of monthly pH values for stations west of the Mississippi River were consistently greater than 5.6. In contrast, monthly values east of the Mississippi River were much more acidic as shown in Figure 3. A comparison of the 1955-56 and 1965-66 isopleths prepared by Cogbill and Likens (1974) shows a marked increase in acidity over the entire eastern half of the United States from 1955 to 1966, with New England being the most acidic region. This alleged spreading of the area affected by acid precipitation was recently questioned by Perhac (1980) on the basis one should use data for trend analysis only from stations which are the same for the different time period. In comparing the 1955-56 and 1965-66 maps (Figure 3), he noted that only 10 stations are common despite the fact that the maps report data from a large number of sites. For those 10 common sites, the acidity increased at four (pH went down), decreased at two and remained unchanged at four. The difference in the precipitation chemistry for a rural, east central Illinois site between 1954 and 1977 was investigated by Stensland (1977) to ascertain whether or not the precipitation became more acidic and, if so, why. The two data sets were collected from October 26, 1953, to August 12, 1954, and from May 15, 1977 to February 6, 1978. For the 1977 study, an automatic wet/dry collector of the HASL design was used on a 24-hour event basis. The 1977 measured median pH was 4.1, as compared with the calculated median pH of 5.9 for the 1954 data. The more basic precipitation in 1954 could have resulted from low levels of acidic ions (e.g., sulfate and nitrate) or from high levels of basic ions (e.g., calcium and magnesium). The comparison yields:

	1954	1977
$SO_4^=$	60	70 μeq/liter
NO_3^-	20	30 μeq/liter
$Ca^{++} + Mg^{++}$	82	10 μeq/liter

With these data there can be little question that the samples in 1954 were much more basic than the 1977 samples. Although both $SO_4^=$ and NO_3^- were apparently lower in the 1954 samples, it was the high levels of soil related species, Ca^{++} plus Mg^{++} (the "hardness"), which produced the high pH in 1954. If the Ca^{++} plus Mg^{++} levels in 1954 had been 10 microequivalent per liter as they were in 1977 at the same site, the calculated pH would have been 4.18, i.e., almost identical to the current 1977 measured pH of 4.1.

The possibility exists, as demonstrated by Stensland (1977) that more calcium and magnesium were present in the atmospheric aerosols in 1954 than in 1977 or that the atmospheric particle loading was higher then. To what extent this "local" conclusion can be extended to the northeastern part of the United States is unknown, so are the meteorological factors that might have contributed to the possible higher atmospheric dust loadings.

Interest in acid rain as an atmospheric chemistry, environmental and ecological issue has dramatically increased in the 1970s, with contributions from individual investigators and from research consortia operating mesoscale precipitation chemistry networks.

In an effort to determine background pH values, Cooper (1976) found the normal rainfall pH over Texas to be 6.5 to 6.6, with extreme variations ranging from 5.8 to 7.3. He also found that the pH decreased as the alkaline $CaCO_3$-bearing particulates were removed. Tabatabai and Laflen (1976) found an average pH of 6.2 in Iowa with high sulfate concentrations. Hoeft et al. (1976) found a similar sulfate dominated rain with the same general values of pH for Wisconsin. Feth et al. (1964) was one of the first American researchers to study the pH of snow, reporting a median of approximately 6.0 for stations in California, Utah, Colorado, Oregon, and Arizona.

Even today there is no high density, synoptic coverage of precipitation chemistry in North America, and the lack of historical data on precipitation composition limits the ability to determine man's effects on the chemical composition of the atmosphere. Currently, programs in Canada and the United States have begun to measure the composition of atmospheric deposition on a long-term basis. These include the Canadian Network for Sampling Precipitation (CANSAP--initiated in 1976), and the United States National Atmospheric Deposition Program (NADP began to collect weekly samples in July 1978), and the United States Multistate Atmospheric Power Production Pollution Study (MAP3S began to collect precipitation on a 24-event basis in October 1976).

The quality and quantity of data available today are highly variable. Nevertheless, the general patterns of spatial distribution of acid precipitation--as a consequence of man-induced and/or natural changes--are reasonably consistent and clear, providing mounting evidence on changes in the ionic composition of precipitation over the past 30 years.

A unique "quality control" comparison was performed by Pack (1980) comparing the results of two overlapping precipitation collection networks: the eight-site MAP3S and the nine-site Electric Power Research Institute networks. Both networks collected precipitation for individual storms (24-hour "events"). There are differences between the two networks including collectors, operators and analytical laboratory procedures (Battelle Pacific Northwest for MAP3S and Rockwell International for the EPRI data). The comparison period extended from August 1978 through June 1979. Table 8 shows the results for five ions and for two different H^+ determinations.

The two networks produce almost identical averages for $SO_4^=$, NO_3^- and NH_4^+. The largest differences for NH_4^+ is only 7% when the coastal sites are included but only 1% for the set of noncoastal locations. In view of the many variables that might have created differences, agreement to within 10% supports data comparability. However, the Cl^- and Na^+ concentrations show significant differences that are likely due to an as yet unidentified system difference. The behavior of the pH data, expressed as H^+_{field} and H^+_{lab} in Table 8 is intriguing. There are differences between the field pH (measured immediately after collection) and laboratory pH (measured days or weeks later as part of the full chemical analysis) in both networks. Kadlecek and Mohnen (1975) first called attention to this now well-established phenomena. Since Pack's (1980) analysis indicated that the two networks produced comparable data for $SO_4^=$, NO_3^-, NH_4^+ and H^+_{lab}, the individual 11 month average values can be combined to produce the isopleths in Figure 4 and Figure 5 for $SO_4^=$ and NO_3^-, respectively: there is a definite north-south gradient with the $SO_4^=$ concentrations at the southern edge of the data lower by 30 to 50 percent than the maximum concentrations. An even more marked gradient is discernible for NO_3^-. These data show that selected precipitation

TABLE 8

Network Average Ion Concentrations (in micromoles per liter), Network Standard Deviations (SD), and EPRI/MAP3S Concentration Ratios.

Data Base	SO_4^{2-}	NO_3^-	NH_4^+	Cl^-	Na^+	H^+(field)	H^+(lab)	$(H^+_{lab} + NH_4^+)/(SO_4^= + NO_3^-)$
EPRI network								
All data								
Concentration	29.26	25.50	17.22	11.22	15.85	97.69	61.79	0.98
SD	7.93	6.79	2.90	7.69	6.35	42.02	19.35	
Noncoastal sites*								
Concentration	28.09	25.46	17.27	8.26	14.08			
SD	6.84	7.26	3.10	3.64	3.69			
MAP3S network								
All data								
Concentration	28.13	25.87	16.08	12.10	9.31	72.35	65.68	0.99
SD	3.92	5.06	4.61	12.68	12.18	12.26	11.09	
Noncoastal sites**								
Concentration	29.68	27.12	17.47	5.61	3.25			
SD	3.18	5.18	4.52	1.11	0.87			
Ratio of EPRI to MAP3S data								
All data	1.04	0.99	1.07	0.93	1.70	1.35	0.94	
Noncoastal sites	0.95	0.94	0.99	1.47	4.33			

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*Indian River, Delaware excluded

**Lewis, Delaware and Brookhaven, New York excluded (this was done to examine the effect of excluding the majority of any sea-salt contributions).

(from Pack, 1980)

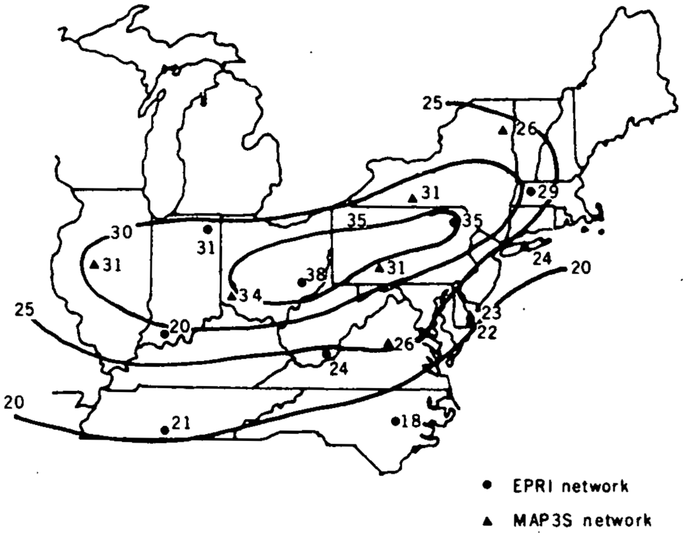


Figure 4. Average SO_4^{2-} concentrations (in micromoles per liter) for the period August 1978 through June 1979. Average concentrations for individual sites are plotted adjacent to the site locations. (from Pack, 1980)

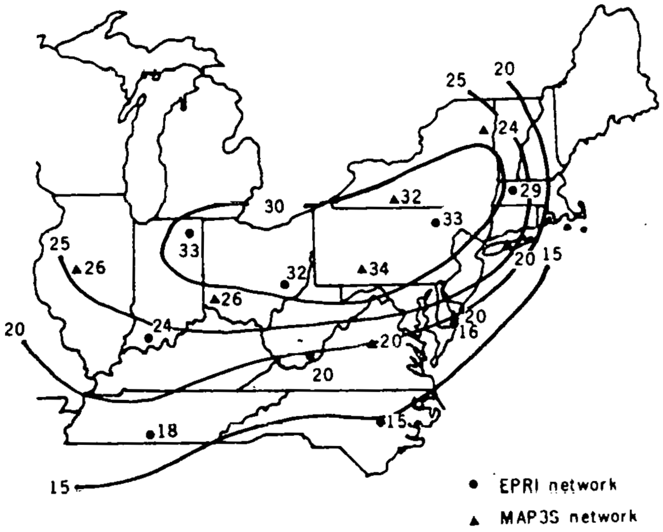


Figure 5. Average NO_3^- concentrations (in micromoles per liter) for the period August 1978 through June 1979. (from Pack, 1980)

chemistry data, carefully collected and rigidly quality controlled can be obtained and intermixed. However, an attempt to incorporate Canadian precipitation chemistry data for the same period of record and the same averaging technique indicated that those data did not compare to either the EPRI or the MAP3S values (Pack, 1980).

These findings also indicate that one cannot compare, without severe limitations, the results of all precipitation analysis including pH obtained by a variety of investigators over a large temporal range and for an almost globally extending area.

With the exception of Houghton (1955), all the studies discussed thus far were made of precipitating clouds with ground based instruments. Oddie (1962) was the first to collect precipitation from an aircraft in a deliberate attempt to prevent below-cloud contamination and/or transformation. He therefore provided the first estimate of the background pH as it exists in clouds as well as the distribution of pH with height. His measurements were made over southern England at varying heights up to 8,500 ft. The pH ranged from 4.4 to 7.2, with a mean of 5.84. One of the most interesting results of the study by Oddie was that the pH for 11 samples taken below 5,000 ft. was 5.4, while the mean pH for 12 samples taken above this height was 6.2, indicating a marked decrease in acidity with height.

An extensive analysis of cloud water pH was performed by Falconer and Falconer (1979). Their results are tabulated in Table 9 and shown in Figure 6. The mean pH for August/September 1977 and 1979 for nonprecipitating clouds was 3.55 and 3.50, respectively, i.e., considerably lower than the pH value for precipitating clouds of 3.96 and 4.01, respectively. The field of cloud chemistry is just emerging in response to the need for a complete atmospheric assessment of all factors affecting acid precipitation.

TABLE 9

Mean hydrogen ion content, $[H^+]$, and pH for precipitating and nonprecipitating clouds at Whiteface Mountain during 1977 and 1979. Variations in $[H^+]$ and pH for dewpoint temperatures (T_d) in excess of $60^\circ F$, as measured at the ASRC Field Station at 610 msl, are also shown.

Data	No. of Observations	Mean $[H^+]$	Mean pH	
All records	824	246 $\mu M\ell^{-1}$	3.61	1977
Precipitating clouds	171	111	3.96	
Nonprecipitating clouds	653	282	3.55	
Nonprecipitating with $T_d \geq 60^\circ F$	192	478	3.32	
Nonprecipitating with $T_d < 60^\circ F$	461	200	3.70	
All records	125	243	3.61	1979
Precipitating clouds	43	98	4.01	
Nonprecipitating clouds	82	320	3.50	
Nonprecipitating clouds with $T_d \geq 60^\circ F$	31	358	3.45	
Nonprecipitating clouds with $T_d < 60^\circ F$	51	296	3.53	

Several important factors have been discussed in this overview that need to be kept in mind when assessing pH or composition of precipitation. These include knowledge of the exact location where sample was taken and the mode of collection. Figure 7 illustrates the various possibilities. In the past, most precipitation samples were collected over a weekly or monthly period at ground level, i.e., within the planetary boundary layer. Hence, rainout, washout, rain splash and dust settling into the collector influenced the local precipitation quality. The current trend is definitely towards event sampling on a storm-by-storm basis with additional support measurements from above the boundary layer and from within clouds. It is recognized that collecting precipitation on an event basis is essential if the source of the acid precursor

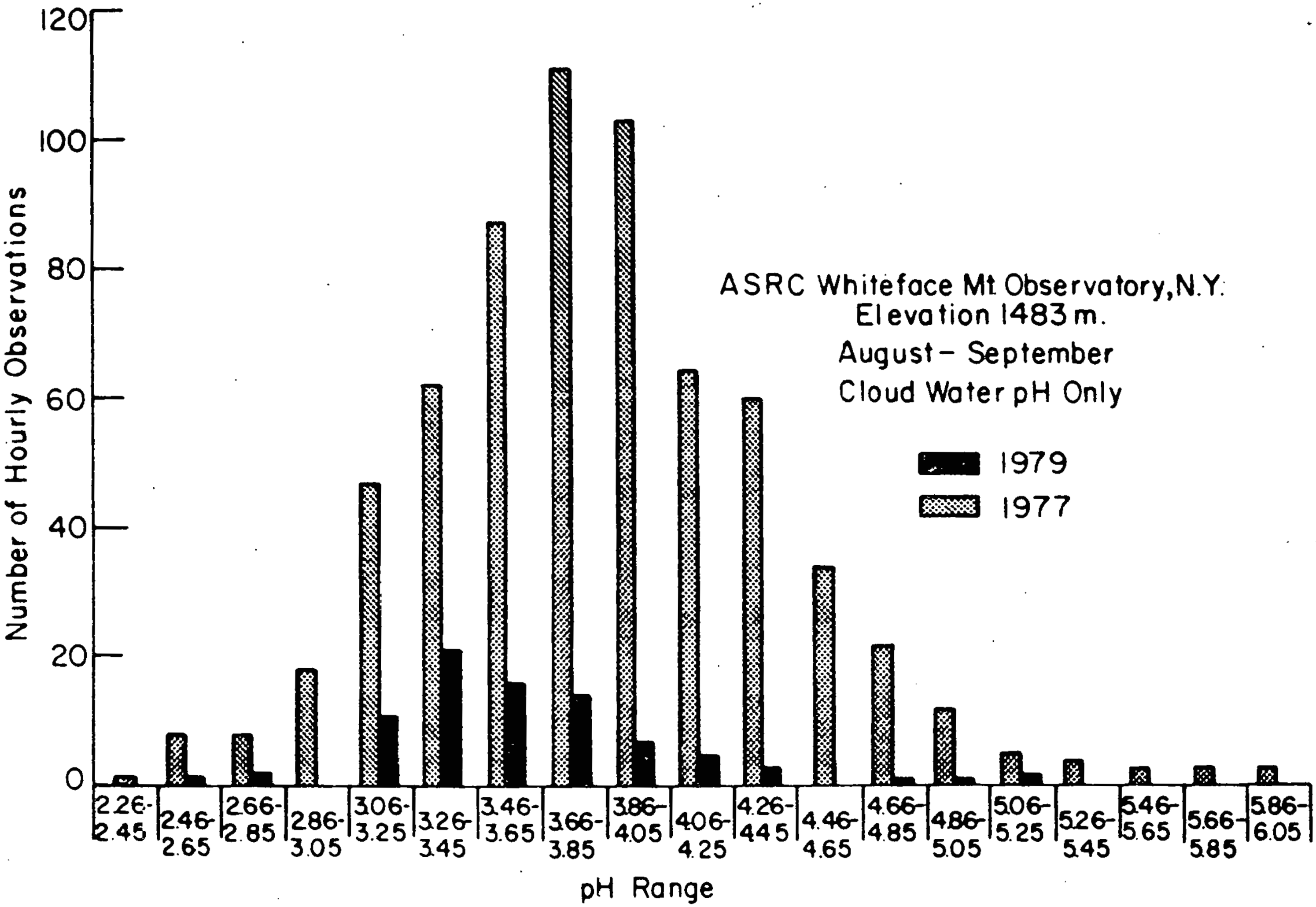
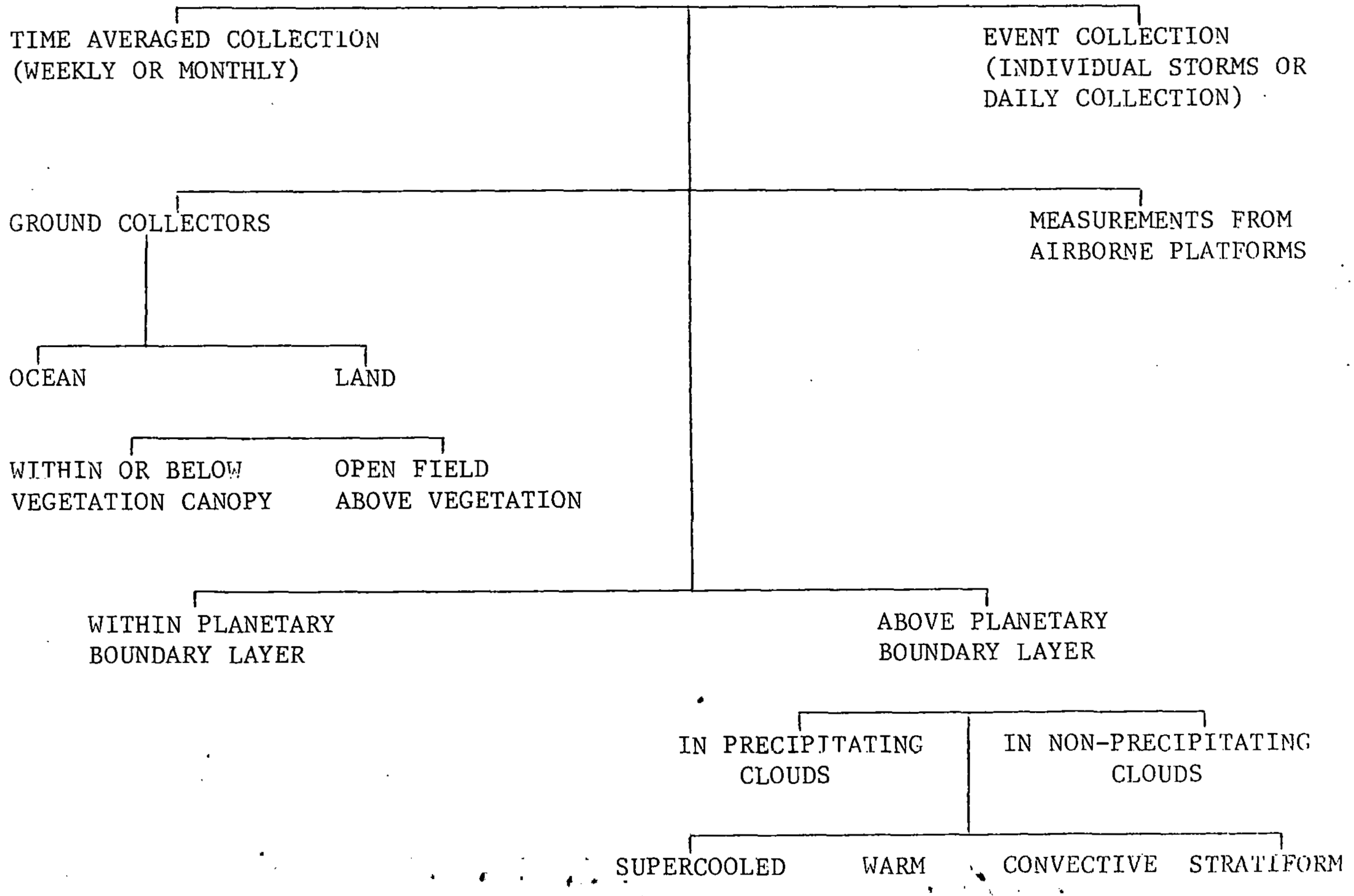


Figure 6. Frequency histograms of hourly pH values for August-September obtained exclusively from non-precipitating cloud events at the Whiteface Mountain Summit Observatory during 1977 and 1979. (Falconer and Kadlecek, 1980)



pH MEASUREMENTS AND CHARACTERIZATION OF CLOUDS AND PRECIPITATION ELEMENTS

Figure 7. pH measurement classification

material are to be identified through trajectory analysis. In addition to source-receptor studies, efforts to determine the dosage statistics for ecological studies require short sampling periods--even shorter than the now accepted 24-hour periods (Peden and Skowron, 1978).

The pH by itself is insufficient to characterize precipitation quality. It is very informative to divide the ionic constituents of precipitation into their categories or components:

- Soil derived minerals Ca^{++}, Mg^{++}. Fe^{3+}, silicate ions, etc.
- Sea salt Na^{+}, Cl^{-1}, $SO_4^{=}$ plus small amounts of K^{+}, Mg^{++} and Ca^{++}.
- Atmospheric conversion products from sulfur and nitrogen bearing molecules, i.e., $SO_4^{=}$, NO_3^{-}, in addition to NH_4^{+} and Cl^{-} (from hydrochloric acid) and, obviously, H^{+}.

Continued and expanded monitoring of precipitation quality is required to better evaluate trends and ultimately to provide a high quality, defensible data base for assessment of effects.

CHAPTER 2

EXAMINATION OF PRECIPITATION CHEMISTRY - 1977-1979

2.1 Sampling Network

The dominant source of data is the Multistate Atmospheric Power Production Pollution Study (MAP3S). In this ongoing study, precipitation chemistry data are obtained on an event basis beginning 1976. The original MAP3S collection sites are:

• Whiteface Mountain/New York	(WFM)
• Ithaca/New York	(ITH)
• Pennsylvania State University	(PEN)
• University of Virginia	(VIR)

In 1977-1978 four more stations were added to the network located at:

• Champaign-Urbana/Illinois	(ILL)
• Lewis/Delaware (coastal site)	(LEW)
• Brookhaven, Long Island/New York (coastal site)	(BRO)
• Oxford/Ohio	(OXF)

The location of all MAP3S stations is shown in Figure 8. The following chemical analysis is reported for each event sample (not a complete listing):

• Sample Volume:	S.V.
• Field pH:	$F[H]^+$
• Laboratory pH:	$L[H]^+$
• Conductivity:	Cond.
• Positive Ions:	NH_4^+, Ca^{++}, Mg^{++}, Na^+, K^+
• Negative Ions:	$SO_4^=$, NO_3^-, Cl^-

It is imperative to first obtain an overview of the chemical climatology of the northeastern United States before entering any detailed discussions on special case studies. Deposition, whenever discussed, will refer to wet deposition only.

Figure 8. The MAP3S precipitation chemistry network site array (from MacCracken, 1979)

2.2 Total Wet Deposition

In order to gain insight into this climatology, total wet deposition was examined for various stations for one and three year periods. For reasons to be discussed later, the stations chosen were Whiteface, Ithaca, Penn State, and Virginia. Table 10 presents the yearly totals for deposition of the dominant ions expressed in mg/m^2 and microequivalents/m^2, along with the anion/cation ratio for 1977-79.

TABLE 10

Total Deposition [mg/m^2] and [μeq/m^2]

		Sample Volume ml	$[SO_4^=]$		$[NO_3^-]$		$[H^+]_L$		$[NH_4^+]$		$\frac{[SO_4]+[NO_3]}{[H]+[NH_4]}$
			mg/m^2	μeq/m^2	mg/m^2	μeq/m^2	mg/m^2	μeq/m^2	mg/m^2	μeq/m^2	
WFM	1977	52674	2333	48604	1495	24111	46.5	46500	201	11123	1.26
	1978	34364	1908	39750	1091	17595	41.2	41200	211	11676	1.08
	1979	52214	1908	39750	1346	21708	47.1	47100	192	10625	1.06
ITHACA	1977	36850	2233	46521	1336	21547	41.5	41500	176	9739	1.33
	1978	36422	2351	48979	1401	22595	49.3	49300	204	11289	1.18
	1979	47275	2429	50604	1346	21708	62.0	62000	248	13723	0.95
PENN STATE	1977	44394	2698	56208	1716	27676	53.7	53700	226	12506	1.27
	1978	42621	2448	51000	1583	25531	56.3	56300	196	10845	1.14
	1979	58933	3188	66416	1983	31982	75.0	75000	341	18870	1.05
VIRGINIA	1977	25742	1744	36333	897	14467	31.5	31500	136	7526	1.30
	1978	41841	2284	47583	1273	20531	55.7	55700	186	10293	1.03
	1979	38906	1620	33750	913	14725	44.0	44000	140	7747	0.94

This table illustrates the variability in wet deposition on both the temporal and spatial scale. Spatial variability is difficult to interpret since the degree of coherency between stations is not usually proven. Pack (1980) showed independent stations could be used to develop regional patterns if one year averages are used. In this context, spatial variability is best discussed for long-term averages or totals of one to three years similar to those of Table 10.

In order to visualize event and monthly contributions to the yearly total, precipitation volume and deposition of the various ions are plotted for Whiteface in Figures 9 through 11. The bar graphs indicate the monthly totals of each constituent.

Precipitation and NO_3^- deposition demonstrates no identifiable sinusoidal or periodic oscillation between the seasons or years. However, H^+, $SO_4^=$m NH_4^+ and the soil components Ca^{++} + Mg^{++} have a definite summer maximum and winter minimum. The enhanced overall transformation of SO_2 to $SO_4^=$, due to the increase in solar radiation and other yet to be determined factors, is a likely reason for $SO_4^=$ being the dominant ion in summer precipitation in the northeastern United States, and therefore becomes the forcing function in the free hydrogen ion concentration. Values of the soil components [Ca^{++} + Mg^{++}] are not plotted for the first part of 1977, since these ions were not part of the routine analysis prior to August 1977.

While a three-year period may not be the optimum time scale for examination of trends in precipitation chemistry, it does nevertheless provide insight into annual variability. The cumulative total for precipitation and deposition by the major ions is shown in Figures 12 through 14. The non-periodic or linear function of precipitation and NO_3^- and the rapid accumulation of $SO_4^=$, H^+, and NH_4^+ is clearly demonstrated. It is also noteworthy that Penn State had the most precipitation and consequently the most wet deposition of each ion. However, Ithaca and Whiteface showed a reversal of this pattern, indicating a higher mean concentration at Ithaca for all the four major ions.

If these accumulations can be assumed to proceed, year after year in a linear fashion, then a simple linear regression equation can be developed that would predict a representative value for the total ion deposition over

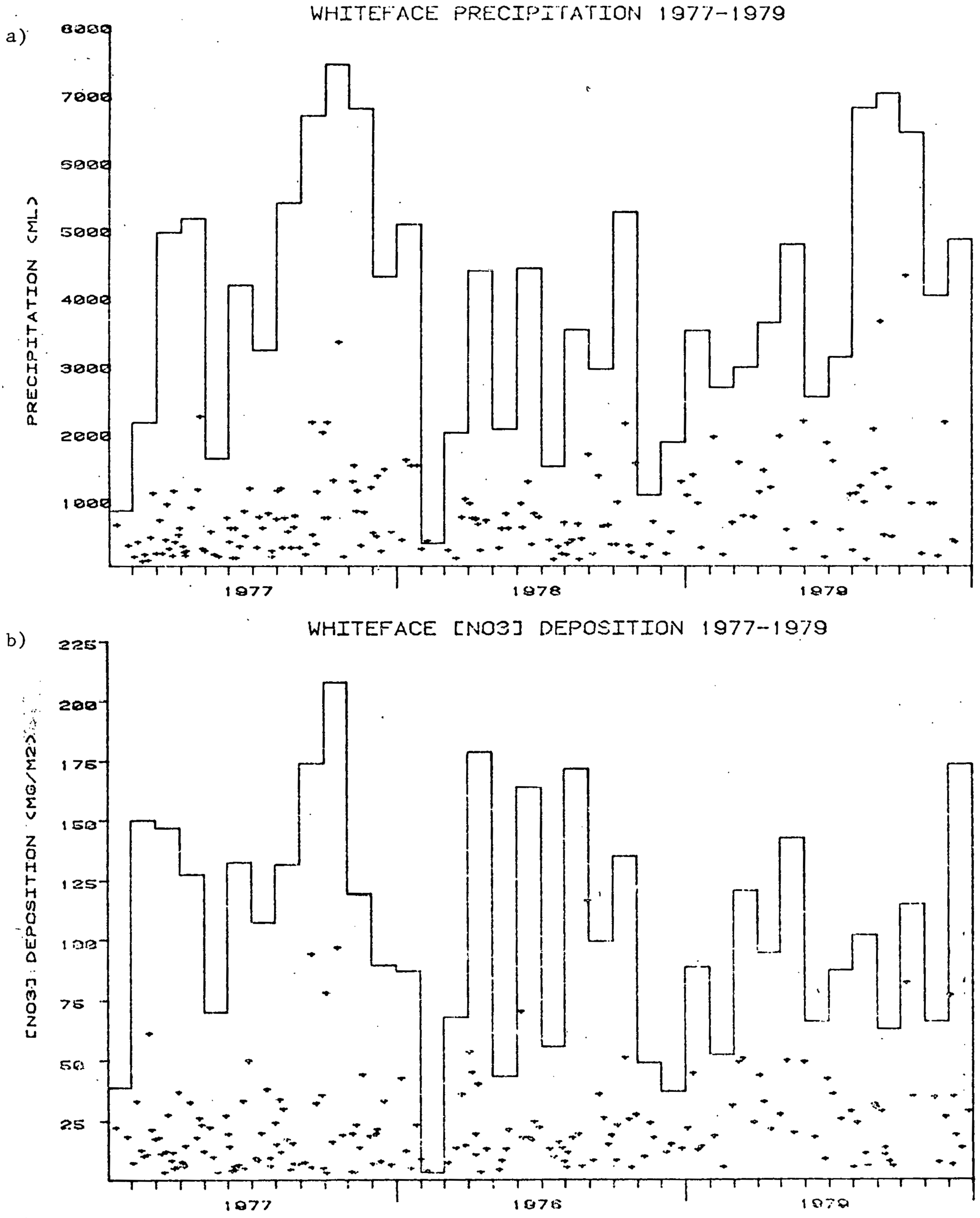


Figure 9. a) Precipitation events and monthly totals, and b) Event and monthly nitrate deposition for Whiteface, 1977-79.

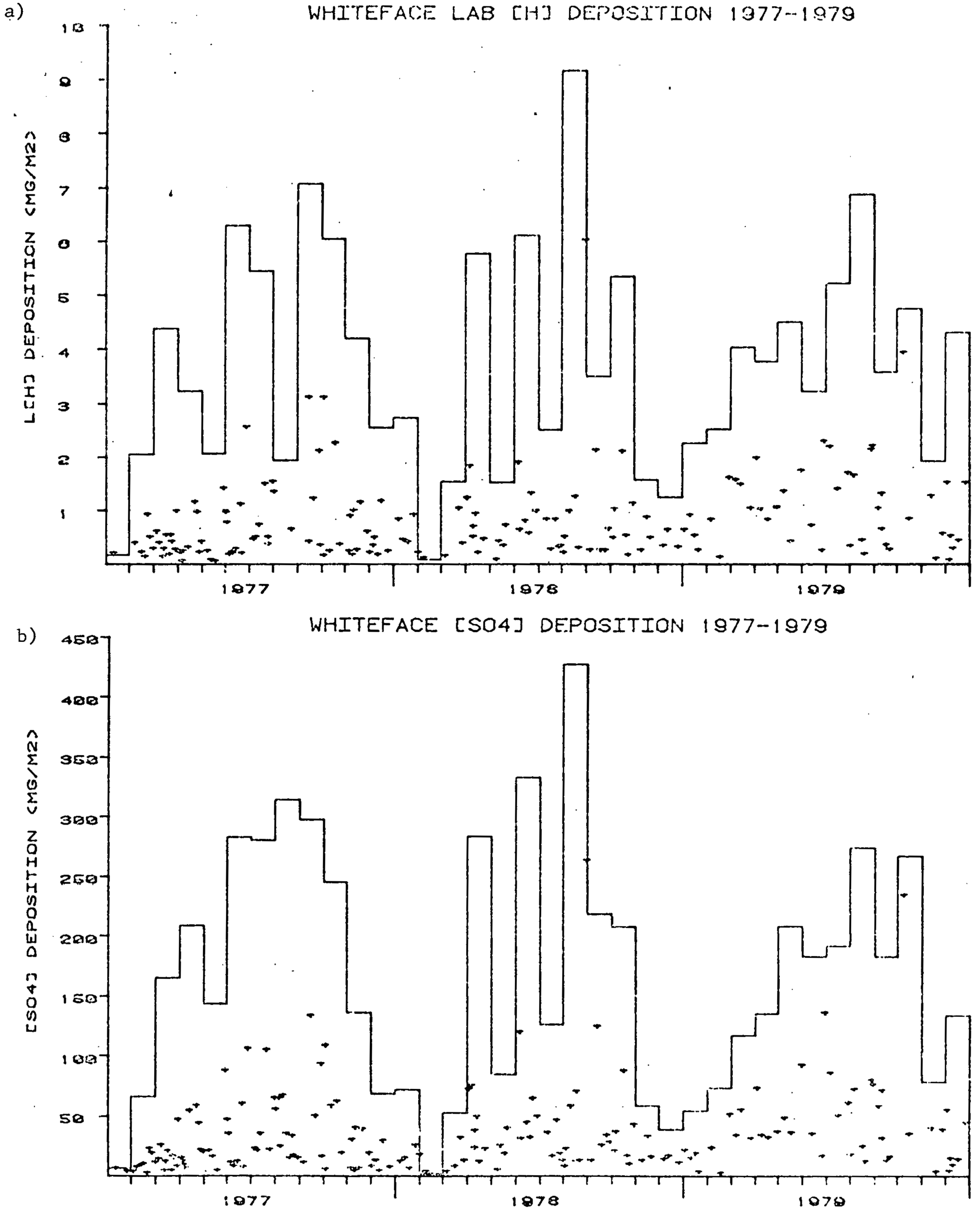


Figure 10. a) Free hydrogen ion event and monthly deposition, and
b) Sulfate event and monthly deposition for Whiteface, 1977-79

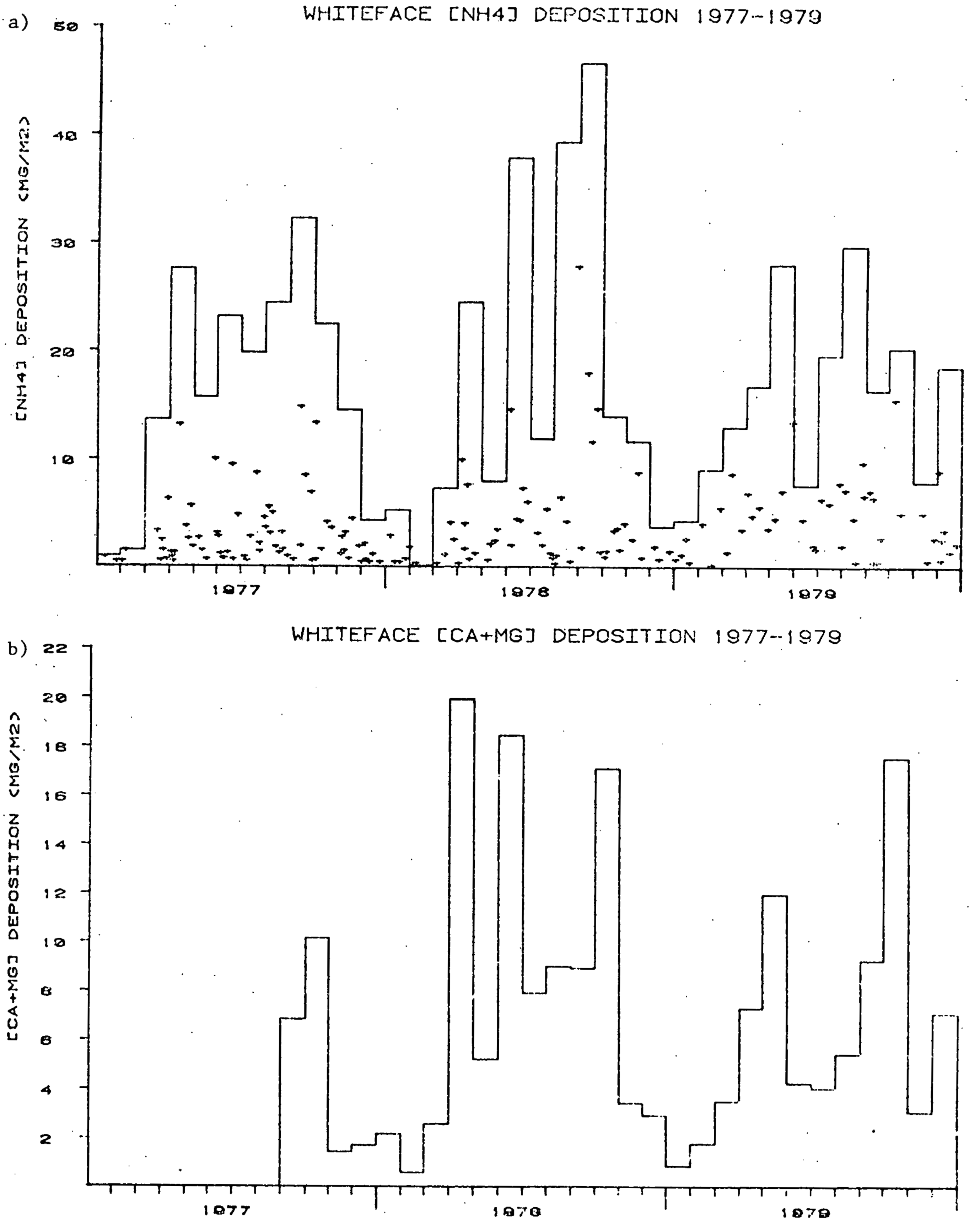


Figure 11. a) Ammonium event and monthly deposition, and b) Soil component monthly deposition for Whiteface, 1977-79

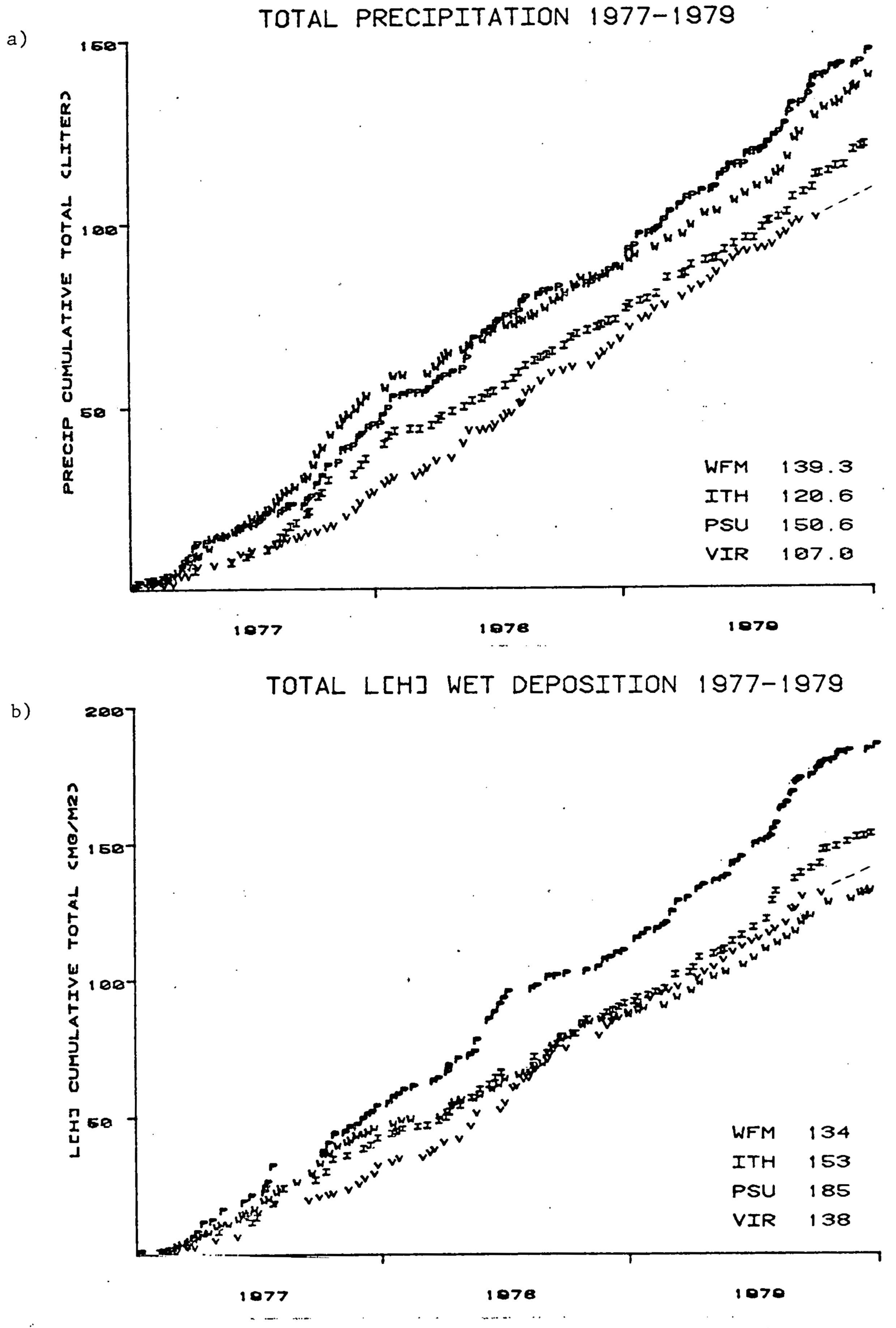


Figure 12. 1977-79 cumulative totals for a) precipitation, and b) free hydrogen ion

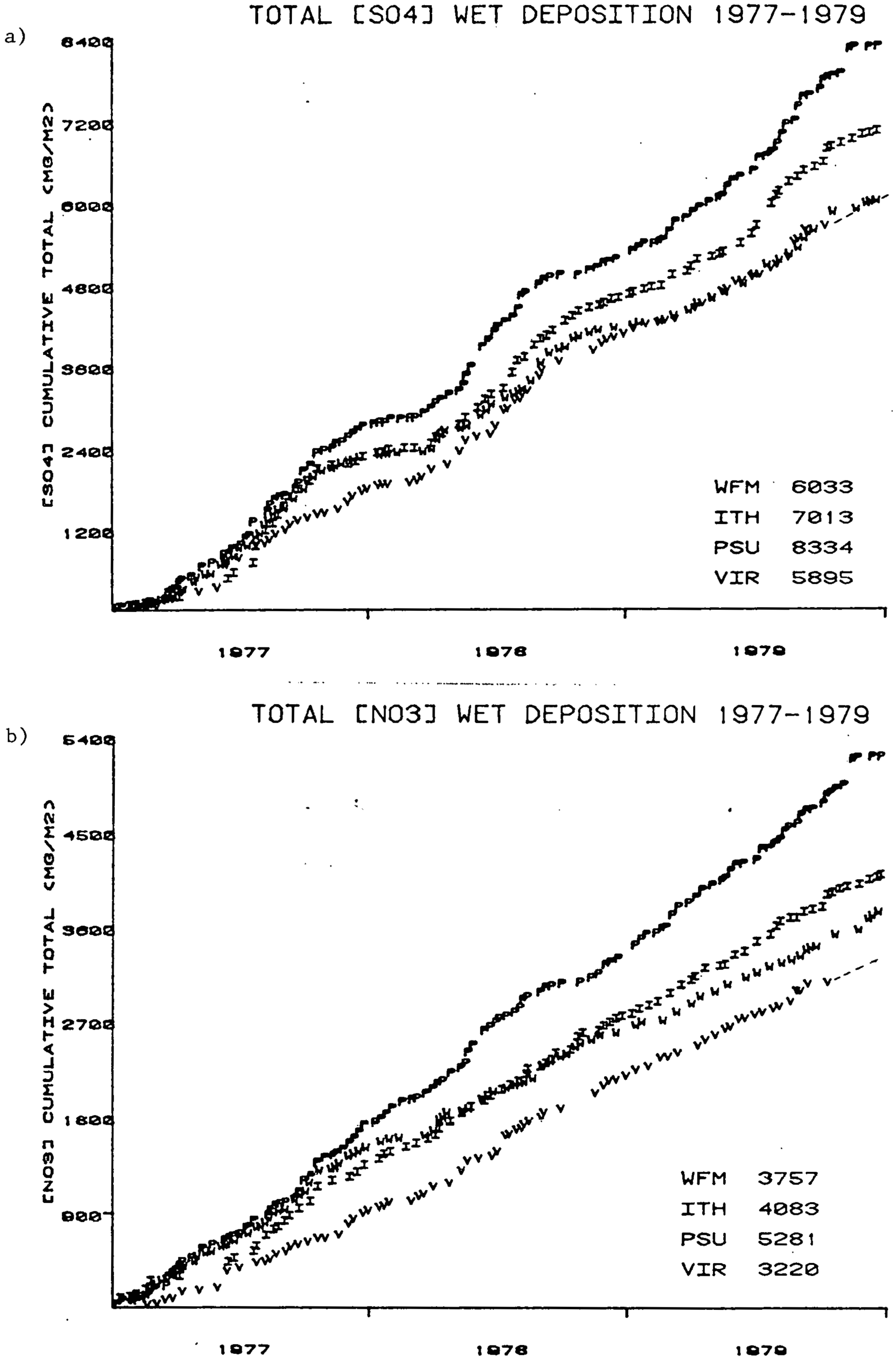


Figure 13. 1977-79 cumulative totals for a) sulfate, and b) nitrate

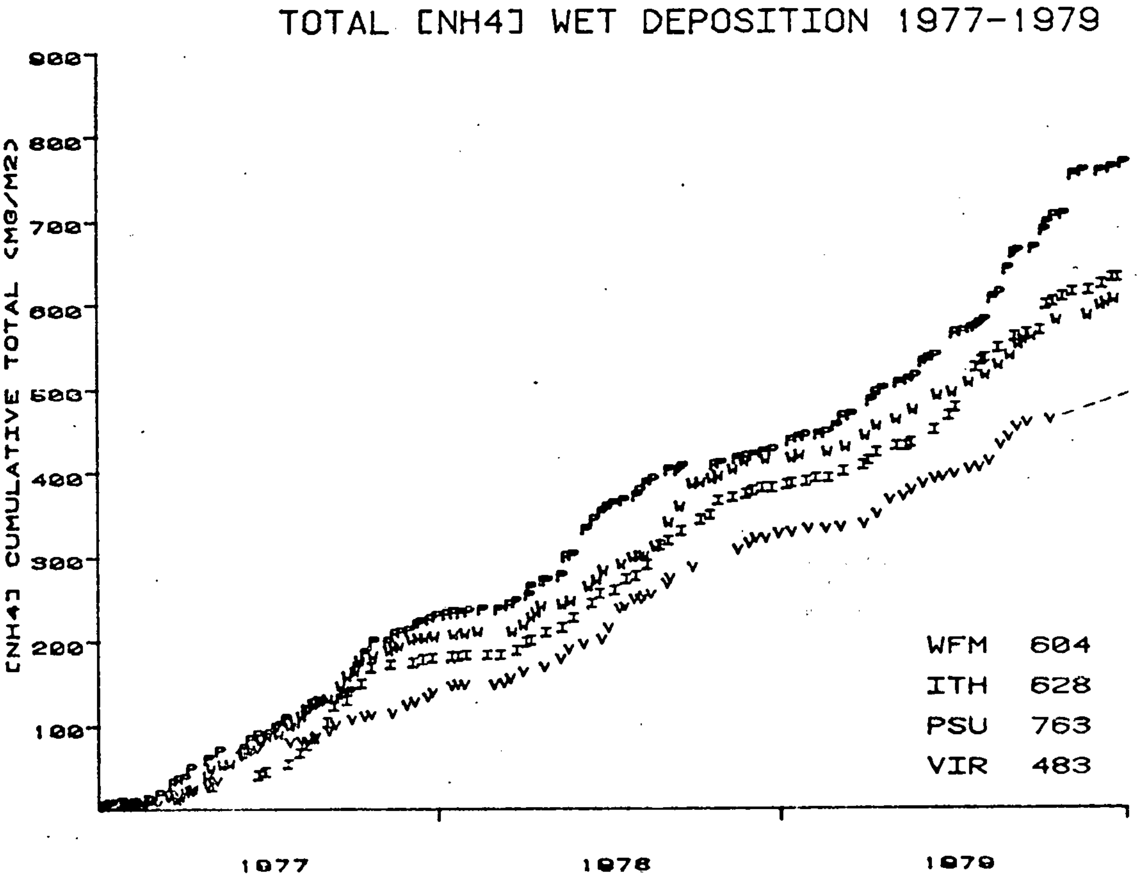


Figure 14. Ammonium cumulative total, 1977-79

a specified time period. Linear regression techniques were applied to Figures 12 through 14, producing the equations listed in Table 11.

TABLE 11

DEPOSITION REGRESSION EQUATIONS

Station	Ion	Regression Equation
WFM	H^+	D = - 3.7 + 45.6 Y
	$SO_4^=$	D = - 65.7 + 2070.6 Y
	NO_3^-	D + - 98.6 + 1247.6 Y
	NH_4^+	D = - 18.7 + 209.6 Y
ITHACA	H^+	D = - 13.8 + 54.4 Y
	$SO_4^=$	D = -274.2 + 2439 Y
	NO_3^-	D = - 92.8 + 1422 Y
	NH_4^+	D = - 47.9 + 217.4 Y
PENN STATE	H^+	D = - 10 + 64.4 Y
	$SO_4^=$	D = -261.6 + 2803.4 Y
	NO_3^-	D = -105 + 1777.6 Y
	NH_4^+	D = - 28.5 + 243.1 Y
VIRGINIA	H^+	D = - 16.9 + 51.7 Y
	$SO_4^=$	D = -344.3 + 2122.6 Y
	NO_3^-	D = -271 + 1207 Y
	NH_4^+	D = - 30.3 + 170.8 Y

D = Deposition (mg/m^2)

Y = Number of years

Admittedly, these equations imply that the emission pattern, the resulting concentration field, and the precipitation distribution would remain relatively constant in future years and close to the three-year mean for 1977-79. The application of such predictive equations will produce more meaningful results when applied over a five to ten year period, since precipitation totals should approximate the mean values used to develop the equations, and any concentration fluctuations would be averaged out.

The regression equations were applied to the individual years between 1977 and 1979 to see if they would apply to time scales of one year. Naturally, a better test would be to apply these equations to periods that were not used to develop the formulas, but data are not available. Table 12 shows the predicted versus measured deposition for each ion for each year between 1977 and 1979. Variations in the ratio of the measured versus predicted can usually be explained by a deviation in the precipitation from the three-year mean.

TABLE 12

PREDICTED VS. MEASURED DEPOSITION (1977-1979)

Station	Ion	Predicted Deposition (mg/m^2)	Measured Deposition (mg/m^2) ($\frac{\text{Measured}}{\text{Predicted}}$)		
			1977	1978	1979
WFM	H^+	41	45 (1.1)	41 (.98)	47 (1.1)
	$SO_4^=$	2005	2233 (1.1)	1908 (.95)	1908 (.95)
	NO_3^-	1346	1495 (1.1)	1090 (.81)	1346 (1.0)
	NH_4^+	191	201 (1.0)	211 (1.1)	192 (1.0)
ITHACA	H^+	41	42 (1.0)	49 (1.2)	62 (1.5)
	$SO_4^=$	2165	2233 (1.0)	2351 (1.1)	2429 (1.1)
	NO_3^-	1329	1336 (1.0)	1401 (1.1)	1346 (1.0)
	NH_4^+	169	176 (1.0)	204 (1.2)	248 (1.5)
PENN STATE	H^+	54	54 (1.0)	56 (1.0)	75 (1.4)
	$SO_4^=$	2542	2698 (1.1)	2448 (1.0)	3186 (1.2)
	NO_3^-	1673	1716 (1.0)	1583 (0.9)	1983 (1.2)
	NH_4^+	214	226 (1.1)	196 (0.9)	341 (1.6)
VIRGINIA	H^+	35	32 (0.9)	55 (1.6)	44 (1.3)
	$SO_4^=$	1778	1744 (1.0)	2285 (1.3)	1620 (0.9)
	NO_3^-	936	897 (1.0)	1273 (1.4)	913 (1.0)
	NH_4^+	140	136 (1.0)	186 (1.3)	140 (1.0)

YEARLY PRECIPITATION/3 YEAR MEAN

	1977	1978	1979
WFM	1.13	0.74	1.12
ITHACA	0.92	0.91	1.18
PENN STATE	0.91	0.88	1.21
VIRGINIA	0.73	1.18	1.10

2.3 Trajectory Sector Analysis

While total deposition for the various ions provides valuable information as to the total input, it is equally necessary to have available a sufficiently documented aerometric data base and supporting meteorological information to determine the trajectories of air masses responsible for the precipitation chemistry at a particular site. To this extent, the Air Resources Laboratories' Atmospheric Transport and Dispersion Model (ARL-ATAD), Heffter (1980), was operated to generate trajectories.

This model uses vertically averaged transport winds from 150 m above terrain to a maximum of 3000 m to calculate trajectories of up to five days duration from any origin in the United States, moving forward or backward in time. Computations are made four times daily at 00 Z, 06 Z, 12 Z, and 18 Z (denoted by symbols A, B, C, and D, respectively).

The transport layer depth initially depends on whether the trajectory begins at day or night. For trajectories beginning at day the daytime scheme is used throughout. The upper air data of each station within a specified radius of each trajectory endpoint is scanned to determine the lowest critical inversion. A critical inversion is defined as having the following characteristics:

$$\frac{\Delta\Theta}{\Delta Z} \geq .005^{\circ}\mathrm{K/m}$$

$$\Theta_{top} - \Theta_{base} \geq 2^{\circ}\mathrm{K}$$

where Θ_{top} and Θ_{base} refer to the top and base of the inversion layer. If an inversion is determined, the transport layer depth is determined as the height of the mid-point of the inversion minus the average terrain height. If no inversion is found, the transport layer depth is assumed to be 3000 m.

The nighttime calculations assume that the transport layer depth (TLD) is approximately equal to:

$$TLD = 2(2K_z \cdot t)^{\frac{1}{2}}$$

where K_z is the vertical coefficient of eddy diffusion and has the numerical value of 1 $m^2 \cdot sec^{-1}$. Nighttime conditions are assumed to persist from 00 Z to 12 Z.

A distance weighting factor is then used to weight the station within a 300 nautical mile radius and advect the air parcels in three-hour time steps.

Since most of the current interest in acid rain is focused on the northeast, or more specifically on the Adirondack region of New York State, Whiteface Mountain was chosen as the prime study candidate. Trajectories were calculated for all of 1978 and 1979 and weighted by precipitation amounts during that six-hour period to determine a dominant direction or origin of air mass for each MAP3S event. Each event was then classified in one of 12-30° sectors. To reduce the sometimes large lateral error associated with trajectories of several days duration, only the final two days of approach trajectory endpoints were considered. This assumption, therefore, could not provide a complete air mass history, but could be used to classify trajectories into various sectors of origin and certainly differentiate between so-called "Ohio Valley" and "Canadian" air masses. Even using these assumptions, not all events could be classified as to sector of origin, since some trajectories traversed several sectors. Furthermore, some MAP3S collection events were actually composed of several smaller separate discrete events with quite different air mass history. However, for 1978, 90% of the events and total deposition could be classified by this method. The percentage for 1979 was slightly less at approximately 85% of the events and

82% of the total deposition assigned to a particular compass sector. The results of 1979 appear to be somewhat atypical due to the influence of hurricanes David and Frederic and therefore will not be extensively discussed here.

Figures 15 though 18 show the event and mean concentration (μmole/liter) for H^+, NH_4^+, $SO_4^=$, NO_3^-, Na^+, Ca^{++}, and Mg^{++} as a function of air mass trajectory sector and precipitation type for Whiteface 1978. The sectors of the northeast quadrant contain relatively few data points and may not be statistically significant, but do provide insight into the composition and origin of several events.

Figure 15a illustrates the precipitation associated with each event and the mean for each sector. The impact of the large coastal snowstorms of a northeasterly component is readily apparent in the 0^o-90^o sector. The remainder of the sectors exhibit a relatively large range in precipitation amounts, as might be expected. Figures 15b through 18b demonstrate the variability in event concentration of various ions, while pointing to a general maximum in the mean concentration of the four major ions for the southwest sector. The wide range in concentration for each sector is partially explained by the variability in precipitation amounts for each event. High concentrations are sometimes associated with relatively low precipitation sample volumes indicating a diluting effect by higher volume. Therefore, caution must be used when extracting results from the concentration plots.

A more meaningful diagram is produced if deposition (mg/m^2) is plotted as a function of trajectory sector. This approach provides a weighting function and reduces the scatter associated with small precipitation volumes.

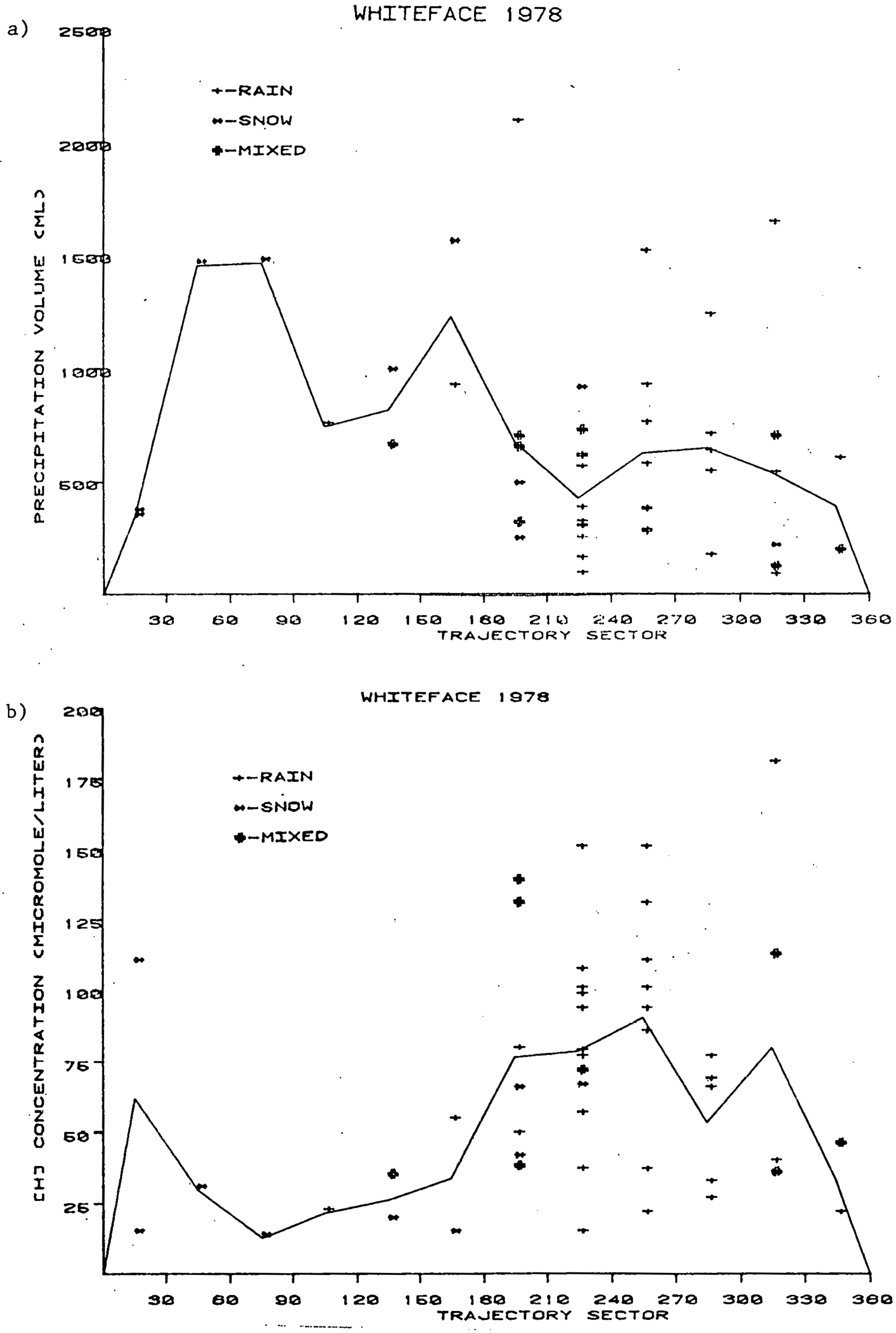


Figure 15. a) Precipitation volume, and b) Free hydrogen ion concentration per 30° trajectory sector for Whiteface, 1978

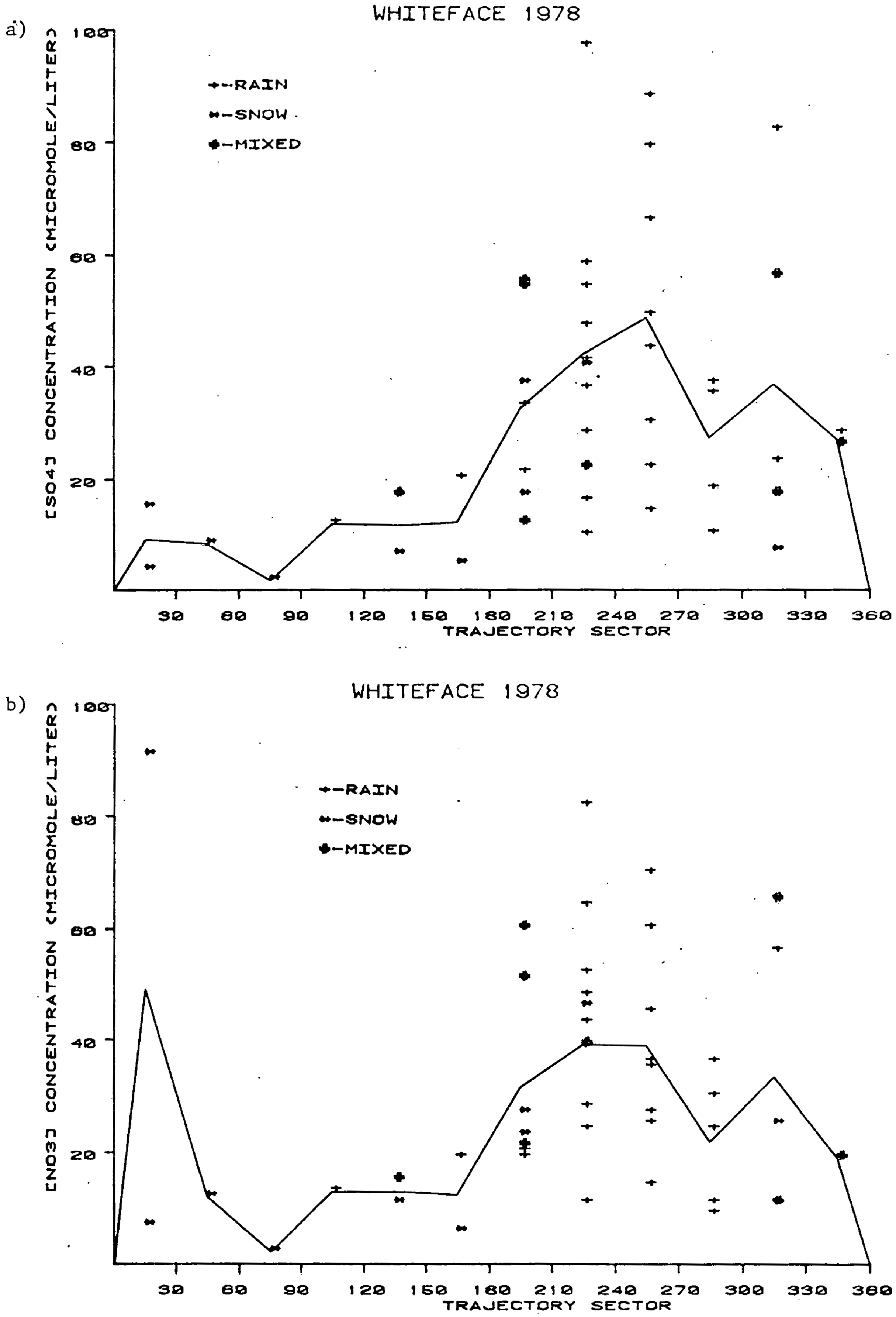


Figure 16. a) Sulfate, and b) Nitrate concentration per 30° trajectory sectors for Whiteface, 1978

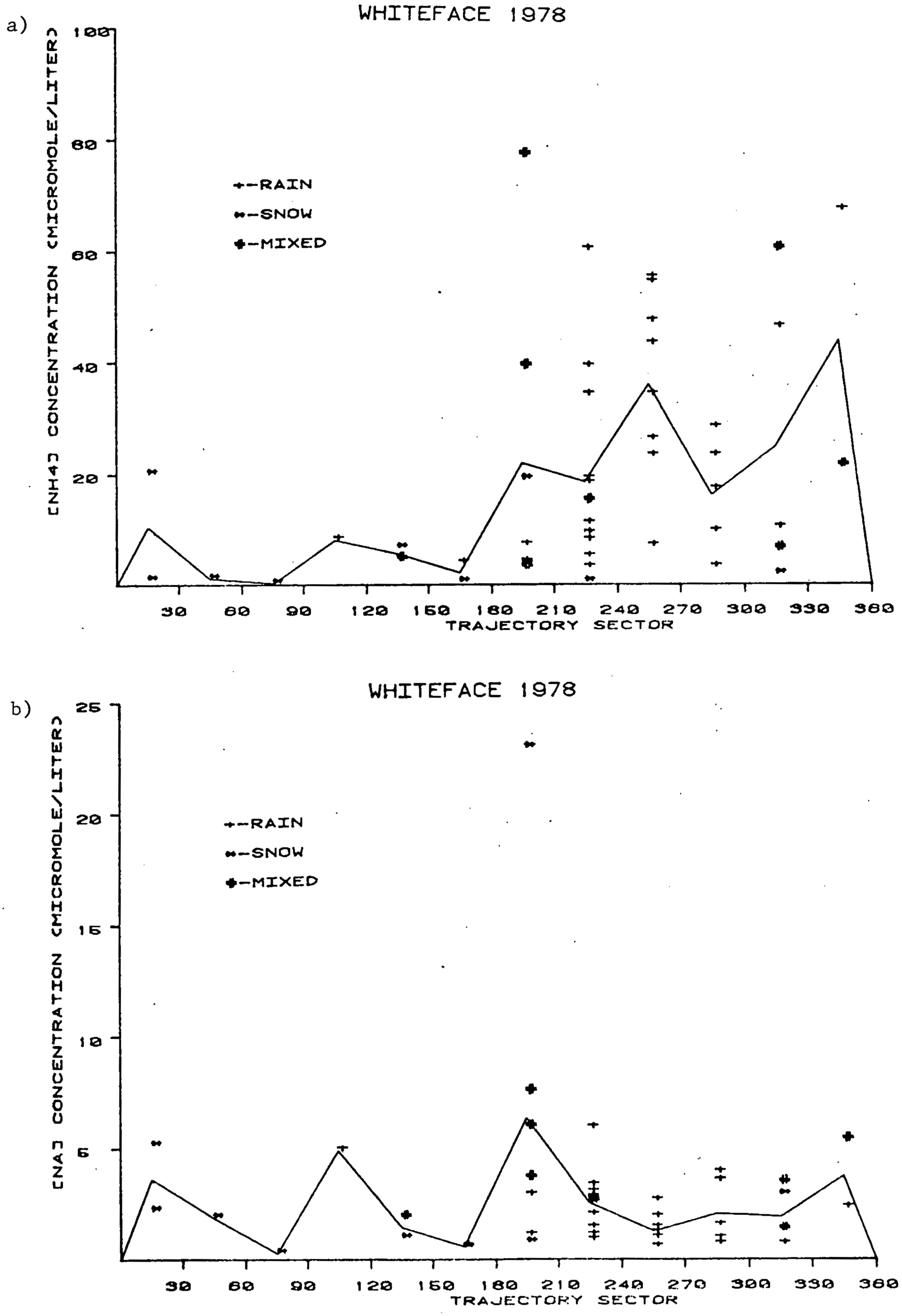


Figure 17. a) Ammonium, and b) Sodium concentrations per 30° trajectory sector for Whiteface, 1978

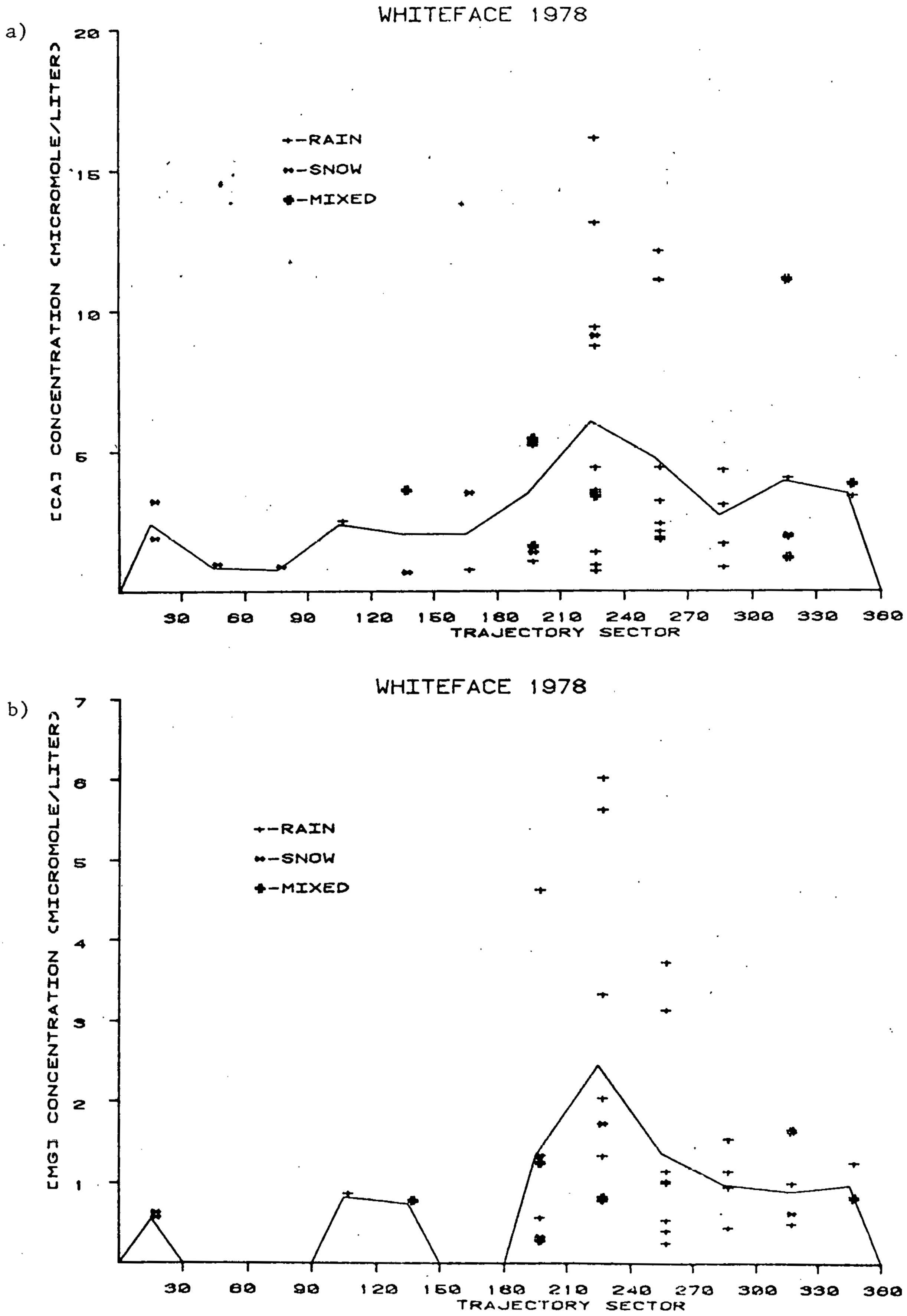


Figure 18. a) Calcium, and b) Magnesium concentrations per 30° trajectory sector for Whiteface, 1978

Figures 19 through 21 show the total deposition for the events that could be classified as a function of trajectory sector or air mass origin. It should be noted that the total deposition indicated on these figures refers to the total of the events definable by air trajectory analysis (the ATAD model).

The majority of the deposition could be further subdivided into two distinct groups: "Ohio Valley/Midwest" events were defined as those having their origin in the sector 165°-285°, while "Canadian/Great Lakes" was designated by the sector 285°-30°. When the total wet deposition is computed (including precipitation itself), the cumulative total of the "Ohio Valley/Midwest" sector accounts for approximately 50-70% of the total deposition from all directions. It cannot be said from these diagrams what the air from this sector is significantly more contaminated or polluted, but rather that the tendence for precipitation and subsequent wet deposition is greatest. This can be explained through synoptic considerations whereby precipitation is generally associated with an advancing upper-level trough and frontal system giving rise to a southwest component prior to its arrival.

These figures illustrate the dependence of deposition upon precipitation volume, since Figure 19a is almost a mirror image of the deposition patterns for the various ions. As shown by the deposition regression equations, if the total precipitation is known, a reasonable estimate can be made as to the total deposition of ions. The dependence of deposition on precipitation volume and concentration can be described further by computing the partial correlation coefficients for each variable. These values for Whiteface and Ithaca for the period 1977-79 are as follows:

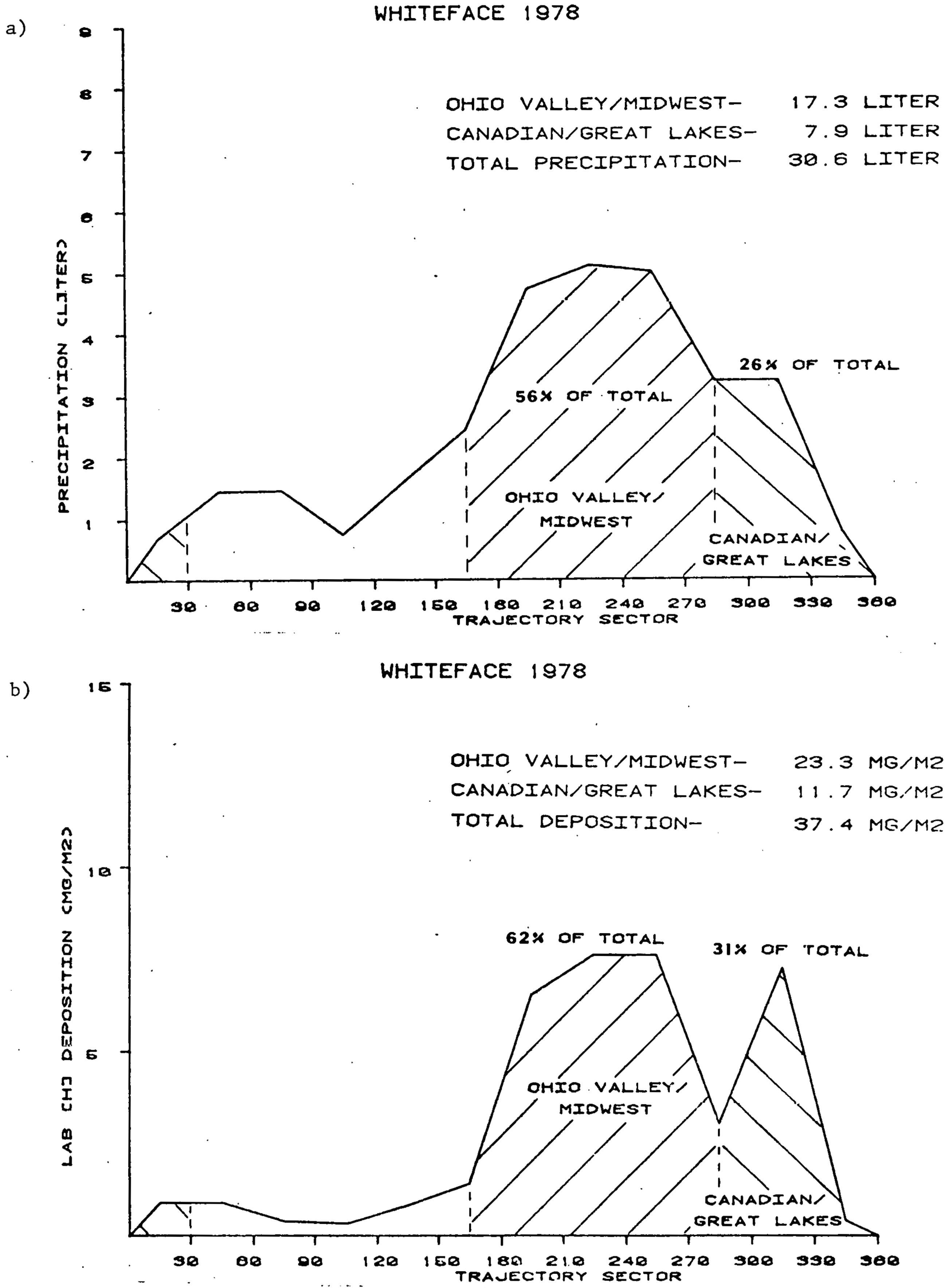
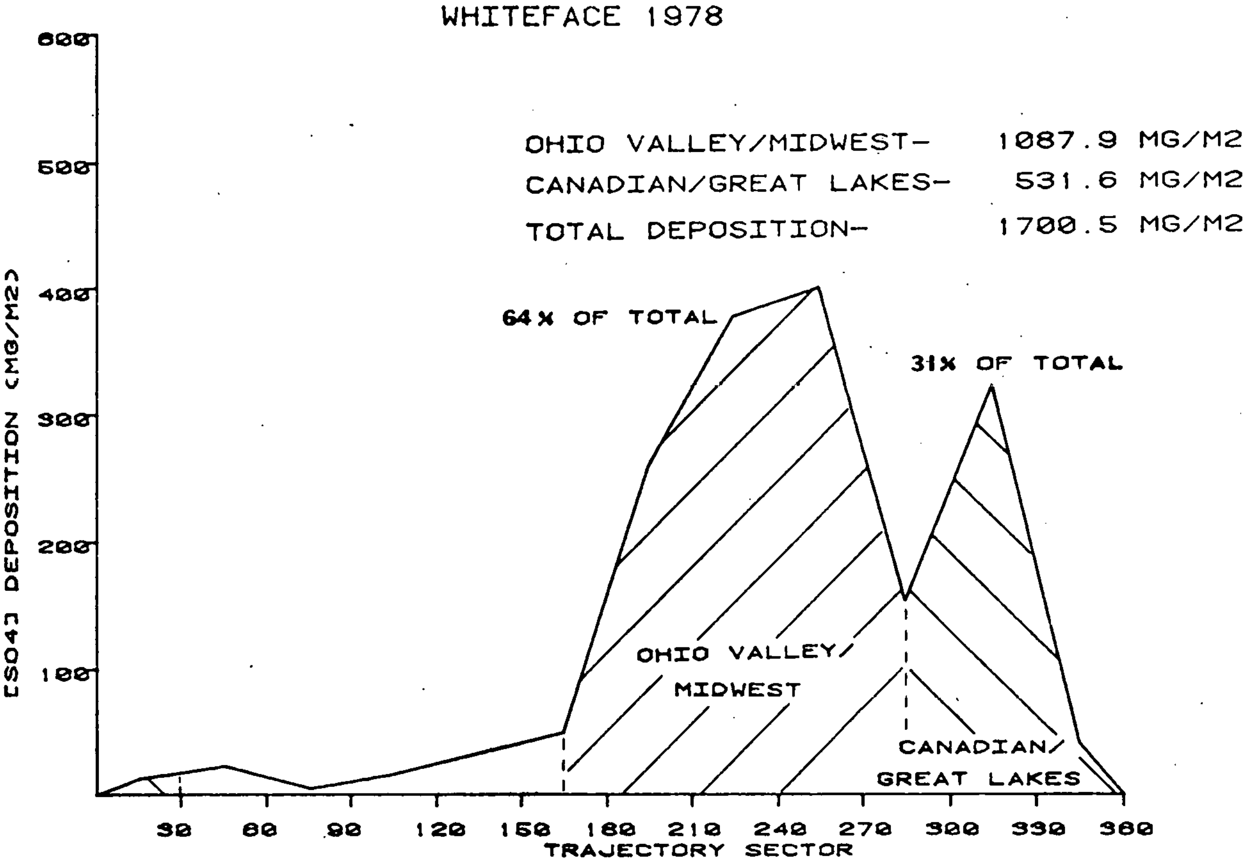


Figure 19. a)Precipitation volume, and b) Free hydrogen ion total wet deposition per 30° trajectory sector for Whiteface, 1978

a)



b)

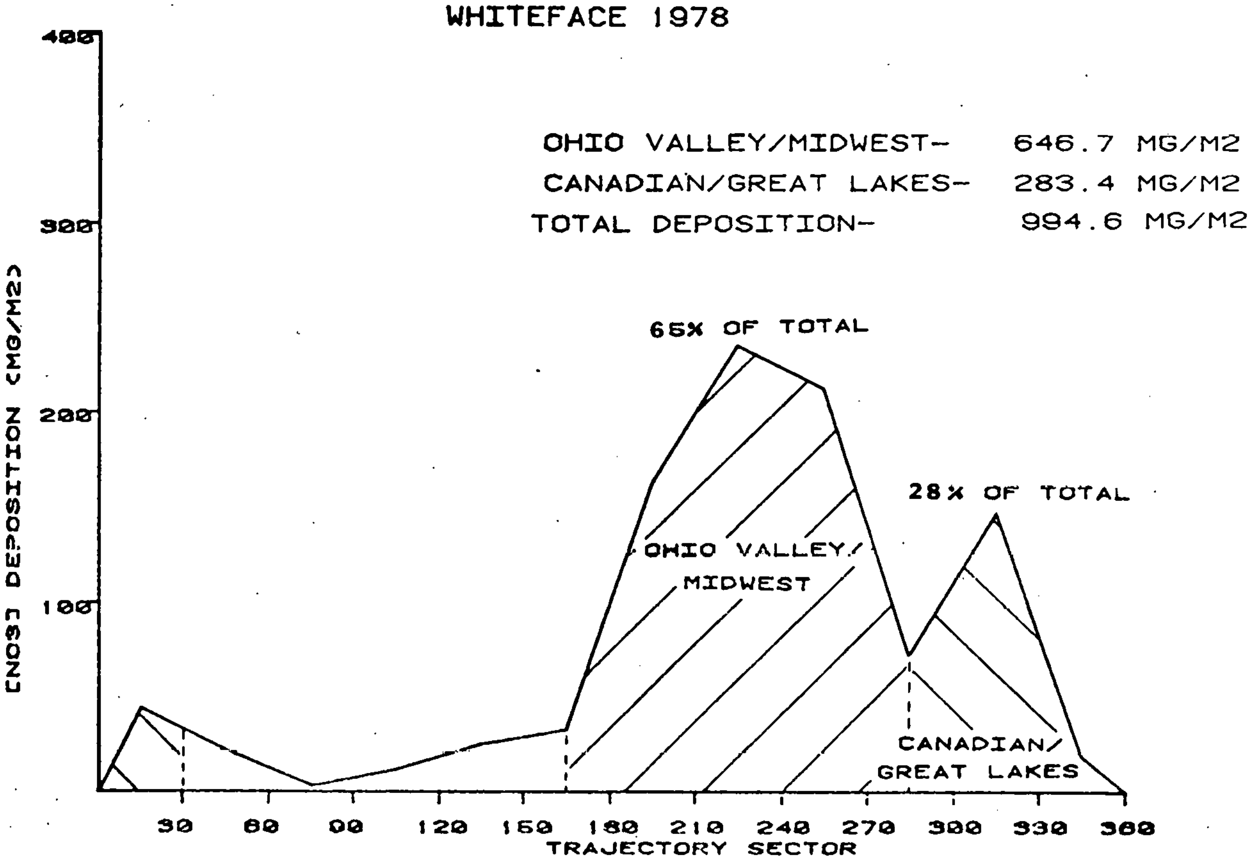


Figure 20. a) Sulfate, and b) Nitrate total wet deposition per 30° trajectory sector for Whiteface, 1978

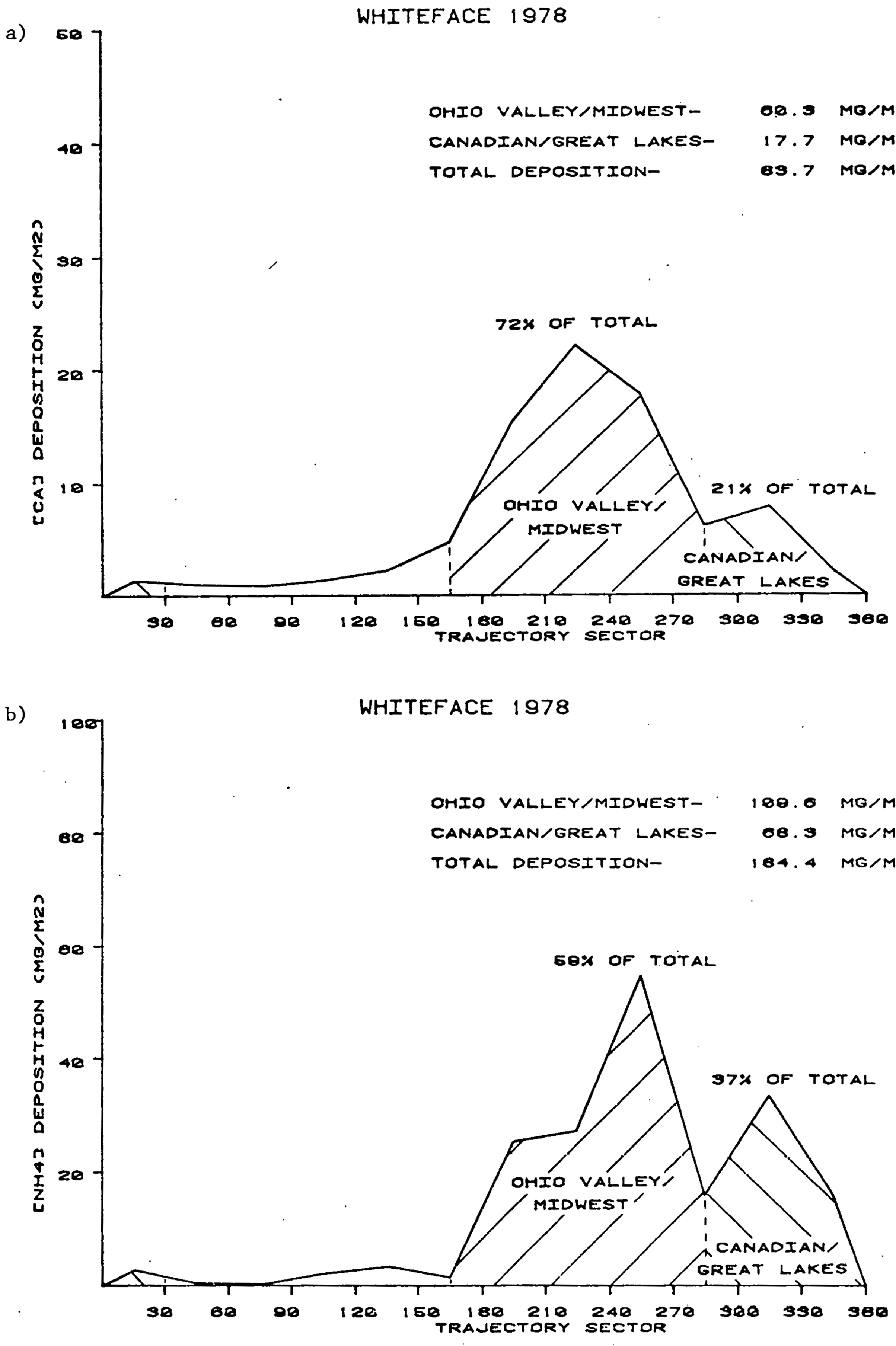


Figure 21. a) Calcium, and b) Ammonium total wet deposition per 30° trajectory sector for Whiteface, 1978

		DEPOSITION PARTIAL CORRELATION COEFFICIENT		
		$[H^+]_L$	$[SO_4^=]$	$[NO_3^-]$
Whiteface	Precip. Volume	0.74	0.72	0.67
	Concentration	0.59	0.57	0.49
Ithaca	Precip. Volume	0.70	0.66	0.62
	Concentration	0.52	0.58	0.45

These values show a relatively good correlation between deposition and precipitation volume, even when the concentration remains constant.

2.4 Summer Deposition - 1978

As shown thus far, the chemistry of precipitation can vary on several time scales. The most noticeable changes obviously occur between winter and summer for both concentration and deposition. From Figure 15, it is justifiable to assume that the summer (May-October) and winter (November-April) trajectories delivered precipitation that was of different air mass origin. It is therefore useful to examine in more detail the total values for summer months of 1978, as summarized in Table 13. The total sampling volume for the seven MAP3S stations during the six month period May-October 1978 was almost the same, i.e., (21056 ± 1728) milliliters. Hence, any modifying effect that might arise due to significantly differing rainfall amounts among the stations is eliminated. Several important factors emerge from the deposition data summarized in Table 13:

- The hydrogen ion is the most dominant positive ion, and the sulfate ion is the most dominant negative ion at all stations.
- The sequence of ion dominance is not the same for all stations. It is, in decreasing order of importance, for the summer of 1978 (May-October):

WFM: F[H], $SO_4^=$, L[H], NO_3^-, NH_4^+, Ca^{++}, Cl^-, K^+, Mg^{++}, Na^+

ITH: F[H], $SO_4^=$, L[H], NO_3^-, NH_4^+, Ca^{++}, Cl^-, Na^+, K^+, Mg^{++}

PEN: F[H], $SO_4^=$, L[H], NO_3^-, NH_4^+, Ca^{++}, Cl^-, Mg^{++}, Na^+, K^+

VIR: F[H], L[H], $SO_4^=$, NO_3^-, NH_4^+, Cl^-, Ca^{++}, Na^+, Mg^{++}, K^+

ILL: $SO_4^=$, F[H], L[H], NO_3^-, NH_4^+, Ca^{++}, Cl^-, Mg^{++}. Ma^+, K^+

LEW: F[H], Cl^-, $SO_4^=$, L[H], Na^+, NO_3^-, NH_4^+, Mg^{++}, Ca^{++}, K^+ (coastal site)

BRO: F[H], $SO_4^=$, L[H], Cl^-, Na^+, NO_3^-, NH_4^+, Mg^{++}, Ca^{++}, K^+ (coastal site)

- The dramatic influence of station location, i.e., inland versus coast, is quite obvious. Lewes/DE and Brookhaven/NY have a precipitation chemistry that is significantly different from the inland stations (the precipitation samples are enriched in Cl^-, Na^+, and Mg^{++}). Furthermore, the most western station of the network, Champaign/IL, shows a distinct "soil component" (Ca) enriched in precipitation and an almost corresponding decrease in free hydrogen ion content.
- For the five inland stations, WFM, ITH, PEN, VIR, AND ILL, the most important ions are H^+, NH_4^+, $SO_4^=$, and NO_3^-. Consequently, the simple stoichiometry relating these four ions summarizes the chemistry observed

$$[H^+] + [NH_4^+] = 2[SO_4^=] + 1[NO_3^-].$$

All of these ions exhibit a large variability from storm to storm, but a seasonal pattern in the concentration means with high values in the summer and low values in the winter emerged for all but nitrate.

- Table 13 lists the field measurement of the pH (listed as F[H]) and the laboratory measurement (listed as L[H]) separately. For no generally accepted reason, these two measurements do not agree. Some material in the collected precipitation samples must slowly change the detailed chemical composition of the samples.

TABLE 13

SUMMER 1978 DEPOSITION [μ equiv./m^2 for 6 month]

(May - October 1978)

	S.V.[ml]	F[H]	L[H]	SO_4	NO_3	NH_4	Ca	Mg	K	Cℓ	Na	Σ all pos for F[H]	Σ all pos for L[H]	Σ all neg
Whiteface	19660	42058	28201	29133	10780	8757	2787	1030	1093	2475	603	56328	42471	42388
Ithaca	21747	47795	31393	37139	13516	8691	2686	739	815	2137	874	61600	45198	52792
Penn State	23732	44284	31969	37084	13883	7685	2688	567	368	1908	483	56075	43760	52875
Virginia	22649	41289	32494	30953	10862	6783	2619	784	685	4472	1127	53287	44492	46287
Illinois	20758	27000	19416	28125	10913	8827	5836	987	315	2141	966	43931	36347	41179
Lewes	18997	28949	-24881	24950	9545	6218	2174	5046	785	27536	20580	63752	59684	62031
Brookhaven	19849	32143	19904	20165	8287	6030	1514	2723	691	10157	9920	53021	40782	38609

ΣS.V. 21056
± 1728 (standardized sampling volume)

SUMMER 1978 DEPOSITION [microequivalent/square meter for 6 month]

(May - October 1978)

Station	SO_4/NO_3	$\frac{(F[H] + NH_4)}{(SO_4 + NO_3)}$	$\frac{\Sigma \text{ all pos for } F[H]}{\Sigma \text{ all negative}}$	$\frac{\Sigma \text{ all pos for } L[H]}{\Sigma \text{ all negative}}$	% of annual 1978 deposition L[H]	NH_4	SO_4	NO_3
W.F.M.	2.7	1.27	1.33	0.93	68	75	73	62
Ithaca	2.7	1.12	1.17	0.79	64	79	76	60
Penn State	2.7	1.02	1.06	0.78	55	71	74	54
Virginia	2.8	1.15	1.15	0.94	58	65	65	53
Illinois	2.6	0.91	1.07	0.72	N.D.	N.D.	N.D.	N.D.
Lewes (Coastal site)	2.6	1.02	1.03	0.90	N.D.	N.D.	N.D.	N.D.
Brookhaven (Coastal site)	2.4	1.34	1.37	0.91	N.D.	N.D.	N.D.	N.D.

- Table 13 indicates that a complete ion balance does not exist between positive and negative ions. The sum of all ions of either sign is significantly larger for positive ions, using the "field pH" $F[H]^+$, than for negative ions. However, if the laboratory pH ($L[H]^+$) is used in adding up all positive ions, then the negative ions exceed the positive ones. There are obviously more ions present in solution than are currently measured, hence the discrepancy.
- While the relationship

  $$[H^+] + [NH_4^+] \overset{\sim}{=} 2[SO_4^=] + [NO_3^-]$$

  holds reasonably well for the stations in the MAP3S network, it by no means is sufficient to understand the precipitation chemistry at a particular site. For example, it is extremely important to know the soil component (in particular Ca) in order to understand the low value for the free hydrogen ion at the rural Illinois site. (As a matter of fact, it can be reasonably well assumed that the above relationship does not hold up anymore in the midwestern parts of the United States where the soil is more alkaline.) At the coastal sites Lewis and Brookhaven, it is the strong maritime component in Na^+, Cl^-, and Mg^{++} that play a significant role in determining the value of the free hydrogen ion. Furthermore, the local meteorology (onshore--offshore flow, i.e., sea breeze effect) might dominate the local air quality and precipitation quality in addition to the regional flow pattern. Hence, a coastal site is not a first choice in assessing regional inland precipitation chemistry.
- A rather surprising result emerges from Table 13 in regard to the deposition of major ions during the six month "summer" period of 1978:

	WFM	VIR	ILL	
F[H]	42058	41289	27000	[μeq/m^2]
L[H]	28201	32494	19416	[μeq/m^2]
SO_4	29133	30953	28125	[μeq/m^2]
NO_3	10780	10862	10913	[μeq/m^2]
NH_4	8757	6783	8827	[μeq/m^2]
Ca	2787	2619	5836	[μeq/m^2]

The above three sites could be looked upon as "corner sites" for the main emission sources referred to as "Ohio Valley." Yet, the sulfur, nitrate, and ammonia depositions during the six summer months of 1978 were almost identical. The free hydrogen ion deposition for Whiteface Mountain/NY and Virginia are again almost identical (so are the soil-derived Ca depositions), but the Illinois site shows a lower free hydrogen ion deposition and a higher soil-derived Ca deposition. The other two stations, Penn State and Ithaca, are in closer proximity to emissions in the "Ohio Valley," yet the deposition values are only slightly larger, except for NH_4 and Ca, which are similar to those found at WFM and VIR.

	ITH	PEN	
F[H]	47795	44284	[μeq/m^2]
L[H]	31393	31969	[μeq/m^2]
SO_4	37139	37084	[μeq/m^2]
NO_3	13516	13883	[μeq/m^2]
NH_4	8691	7685	[μeq/m^2]
Ca	2686	2688	[μeq/m^2]

Note that the daily trajectory analysis for the entire year 1978 shows predominantly southwesterly to westerly flow for precipitation producing air masses arriving at WFM in the "summer season." Under these conditions the resulting sulfate and nitrate depositions at WFM are about 20 percent lower than those for Ithaca and Penn State. Furthermore, Table 13 indicates that the SO_4/NO_3 deposition ratio of 2.7 is exactly the same for WFM, ITH, and PEN and differs only insignificantly from the ratios found at all the other sites. Therefore, a steep gradient for the deposition of pollution-related materials over the entire northeastern part of the United States cannot be detected.

- The percent of annual deposition that occurred during the six "summer" months is consistent with the annual change of the concentration for the pollution-related ions $[H^+]$, $SO_4^=$, and NO_3^-. Table 13 indicates that 65 to 75% of the sulfate, 50 to 60% of the nitrates, and 55 to 65% of the hydrogen ions are deposited during the summer months (May-October), 1978.

2.5 Ion Balances

Linear correlation and regression analysis was performed to determine the degree of association between various ions or pairs of ions. The results are presented as follows:

- $[H^+] + [NH_4^+] = 2[SO_4^=] + [NO_3^-]$

  (concentration values, Figure 22)
  correlation coefficient R = 0.95

- $[H^+] + [NH_4^+] = 2[SO_4^=] + [NO_3^-] - 2[Ca^{++} + Mg^{++}]$

  (concentration values, Figure 23)
  correlation coefficient R = 0.98 increased slightly when the soil component was subtracted.

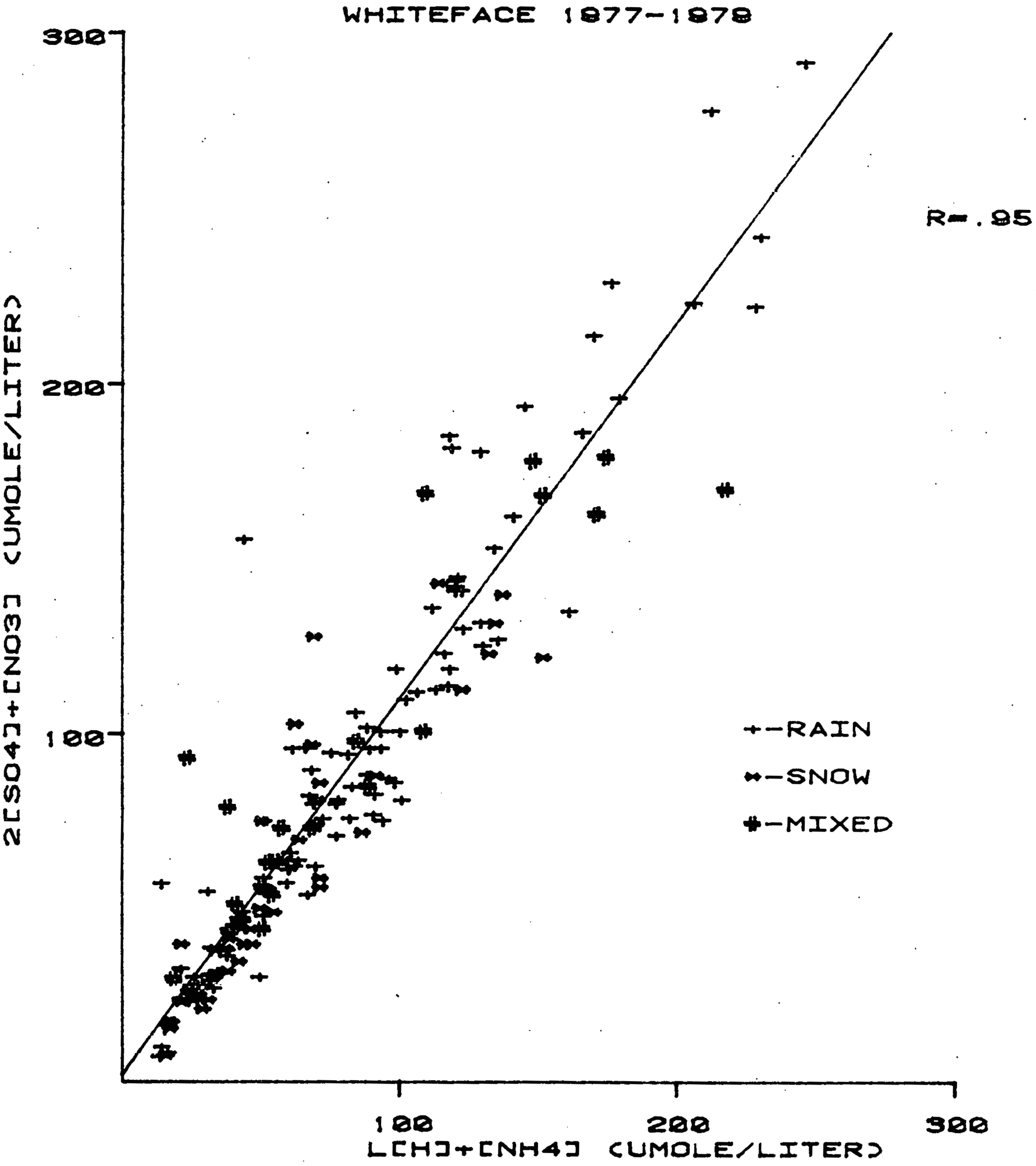


Figure 22. Hydrogen + Ammonium vs. 2(Sulfate) + Nitrate for Whiteface, 1977-79

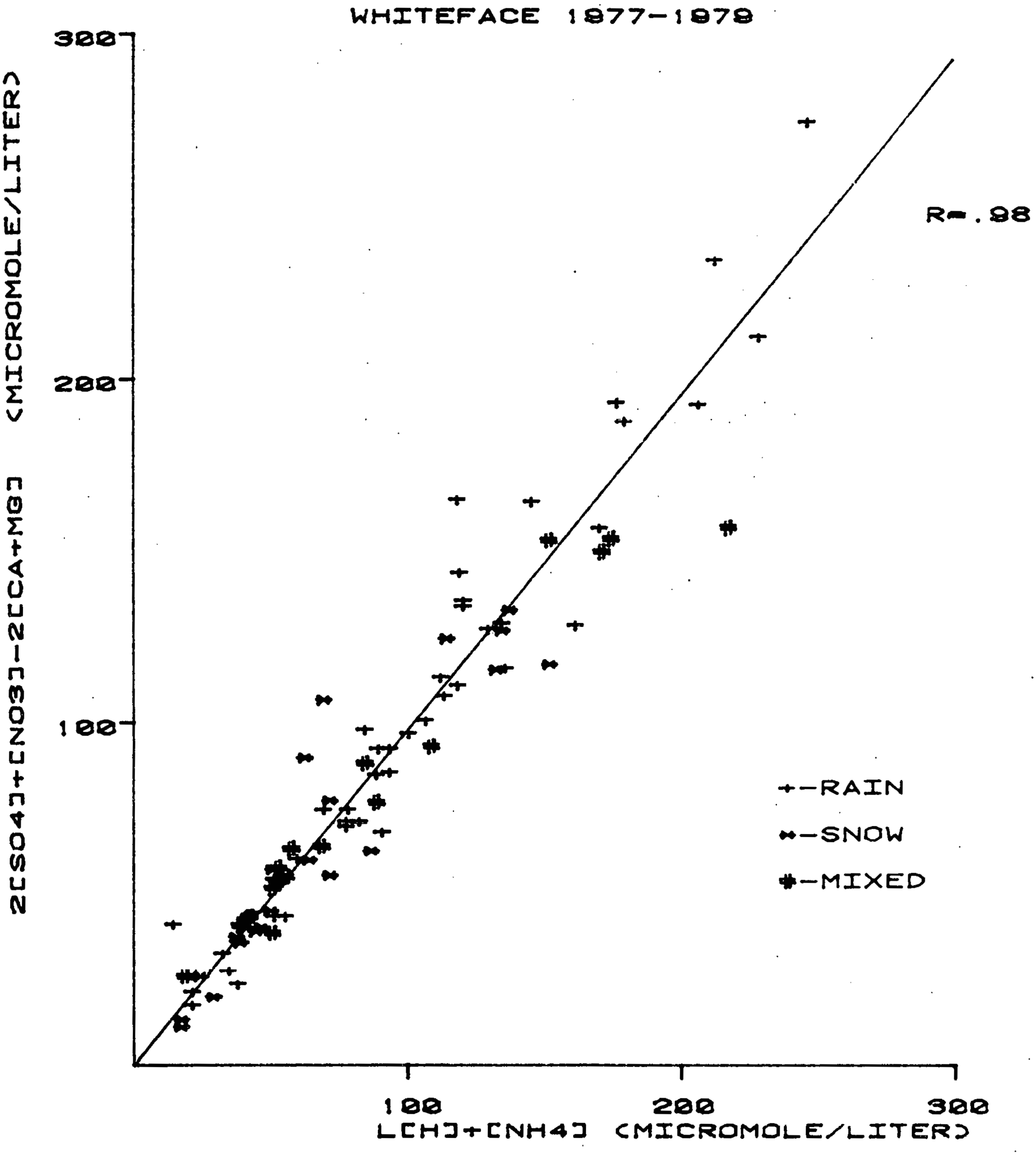


Figure 23. Hydrogen + Ammonium vs. 2(Sulfate) + Nitrate - 2(Soil Components) for Whiteface, 1977-79

- $[H^+]$ versus $[NH_4^+]$

  (concentration values, Figure 24)
  correlation coefficient R = 0.68

- $[H^+]$ versus $[NO_3^-]$

  (concentration values, Figure 25)
  correlation coefficient R = 0.72

- $[H^+]$ versus $[SO_4^=]$

  (concentration values, Figure 26)
  correlation coefficient R = 0.88

The high correlation that exists between $[H^+] = 2[SO_4^=] + [NO_3^-] - [NH_4^+]$ suggests that a significant portion of the sulfate and nitrates at WFM existed in the form of sulfuric and nitric acid.

There is no strong relationship between precipitation volume and ion concentration. It is recognized that the only measured parameters of "precipitation sample volume" is a very poor indicator of "precipitation rate" and hence the scavenging behavior is not easily discernable from the observed data. An inverse relationship between sample volume and ion concentration in precipitation is suggested from the data presented in Figures 27 through 30 for the $[H^+]$, $[SO_4^=]$, $[NH_4^+]$, and $[NO_3^-]$ ions. These figures illustrate the inverse dependence of concentration and precipitation volume and help explain the wide range of values for each ion concentration per trajectory sector in Figures 15 through 18.

2.6 Weighted Concentration and Mean Deposition - 1977-79

Thus far deposition and concentration patterns have been described in detail for time scales of months and years. It is apparent that a comprehensive treatment of individual events and/or episodes is also necessary in order to understand the chemical climatology of precipitation. In order to define a significant event or episode, a definition as to the exact nature

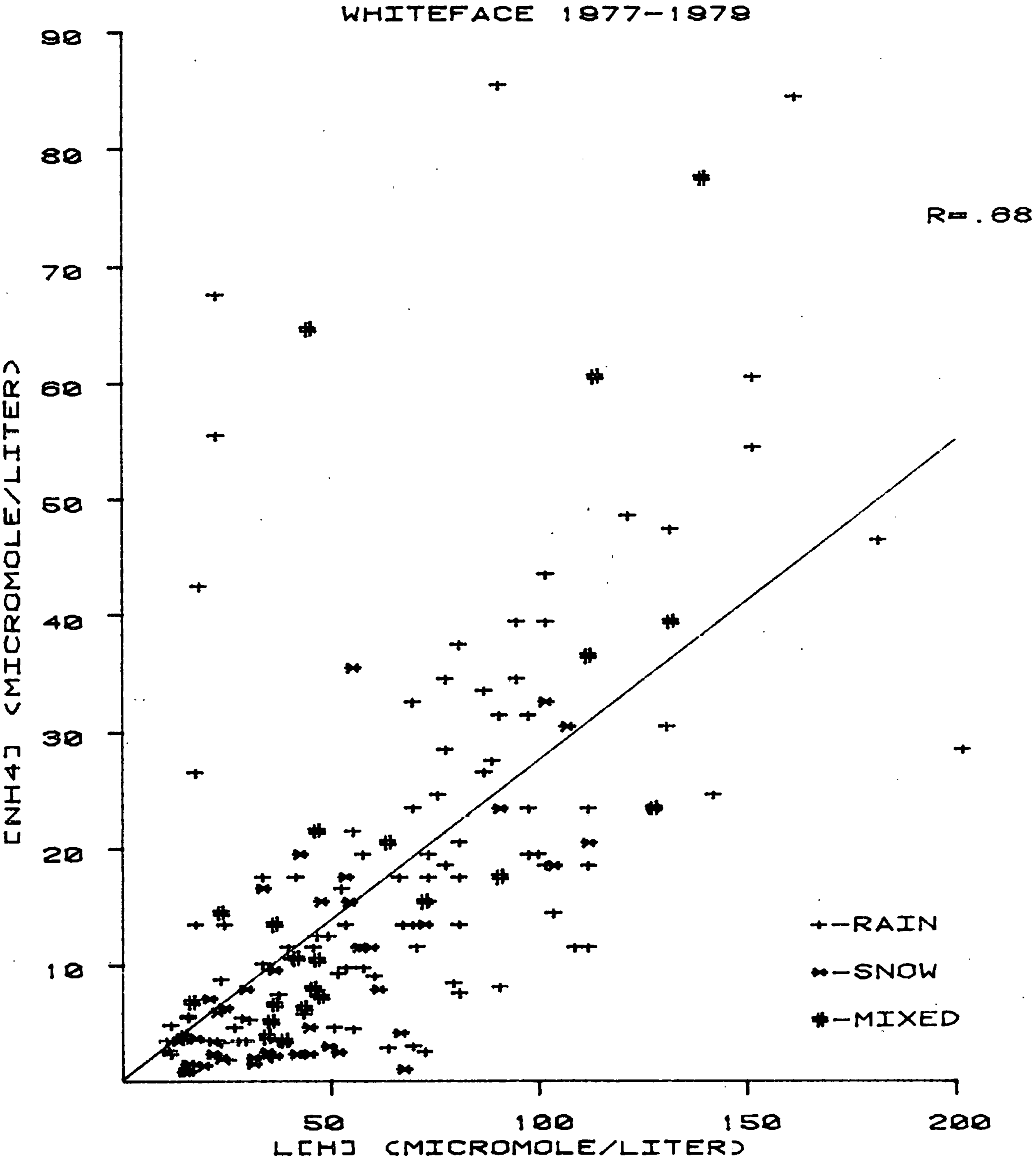


Figure 24. Hydrogen vs. Ammonium for Whiteface, 1977-79

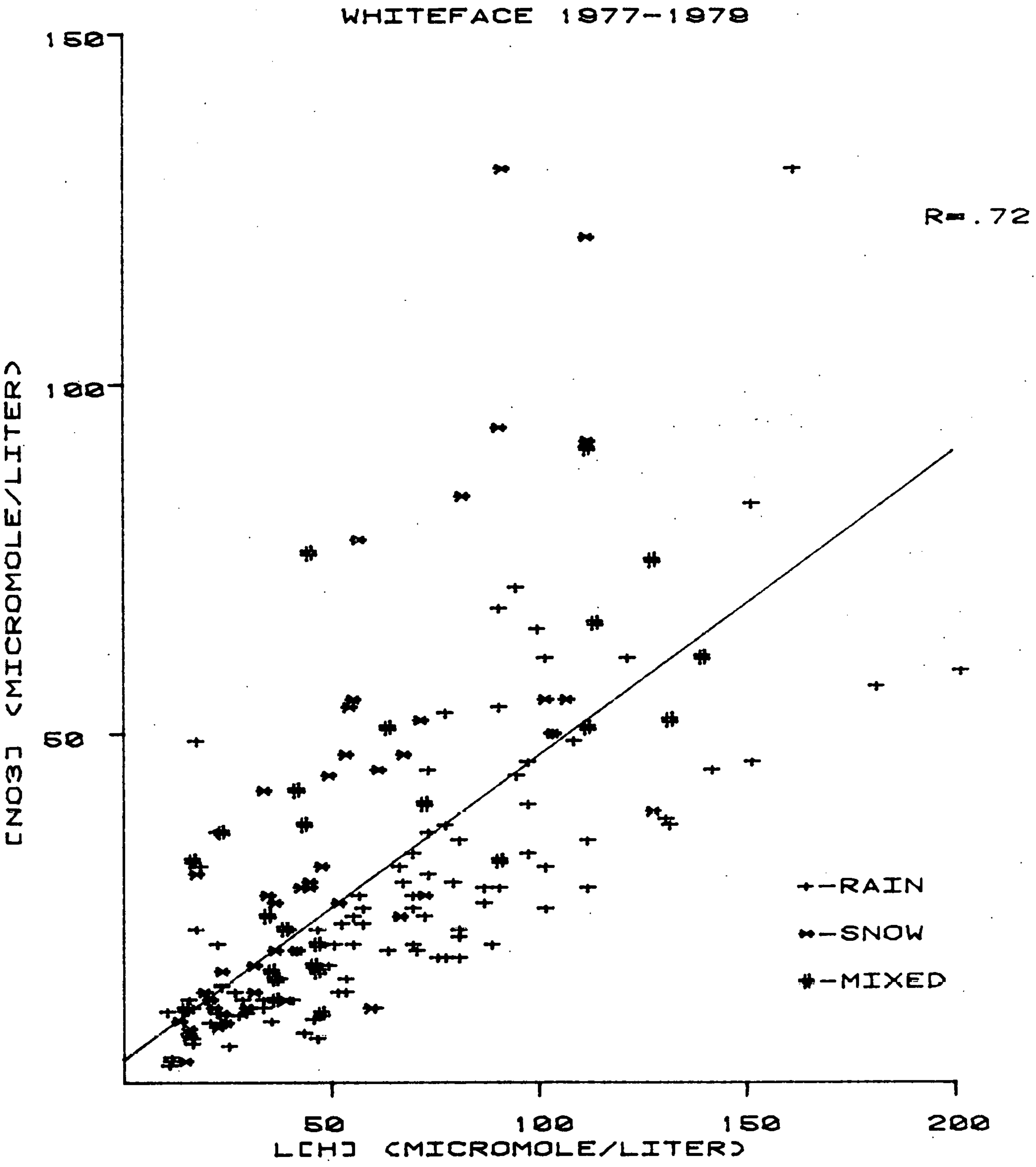


Figure 25. Hydrogen vs. Nitrate for Whiteface, 1977-79

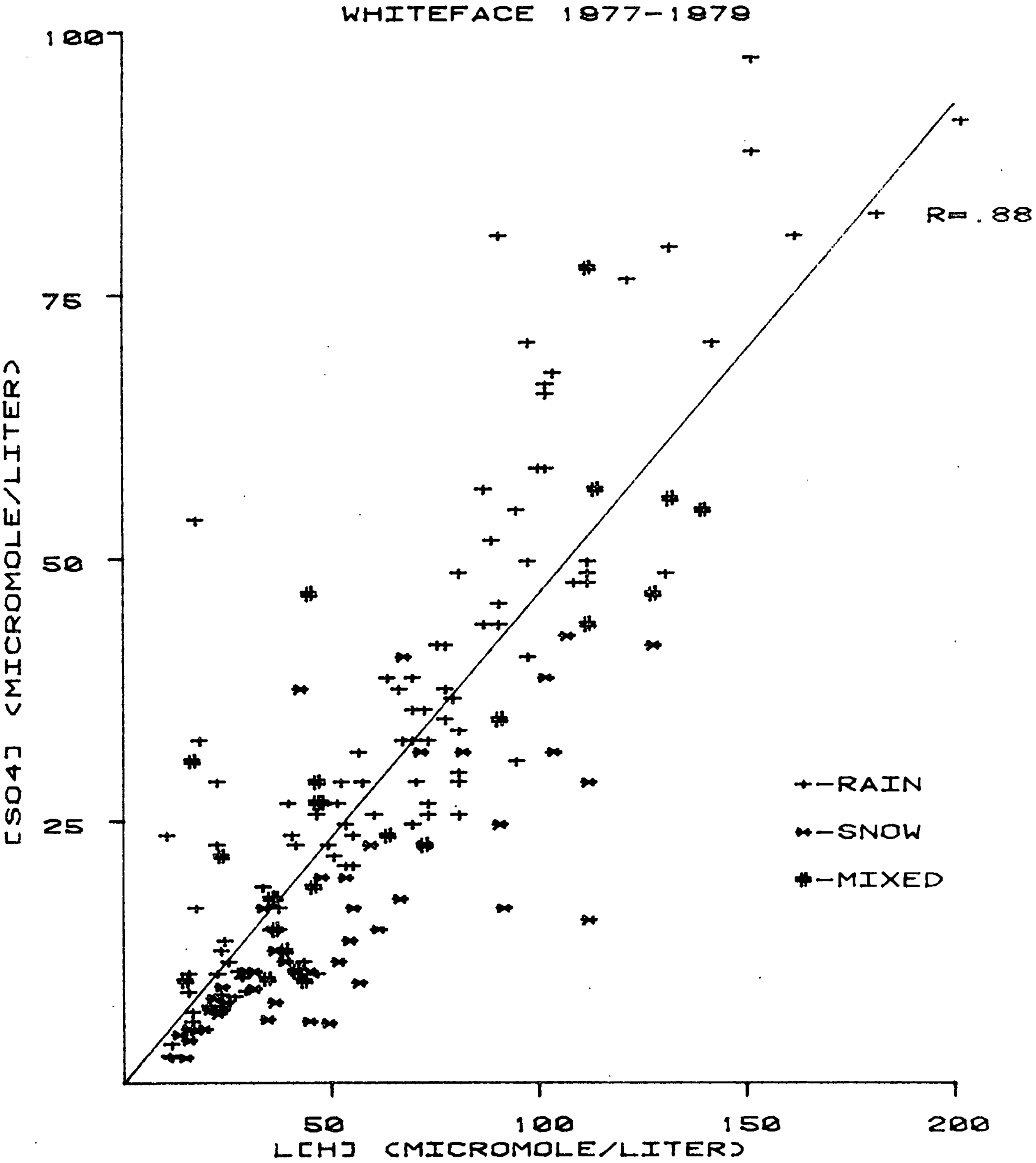


Figure 26. Hydrogen vs. Sulfate for Whiteface, 1977-79

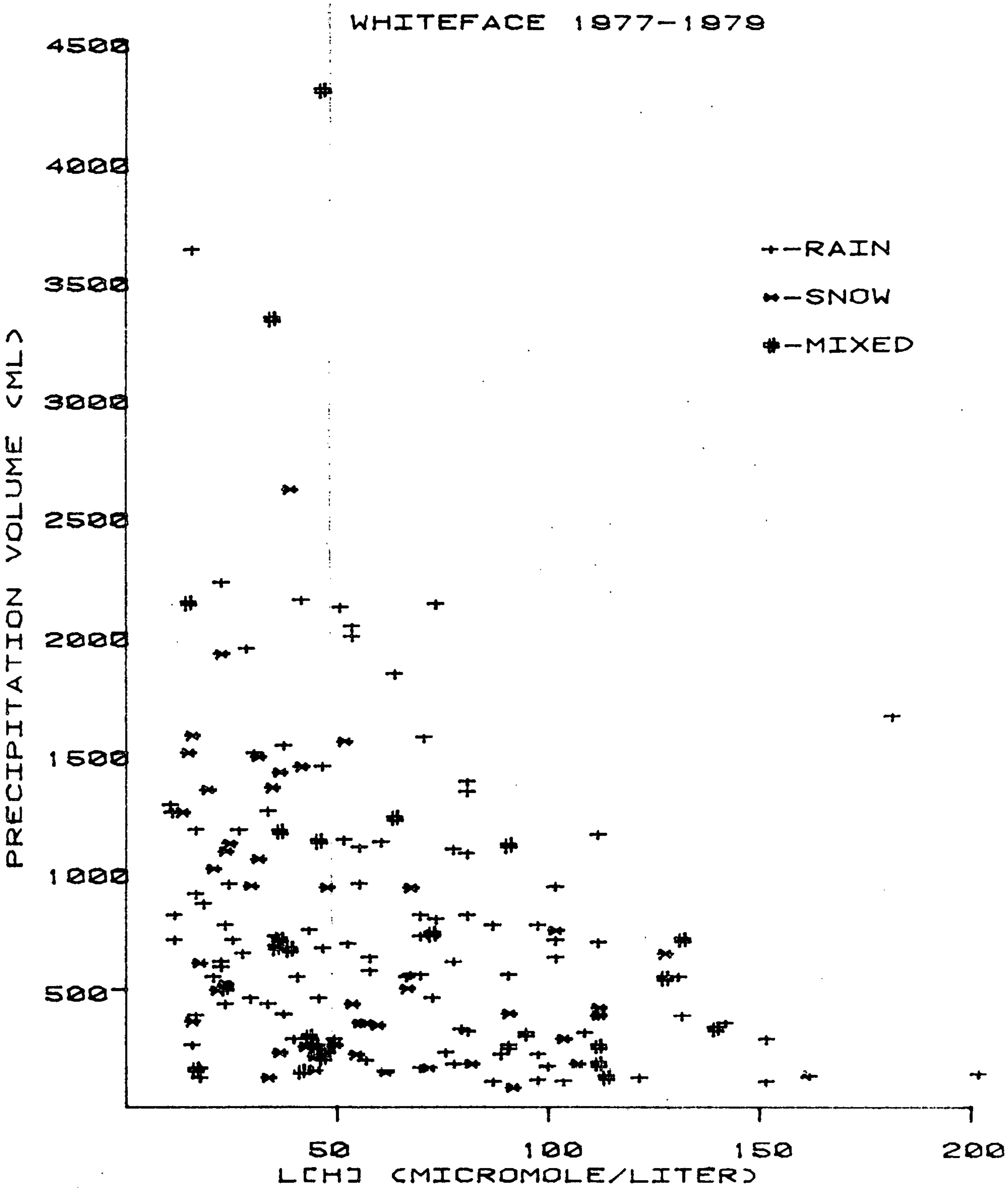


Figure 27. Precipitation Volume vs. Free Hydrogen Ion Concentration for Whiteface, 1977-79

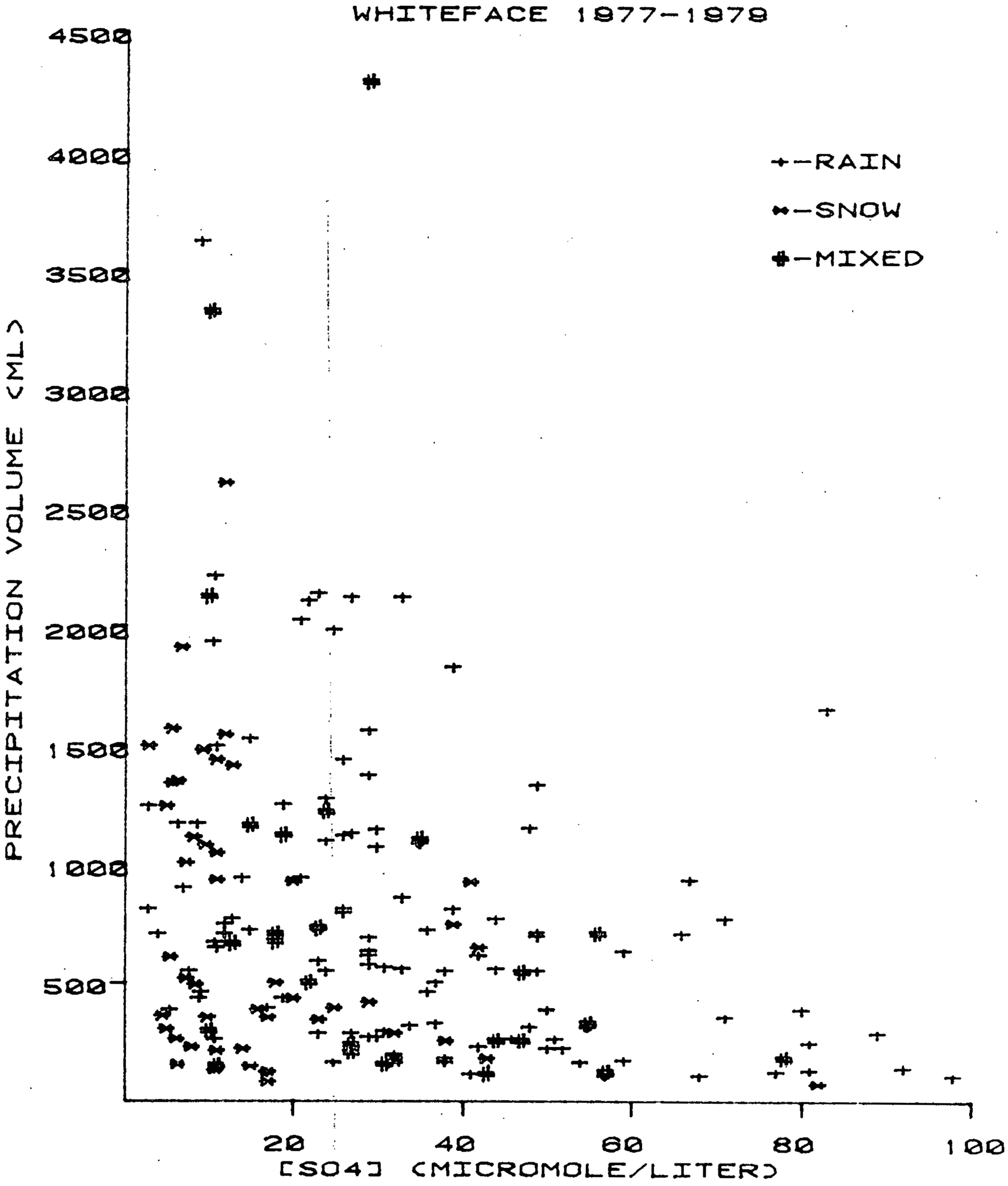


Figure 28. Precipitation Volume vs. Sulfate Concentration for Whiteface, 1977-79

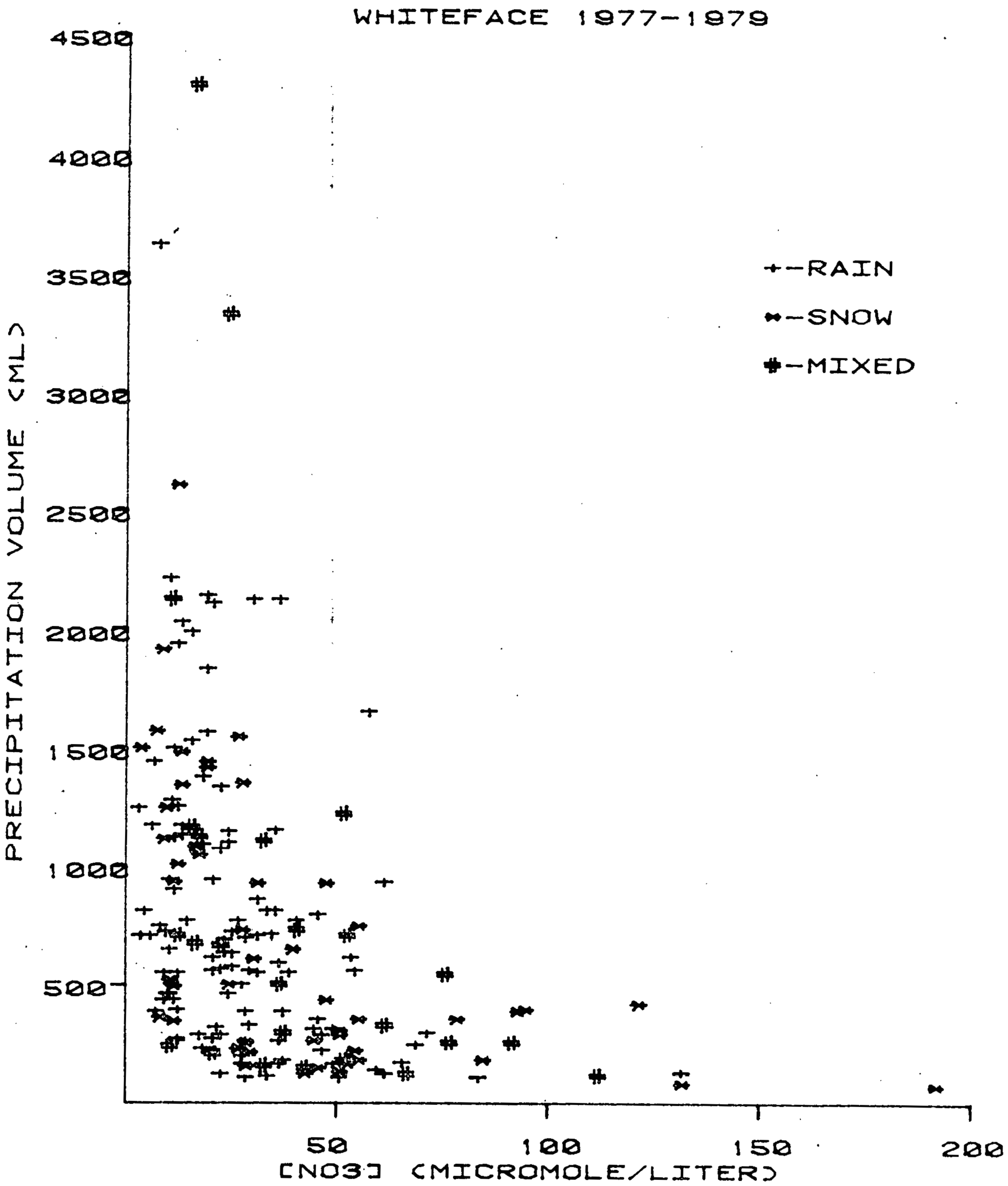


Figure 29. Precipitation Volume vs. Nitrate Concentration for Whiteface, 1977-79

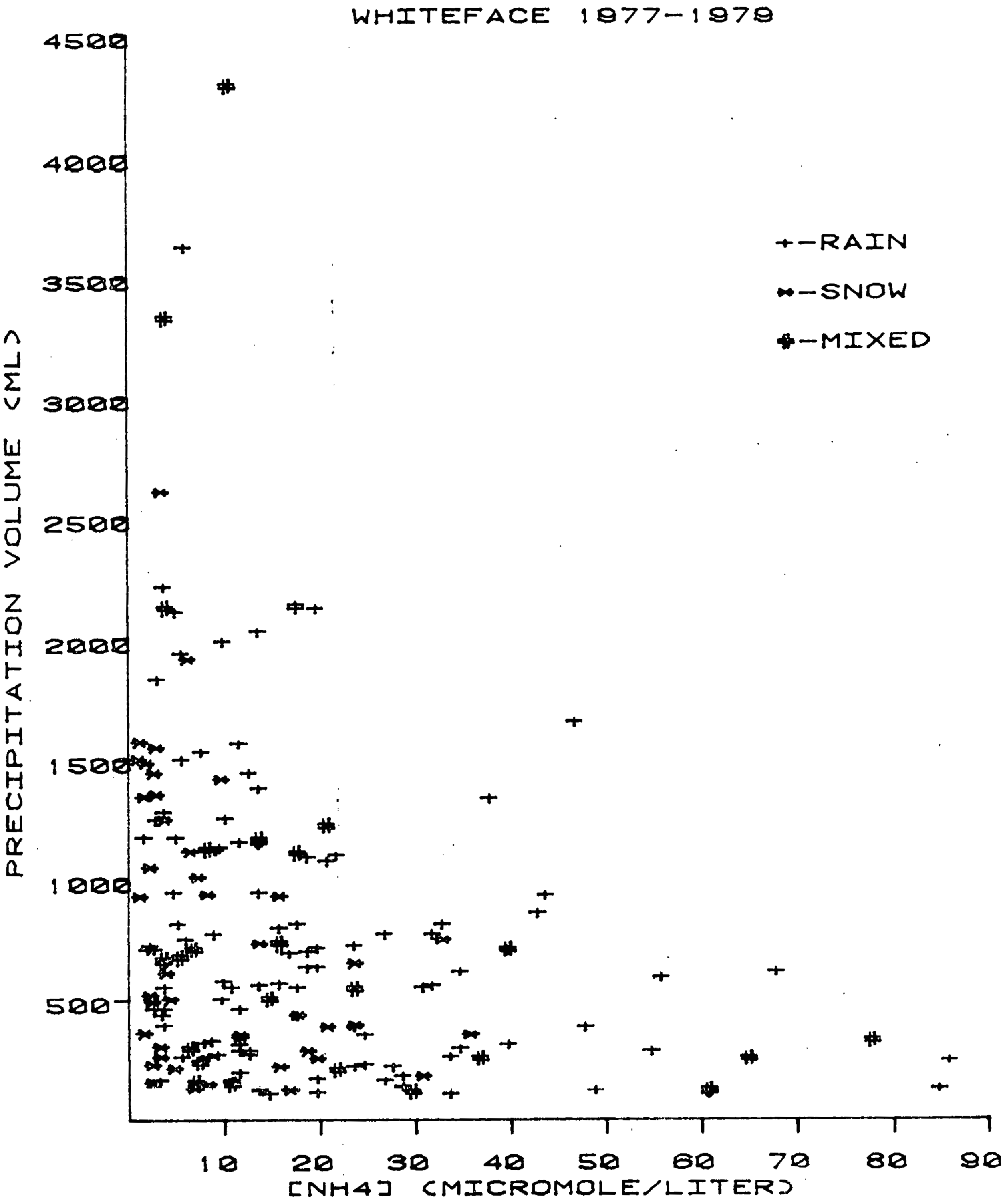


Figure 30. Precipitation Volume vs. Ammonium Concentration for Whiteface, 1977-79

of this occurrence must first be proposed. An objective method was used whereby any event value greater than the annual mean plus one standard deviation was considered to be "episodic" or "significant." This procedure was used to select episodes for case studies as well as to examine the effect of the percent of total deposition of the elevated events. The results of this procedure is shown in Tables 14 and 15, along with the mean values of concentration, deposition, and precipitation for each year. The concentration values were weighted according to the formula

$$\overline{C} = \frac{\Sigma P_i C_i}{\Sigma P_i}$$

where P_i = event precipitation volume

C_i = event concentration value

$\overline{C}$ = weighted mean.

It is interesting to note that the concentration weighted values for Whiteface, Table 14, are the lowest of the four stations considered. This could be due to the proximity of the other stations to pollutant sources, while Whiteface is essentially an isolated location, or it could be due to the elevation of Whiteface Mountain being over 4000 feet higher than the other stations. The three year means of Table 15 represent essentially an event average for deposition values so that the number of events per year must be considered when comparing station values to obtain a pattern consistent with the total deposition values of Figures 12 through 14. That is, the larger number of events or total sample volume produce a larger total deposition for Whiteface than Virginia, even though the mean values are greater for the latter station. The ratio of cations to anions of both Tables 14 and 15 indicate an approximate balance for these mean values for the yearly and three year averages. (The balance refers only to the four major ions, H^+, NH_4^+, $SO_4^=$, and NO_3^-.)

TABLE 14

CONCENTRATION [µmole/liter]

		Total Sample Volume	Intensity weighted SO_4 Mean (µmole/liter)	Intensity weighted SO_4 Mean [1]No. of significant events/total events	Intensity weighted NO_3 Mean (µmole/liter)	Intensity weighted NO_3 Mean [1]No. of significant events/total events	Intensity weighted L[H] Mean (µmole/liter)	Intensity weighted L[H] Mean [1]No. of significant events/total events	Intensity weighted NH_4 Mean (µmole/liter)	Intensity weighted NH_4 Mean [1]No. of significant events/total events
WFM	1977	52674	21.45	17/82	22.48	9/83	42.39	17/71	10.36	13/73
	1978	34364	28.32	11/55	25.08	12/55	58.79	11/54	16.67	12/55
	1979	52214	18.86	9/45	18.13	12/45	44.97	10/45	10.13	5/45
ITHACA	1977	36850	30.91	4/44	28.65	6/44	55.21	6/30	12.97	8/42
	1978	36422	32.93	15/59	30.40	10/60	66.32	12/56	15.22	9/57
	1979	47275	27.27	11/61	23.92	13/60	67.84	8/59	14.69	9/60
PENN STATE	1977	44394	31.00	19/83	30.55	17/83	59.22	8/51	13.83	14/74
	1978	42621	29.30	17/71	29.34	11/71	64.74	14/58	12.98	8/70
	1979	58879	27.93	10/77	27.01	13/77	63.41	14/74	15.85	10/76
VIRGINIA	1977	25742	34.57	9/48	27.53	7/48	60.04	5/35	14.31	8/45
	1978	41691	28.29	9/54	24.74	3/54	66.68	3/50	12.26	5/54
	[2]1979	38906	24.08	10/53	21.10	8/52	63.70	8/51	11.08	5/52

Intensity weighted averages for 1977-1979 period

	Total Sample Volume	SO_4 (µmole/liter)	NO_3 (µmole/liter)	L[H] (µmole/liter)	NH_4 (µmole/liter)	$\frac{2[SO_4^=]+[NO_3^-]}{L[H^+]+[NH_4^+]}$
WFM	46417	22.88	21.90	48.72	12.39	1.11
ITHACA	40182	30.37	27.66	63.12	14.29	1.14
PENN STATE	48631	29.41	28.97	62.46	14.22	1.14
VIRGINIA	35513	26.98	24.46	63.47	12.54	1.08

[1] A significant event is defined as one whose value is greater than the intensity weighted mean plus one standard deviation.

[2] Virginia 1979 was corrected for events missed between 10 October and 26 November.

TABLE 15

Mean Deposition [mg/m²] and [microequivalent/m²]

		$\overline{SO_4^{=}}$			$\overline{NO_3^{-}}$			$\overline{L[H^{-}]}$			$\overline{NH_4^{+}}$		
		mg/m²	µeq/m²	[1]Significant Events/ Total Events	mg/m²	µeq/m²	[1]Significant Events/ Total Events	mg/m²	µeq/m²	[1]Significant Events/ Total Events	mg/m²	µeq/m²	[1]Significant Events/ Total Events
WFM	1977	27	563	13/82	18	291	7/83	0.64	640	9/71	2.8	152	9/73
	1978	35	723	4/55	20	320	7/55	0.75	763	5/54	3.8	213	6.55
	1979	42	884	4/45	26	420	7/45	1.05	1047	6/45	4.3	237	6/45
ITHACA	1977	51	1057	6/44	30	490	4/44	1.38	1383	5/30	4.2	232	6/42
	1978	40	830	8/59	23	376	7/60	0.88	880	8/56	3.6	198	8/57
	1979	40	830	6/61	22	356	8/60	1.06	1058	7/59	4.1	228	5/60
PENN STATE	1977	32	677	13/83	21	333	11/83	1.05	1052	9/51	3.1	169	6/74
	1978	35	718	10/71	22	366	9/71	0.97	970	7/58	2.8	155	5/70
	1979	41	862	9/77	26	415	8/77	1.02	1018	11/74	4.5	248	7/76
VIRGINIA	1977	36	757	3/48	19	301	5/48	0.91	901	4/35	3.0	167	2/45
	1978	42	881	11/54	24	380	7/54	1.11	1113	10/50	3.5	191	9/54
	1979[2]	35	731	5/53	20	319	7/53	1.00	1004	5/51	3.1	171	7/52

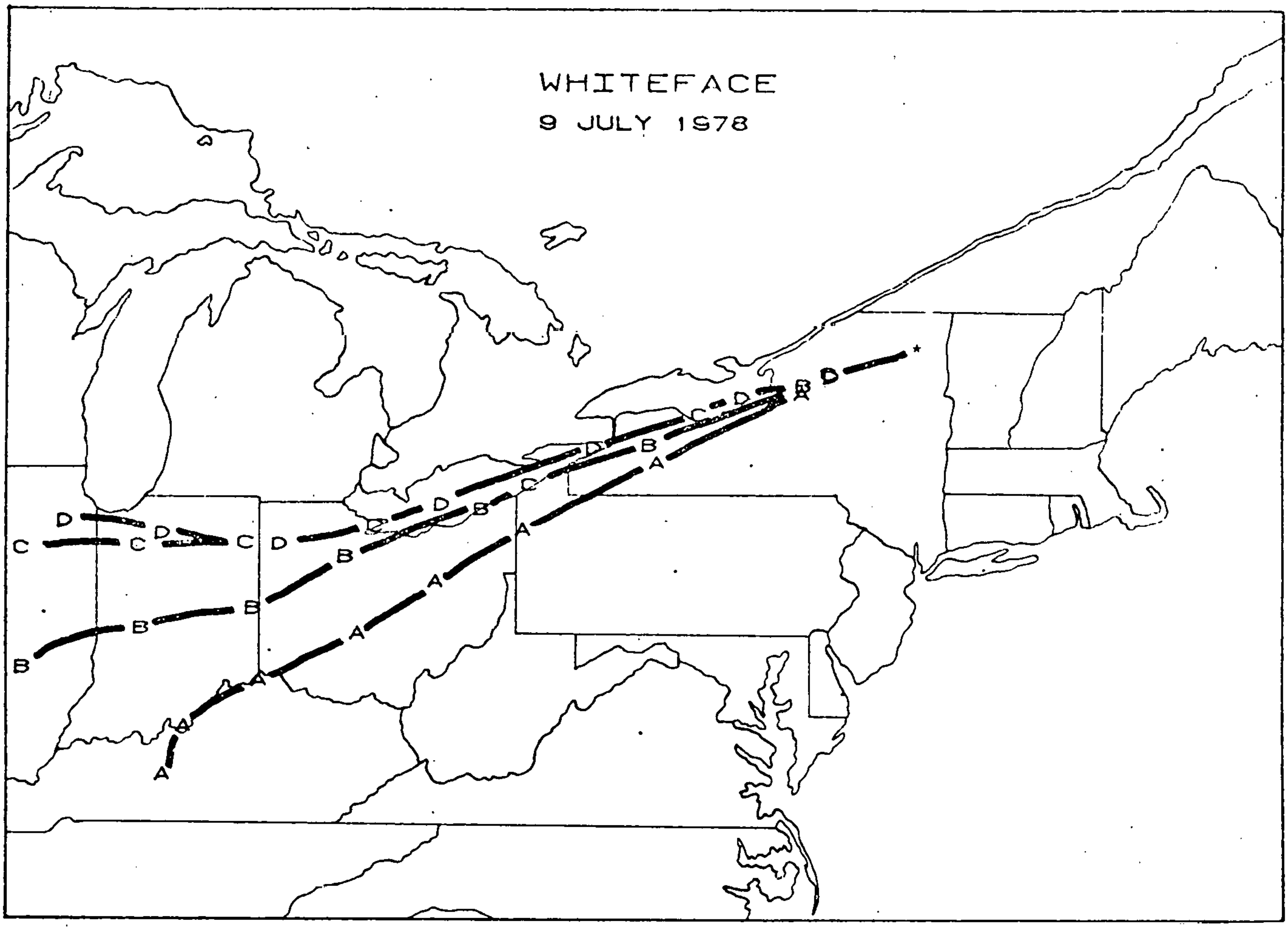
		Total Sample Volume [ml]		C = $(\overline{SO_4} + \overline{NO_3})$ [µeq/m²]		A = $(\overline{L[H]} + \overline{NH_4})$ [µeq/m²]		C/A (cations/anions)	
WFM	1977	52674		854	3 yr. mean 1070	792	3 yr. mean 1015	1.08	3 yr. mean 1.05
	1978	34364		1043		967		1.08	
	1979	52214	Total - 139252	1304		1284		1.06	
ITHACA	1977	36850		1547	3 yr. mean 1313	1615	3 yr. mean 1321	0.96	3 yr. mean 0.99
	1978	36422		1206		1087		1.12	
	1979	47275	Total - 120547	1186		1286		0.92	
PENN STATE	1977	44394		1010	3 yr. mean 1124	1221	3 yr. mean 1203	0.83	3 yr. mean 0.93
	1978	42621		1084		1125		0.96	
	1979	58933	Total - 145948	1277		1266		1.01	
VIRGINIA	1977	25742		1058	3 yr. mean 1123	1068	3 yr. mean 1162	0.99	3 yr. mean 0.95
	1978	41841		1262		1304		0.97	
	1979	38906	Total - 106489	1050		1175		0.95	

[1] A significant event is defined as one whose value is greater than the mean plus one standard deviation.
[2] Virginia 1979 was corrected for events missed between 10 October and 26 November.

2.7 The July 1978 "Intensive"

During the month of July 1978, intensive monitoring of air pollution parameters was initiated throughout the midwest to northeastern part of the United States. Several air pollution episodes occurred during this month, triggered by the high photochemical potential that coincides with high pressure systems. Precipitation events that follow such anticyclonic events could conceivably lead to rain that is enriched in pollution-related ions ($SO_4^=$, NO_3^-, H^+. etc.) In order to investigate this hypothesis, it is very crucial to know the origin of air masses. The MAP3S site at Whiteface Mountain is again selected as the study site in order to see whether or not air pollution episodes concentrated in the "Ohio Valley" region and occurring under anticyclonic conditions do have an impact on the northeastern United States (Adirondack region) precipitation chemistry.

The July 1978 back trajectories for Whiteface as developed by the ARL-ATAD model are shown in Figures 31 through 35. Each letter of the trajectory indicates a six hour endpoint whereby the A-trajectory denotes 00 Z, the B denotes 06 Z, the C denotes 12 Z, and the D denotes 18 Zulu time. Therefore, relative speed of the air parcels as well as direction is obtainable from these figures. Trajectories which terminate with less than eight endpoints are usually caused by insufficient transport layer depth or lack of usable meteorological upper air data. As mentioned earlier, trajectories were not extrapolated past two days. Included in each figure is the MAP3S collection date, event concentration and deposition of the four major ions, sample volume, and ion ratio. Figure 36 gives the detailed six hour precipitation totals for Whiteface for June and July of 1978 which can be used to volume-weight the trajectories in order to determine the dominant



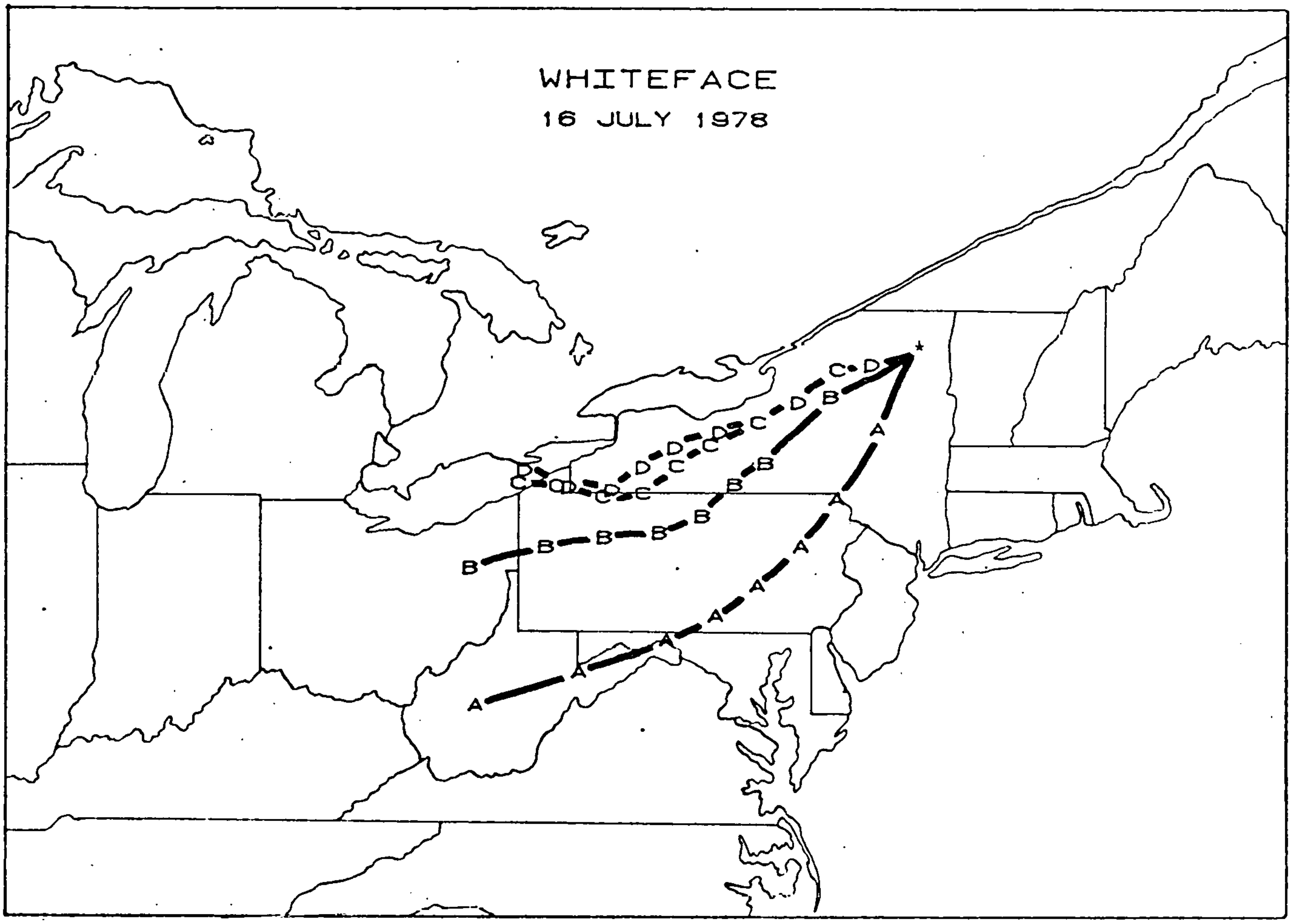
MAP3S Event - 11 July 1978

	$[H^+]_L$	$[SO_4^=]$	$[NO_3^-]$	$[NH_4^+]$
Concentration (μmole/liter)	110	49	27	23
Deposition (mg/m^2)	0.81	35	12	3.1

Sample volume - 362 ml

$[H^+]_L + [NH_4^+]/2[SO_4^=] + [NO_3^-] = 1.01$

Figure 31



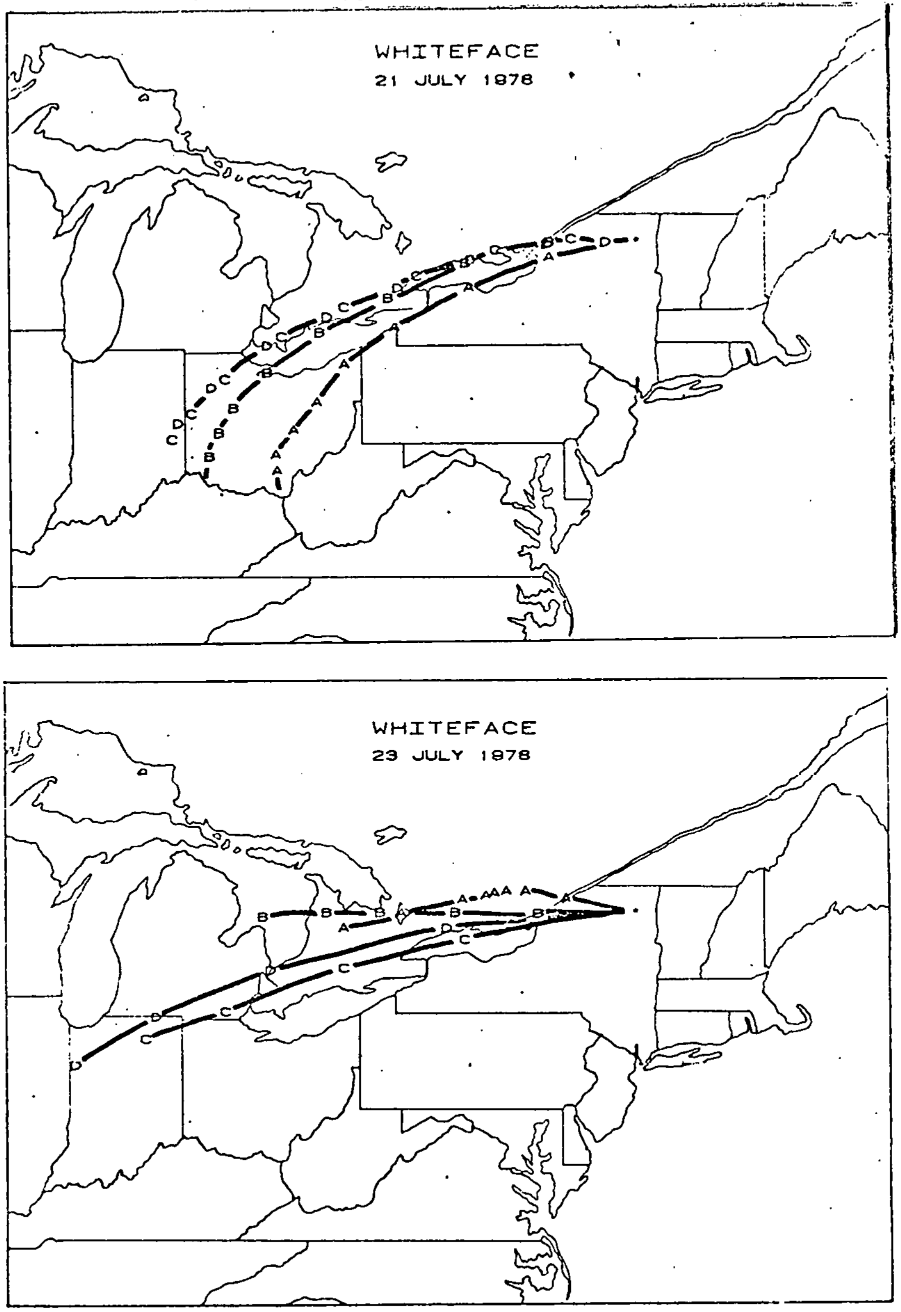
MAP3S Event - 18 July 1978

	$[H^+]_L$	$[SO_4^=]$	$[NO_3^-]$	$[NH_4^+]$
Concentration (μmole/liter)	150	97	82	60
Deposition (mg/m^2)	0.26	16	8	1.9

Sample volume - 84 ml

$[H^+]_L + [NH_4^+]/2[SO_4^=] + [NO_3^-] = 0.76$

Figure 32



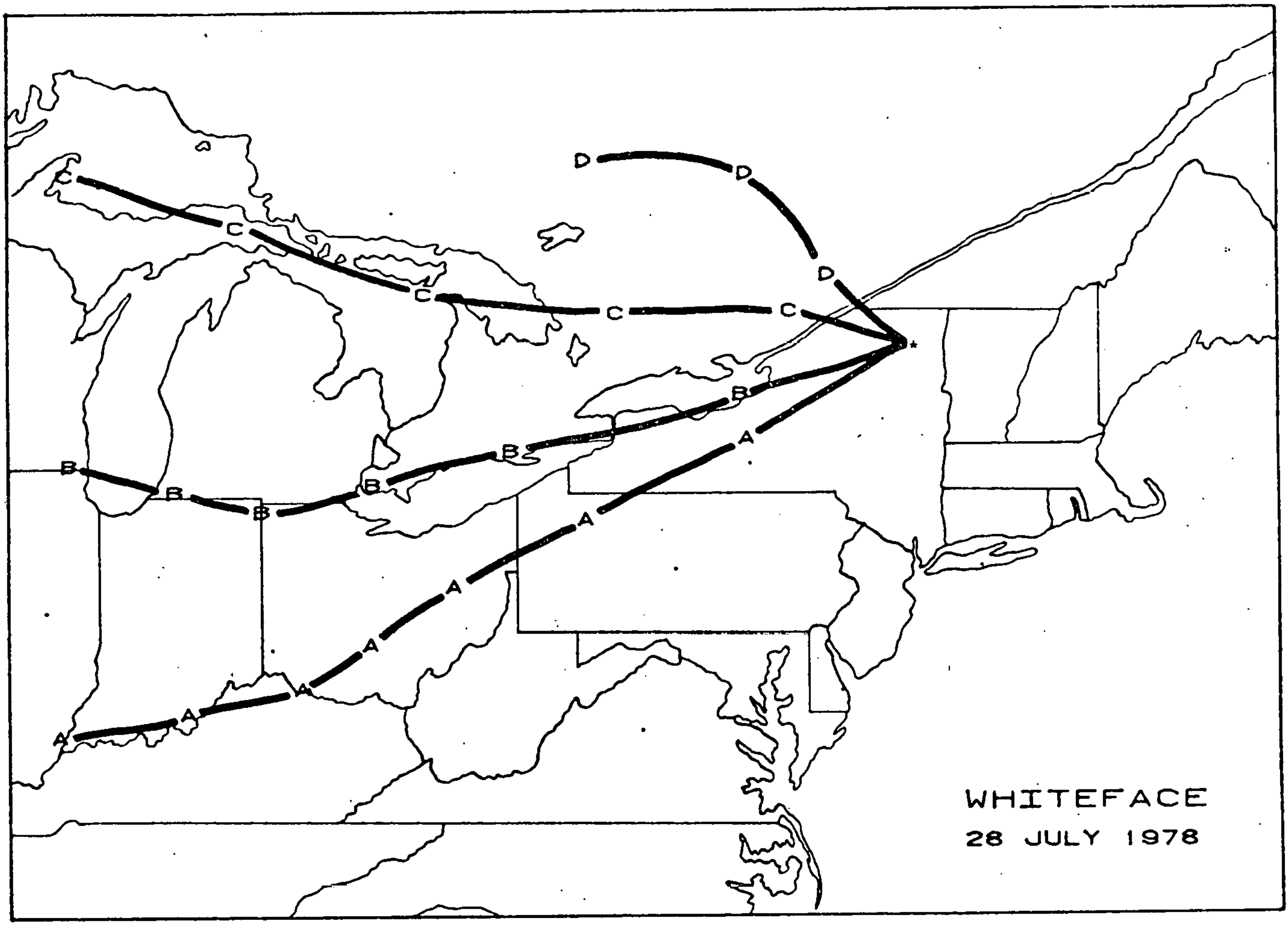
MAP3S Event - 24 July 1978

	$[H^+]_L$	$[SO_4^=]$	$[NO_3^-]$	$[NH_4^+]$
Concentration (μmole/liter)	150	88	45	54
Deposition (mg/m^2)	0.81	45	14	5.2

Sample volume - 264 ml

$[H^+]_L + [NH_4^+]/2[SO_4^=] + [NO_3^-] = 0.92$

Figure 33



MAP3S Event - 28 July 1978

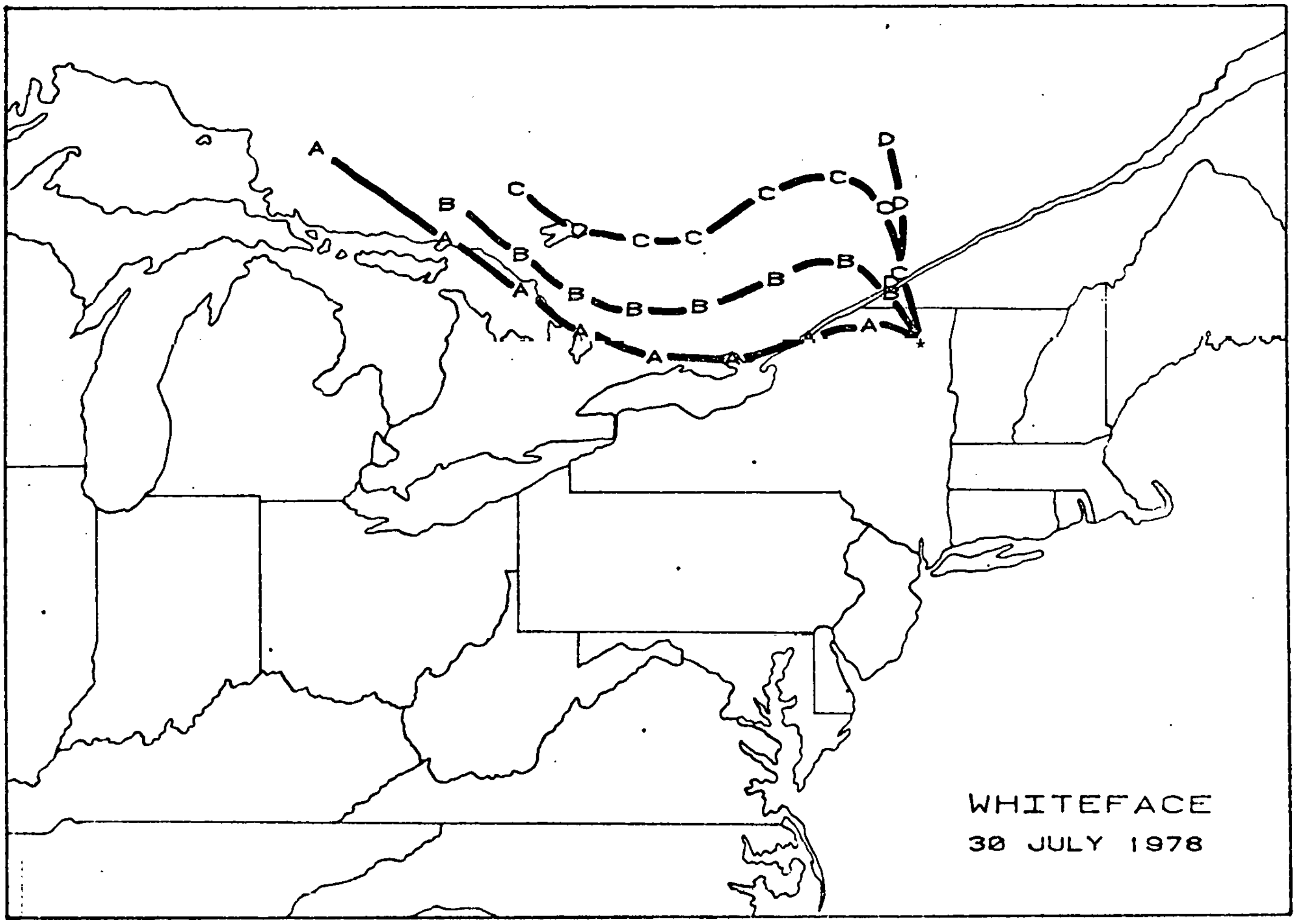
	$[H^+]_L$	$[SO_4^=]$	$[NO_3^-]$	$[NH_4^+]$
Concentration (μmole/liter)	98	58	64	19
Deposition (mg/m^2)	0.9	52	36	3.3

Sample volume - 450 ml

$[H^+]_L + [NH_4^+]/2[SO_4^=] + [NO_3^-] = 0.65$

(Note: total cation/total anion = 0.84)

Figure 34



MAP3S Event - 31 July 1978

	$[H^+]_L$	$[SO_4^=]$	$[NO_3^-]$	$[NH_4^+]$
Concentration (μmole/liter)	26	10	8.9	3.1
Deposition (mg/m^2)	0.33	12	6.8	0.7

Sample volume - 623 ml

$[H^+]_L + [NH_4^+]/2[SO_4^=] + [NO_3^-] = 1.01$

Figure 35

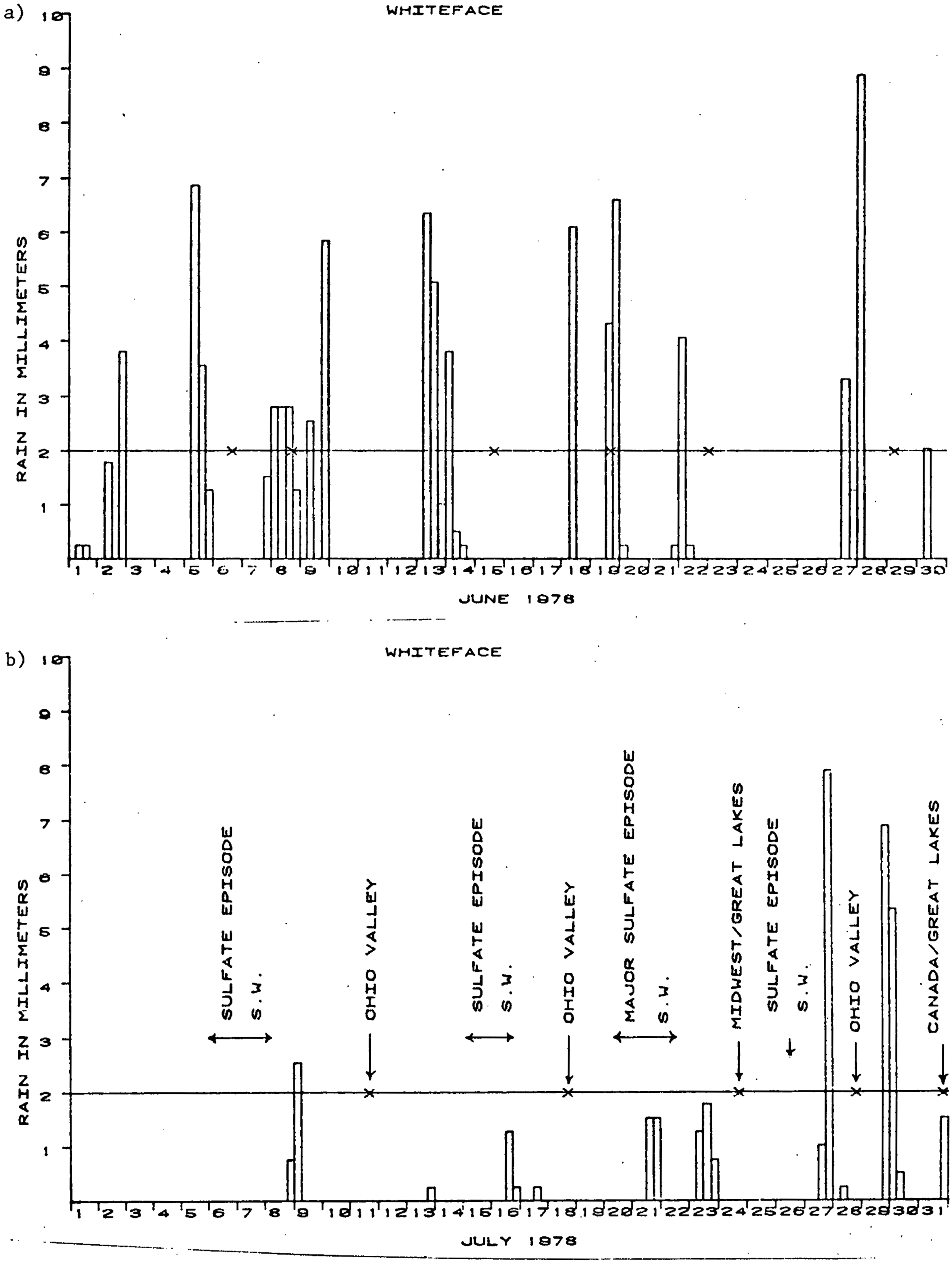


Figure 36. Six hour precipitation amounts for Whiteface, a) June, and b) July 1978

contributor(s) in the case of conflicting or diverse directions. Note that Figure 36 refers to local standard time, while trajectory calculations are based on GMT (Zulu time).

The Sulfate Regional Experiment (SURE) air quality date for July 1978 were used to determine ambient air quality conditions, and in particular to delineate sulfate episodes worthy of examination. Figures 37, 37a, 38 and 38a illustrate ambient conditions based on 24 hour HIVOL sampling and rainfall for Whiteface and Ithaca. There were essentially four sulfate episodes during July 1978 that are reflected in the total suspended particulates, SO_4 (aerosol) and SO_2. The aerosol nitrate concentration demonstrates no significant trend or, in the case of Ithaca, exhibits an anti-correlation with concentration values of the other aerosol constituents.

The cleansing mechanisms of rainout and washout and/or the change of air mass (anti-cyclonic versus cyclonic) are apparent, causing a significant decrease in total suspended particulates and in other pollution-related materials. The early part of July for Ithaca is somewhat confusing in this respect, since the National Climatic Center data indicate no rainfall between 5 July and 9 July, but a MAP3S collection accounted for 2.65 mm, suggesting at least some precipitation activity during this period. Rainfall amounts in Figure 38 are taken from National Climatic Center Daily Precipitation Summaries.

With this information, the individual precipitation events and preceding ambient conditions at WFM can be classified as follows:

Rain Event at WFM	MAP3S Collection	Origin of Air Mass/Characterization
7/8	7/11	"Ohio Valley" preceded by sulfate episode
7/16	7/18	"Ohio Valley" preceded by sulfate episode
7/21 and 7/23	7/24	"Midwest/Great Lakes" preceded by a major sulfate episode
7/27	7/28	"Ohio Valley" preceded by a sulfate episode
7/29	7/31	"Canada/Great Lakes"

There is a striking difference in concentration values between the air masses arriving at Whiteface from the "Midwest" to "Ohio Valley" region and the "Canada" to "Great Lakes" region. The intensity weighted [$SO_4^=$], [NO_3^-], and [H^+] concentration for these two different regions are:

	Concentration			
	H^+ µmole/L	$SO_4^=$ µmole/L	NO_3^- µmole/L	MAP3S Events
WFM	$\overline{146}$	$\overline{65}$	$\overline{50}$	Combined July 11, 18, 24 and 28 MAP3S events (The bar indicates the mean)
	46	10	8.9	Canada/Great Lakes
ITH	$\overline{138}$	$\overline{55}$	$\overline{34}$	Combined July 9, 17, 22, 27, 28 (The bar indicates the mean)
	46	16	22	July 4 "Canadian" air
	25	9.4	6.7	August 7 events
PEN	$\overline{170}$	$\overline{71}$	$\overline{45}$	Combined July 7, 11, 15, 24, 28, 30 events (The bar indicates the mean)
	71	25	13	July 4 event "Canadian" air

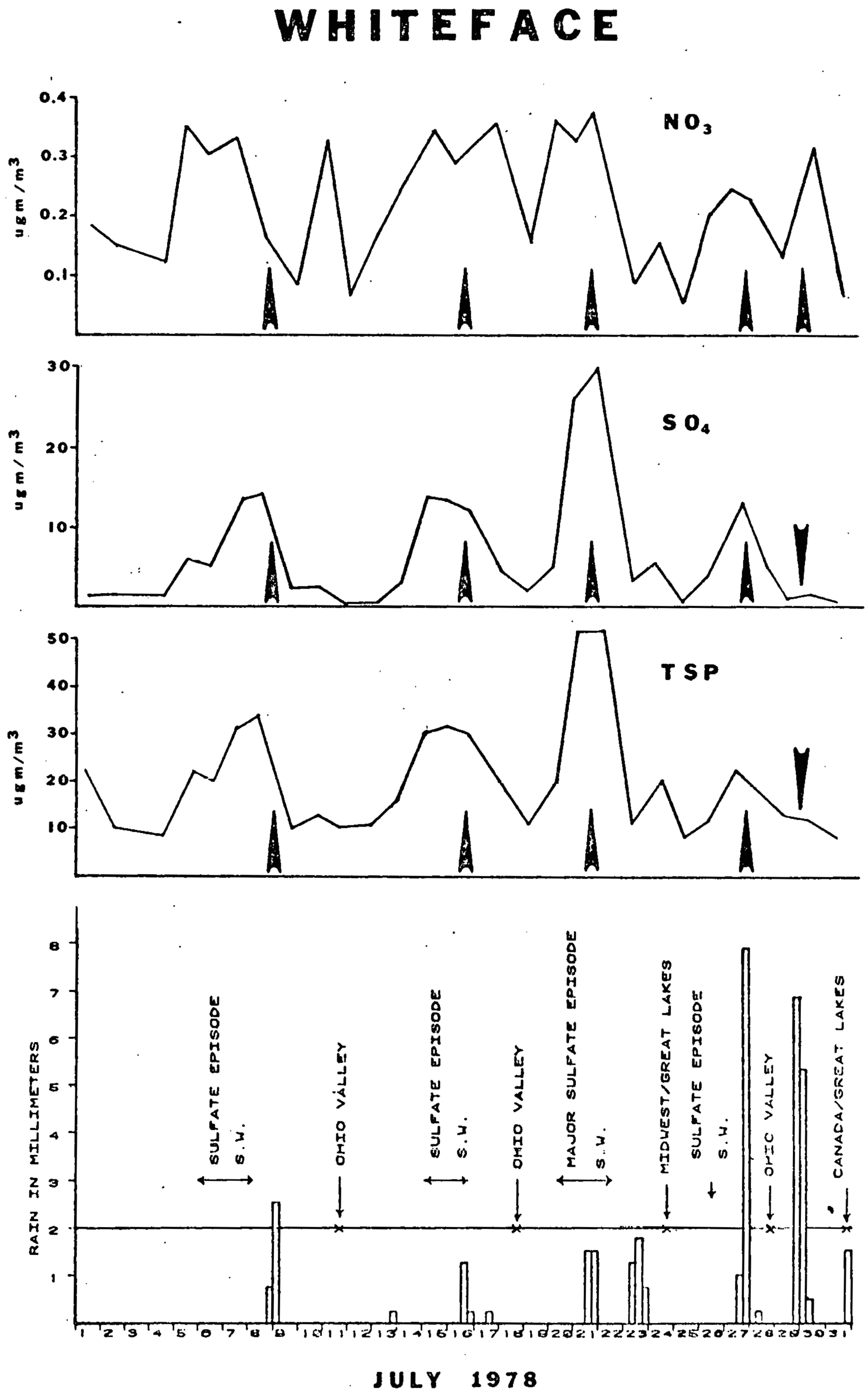


Figure 37. SURE air quality data and rainfall for Whiteface - July 1978

Whiteface Air Quality Data July 1978

Date	$[\mu g/m^3]$				Daily Rainfall (inch)	(μmole/L) MAP3S			
	TSP	NO_3	SO_4	SO_2		$L[H^+]$	$[SO_4^=]$	$[NO_3^-]$	$[NH_4^+]$
1	22.934	0.187	1.464	16.921					
2	10.756	0.163	1.746	18.013					
3	--	--	--	19.432					
4	9.315	0.120	1.086	18.340					
5	23.454	0.341	6.130	21.178					
6	20.623	0.316	5.301	21.506					
7	32.780	0.333	13.770	28.618					
8	35.301	0.183	15.889	--	.13				
9	11.966	0.097	2.445	--					
10	13.790	0.316	3.315	--					
11*	10.272	0.080	0.909	--		110	49	27	23
12	11.739	0.176	0.958	--					
13	17.064	0.239	3.745	--	.01				
14	31.642	0.322	14.100	--					
15	32.010	0.293	13.925	--					
16	30.587	0.320	12.206	--	.06				
17	19.776	0.369	6.334	--	.01				
18*	13.462	0.176	2.316	--		150	97	82	60
19	22.108	0.352	6.523	--					
20	53.124	0.309	25.936	--					
21	53.180	0.356	29.347	--	.12				
22	13.206	0.099	3.634	--					
23	22.222	0.153	7.229	--	.15				
24*	10.821	0.088	0.671	--		150	88	45	54
25	14.359	0.205	3.339	--					
26	26.878	0.229	12.045	--					
27	19.255	0.222	6.700	--	.35				
28*	14.865	0.116	0.920	--	.01	98	58	64	19
29	13.963	0.290	1.390	--	.43				
30	9.714	0.084	0.655	--	.07				
31*	--	--	--	--	.11	26	10	8.9	3.1

*MAP3S Event

Figure 37a. Whiteface air quality data - July 1978

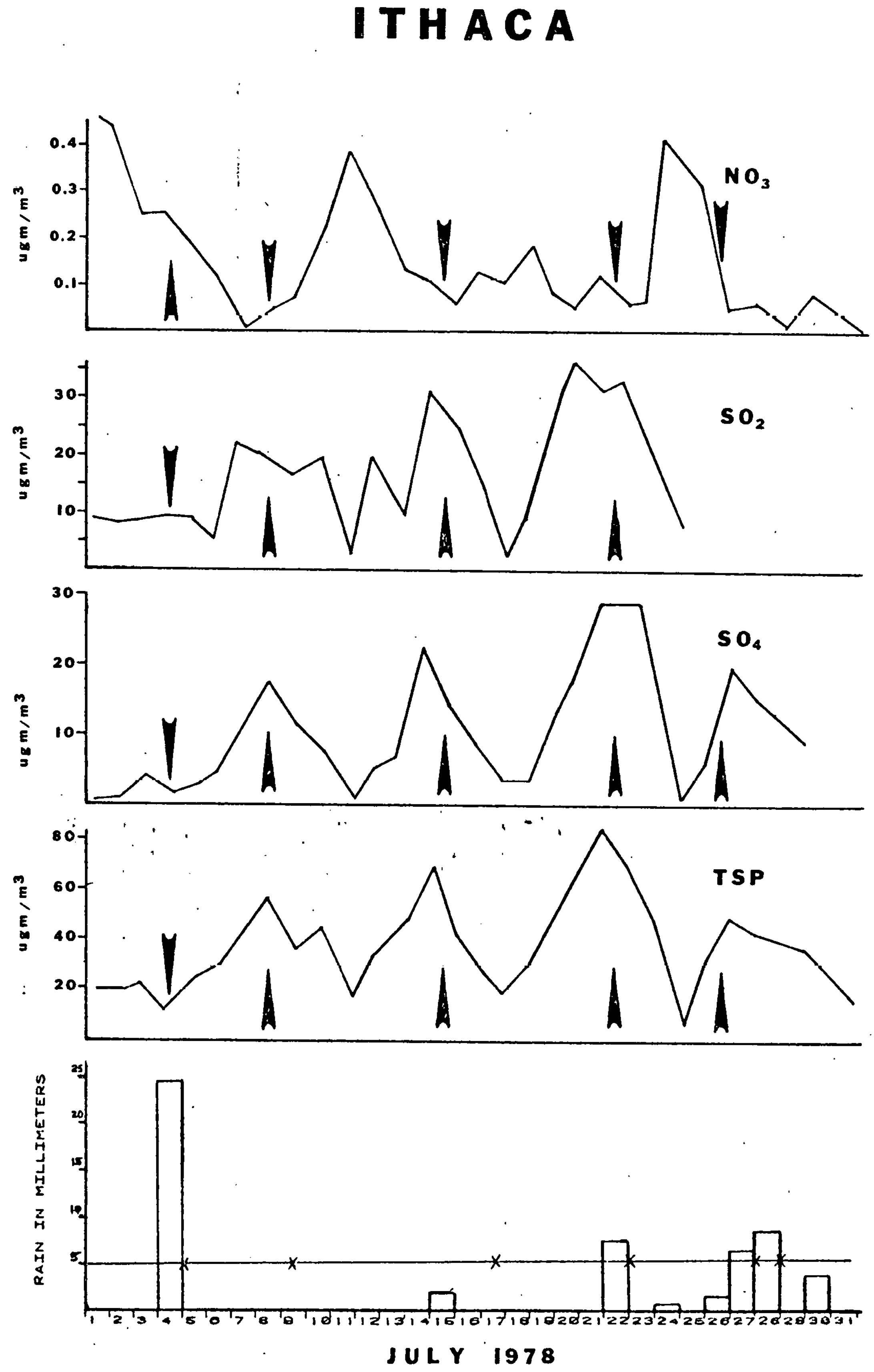


Figure 38. SURE air quality data and rainfall for Ithaca - July 1978

ITHACA AIR QUALITY DATA JULY 1978

	micro gram/m^3						Rainfall (inch)	(μ mole/l) MAP3S			
Date	TSP	Cl^-	NH_4^+	NO_3^-	$SO_4^=$	SO_2		L[H^+]	$SO_4^=$	NO_3^-	NH_4^+
1	19.3	--	--	0.477	1.792	8.813	--				
2	19.8	--	--	0.434	1.439	7.423	--				
3	21.4	--	--	0.246	4.442	8.952	--				
4*	11.4	--	--	0.268	2.212	9.061	.96	66	16	22	3.5
5	22.5	--	--	0.192	3.456	8.842	--				
6	29.5	--	--	0.133	4.826	5.677	--				
7	--	--	--	0.002	--	22.487	--				
8	56.2	--	--	0.057	18.915	21.833	--				
9*	38.7	--	--	0.073	12.572	18.668	--	169	74	37	28
10	44.7	--	--	0.213	9.020	21.178	--				
11	17.5	--	--	0.399	1.953	4.803	--				
12	33.6	--	--	0.274	5.061	21.615	--				
13	45.0	--	--	0.177	7,831	10.644	--				
14	68.3	--	--	0.128	23.620	31.986	--				
15	44.7	--	--	0.087	16.830	25.872	.12				
16	29.8	--	--	0.187	9.234	14.082	--				
17*	20.5	0.005	0.221	0.110	4.479	3.930	--	129	58	26	23
18	30.1	0.005	0.171	0.192	4.479	11.135	--				
19	--	0.005	2.262	0.100	15.362	25.982	--				
20	62.1	0.005	4.416	0.070	18.785	36.134	--				
21	85.3	0.021	5.001	0.113	28.018	32.465	--				
22*	65.3	0.033	7.616	0.063	28.817	33.296	.35	170	63	3.5	.18
23	45.0	0.005	3.939	0.073	16.902	24.890	--				
24	8.1	0.052	0.012	0.401	1.968	8.187	.02				
25	27.4	--	--	0.318	5.186	--	--				
26	46.6	--	--	0.049	20.159	--	.07				
27*	41.8	--	--	0.061	18.003	--	.30	200	87	57	34
28*	--	--	--	0.001	--	--	.36	112	42	35	27
29	30.6	--	--	0.096	10.076	--	--				
30	--	--	--	--	--	--	.15				
31	12.7	--	--	0.002	--	--	--				

*MAP3S Event

Figure 38a. Ithaca air quality data - July 1978

Concentration (μmole/L) of pollutant material is one way of characterizing the impact of precipitation on a region. Deposition (mg/m^2 or μequiv/m^2) is another equally, if not more, important parameter. For July 1978, the following deposition picture emerges for the "Midwest/Ohio Valley" versus "Canada/Great Lakes" region:

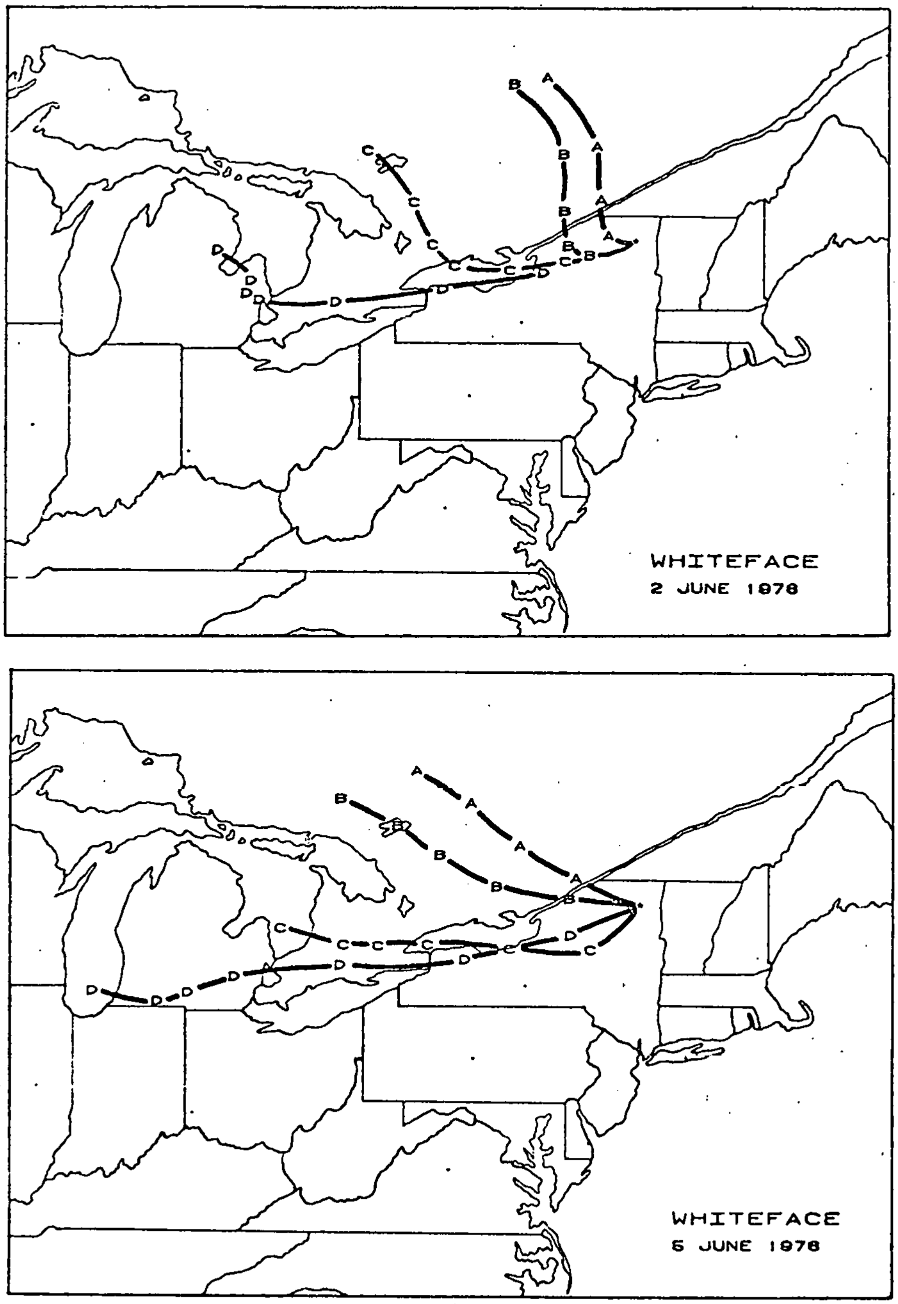
	Deposition			
	H (mg/m^2)	SO_4 (mg/m^2)	NO_3 (mg/m^2)	MAP3S Events
WFM	$\overline{0.61}$ per event 2.44 total for July 78	$\overline{28.4}$ per event 113.6 total for July 78	$\overline{11.7}$ per event 46.8 total for July 78	Combined July 11, 18 and 24 and 28 Midwest/Ohio Valley (The bar refers to the mean)
	1.58 or 24% of total July	12.2 11% of total	6.8 15% of total	July 31 event Canada/Great Lakes
ITH	$\overline{2.18}$ per event 207 of total for July 78	$\overline{84.3}$ per event 241.5 total	$\overline{31.2}$ per event 156 total	Combined July 9, 17, 22, 27, 28 Midwest/Ohio Valley (The bar refers to the mean)
	1.29 or 12% of total July 78	43.3 or 18% of total	37.2 or 24% of total	July 4 Canadian air
PEN	$\overline{0.95}$ per event 4.76 total for July 78	$\overline{38.4}$ per event 192 total	$\overline{15.2}$ per event 76 total	Combined July 7, 11, 15, 24, 28, 30 Midwest/Ohio Valley (The bar refers to the mean)
	1.83 39% of total July	62 or 32% of total July	20 or 26% of total	July 4 Canadian air

It can be summarized that the impact of precipitation in July of 1978 originating from the "Great Lakes/Canadian" sector is significantly lower than the impact caused by "Midwest/Ohio Valley" air in regard to the concentration, but comparable in regard to deposition per event. There have been four to five times more events during July 1978 involving air masses from the "Midwest/Ohio Valley." Accordingly, the percent contribution of the precipitation from air masses passing over the Canadian/Great Lakes region is appreciably lower. For example, during July of 1978, 76% of the hydrogen ion, 89% of the sulfate ion and 85% of the nitrate ion were deposited at WFM from air mass systems that had previously passed over the Midwest/Ohio Valley region. Surprisingly enough, however, a much lower fraction, namely 61% of the hydrogen ion, 68% of the sulfate ion and 75% of the nitrate ions had been deposited at Penn State from similar air masses.

2.8 June 1978 Case Studies

The events of June 1978 were also examined to determine if the same deposition proportionalities existed between the different air masses. SURE air quality data were not available; therefore, ambient air quality, pollutant episode, and loading of the atmosphere could not be determined. The two day back trajectories for WFM MAP3S events during June 1978 are shown in Figures 39 through 44. Contrary to July, there were no comparisons possible between different air masses since almost every air mass leading to an event at WFM had at some time passed over the "Midwest/Ohio Valley" area. Even though all events for June have a similar sector of origin, it is still interesting to compare the concentration and deposition patterns. Aside from the diluting effect of precipitation volume on the concentration of various ions, it is apparent that the ion concentration measured at WFM is not uniquely defined by air mass origin and air trajectory alone.

A detailed study of emissions, chemical and removal transportations processes along the trajectory path is needed to account for fluctuations in concentration of samples of relative magnitude which originated in the same general sector.



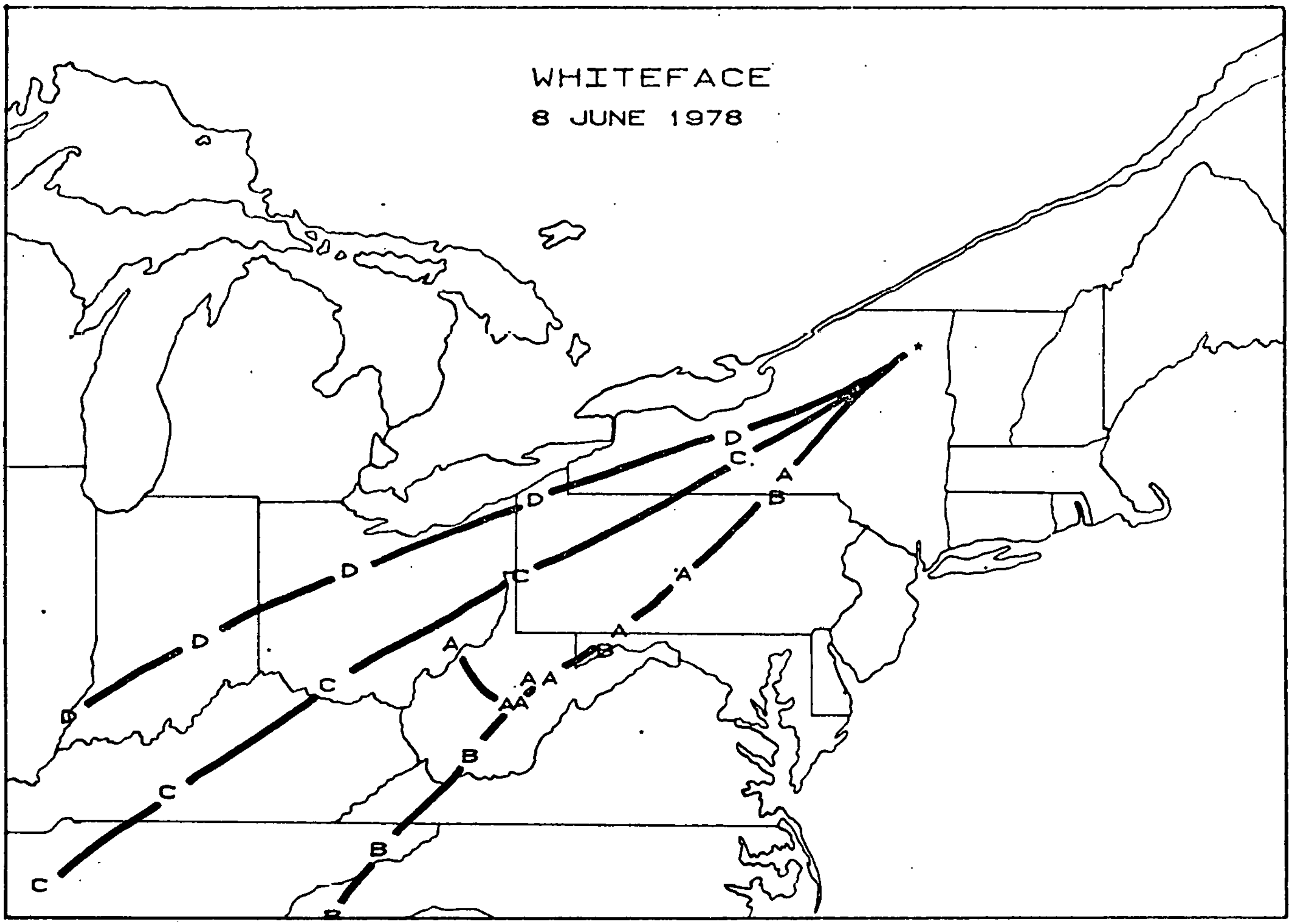
MAP3S Event - 6 June 1978

	$[H^+]_L$	$[SO_4^=]$	$[NO_3^-]$	$[NH_4^+]$
Concentration (μmole/liter)	100	66	60	43
Deposition (mg/m^2)	1.86	118	67	16

Sample volume - 914 ml

$[H^+]_L + [NH_4^+]/2[SO_4^=] + [NO_3^-] = 0.74$

Figure 39



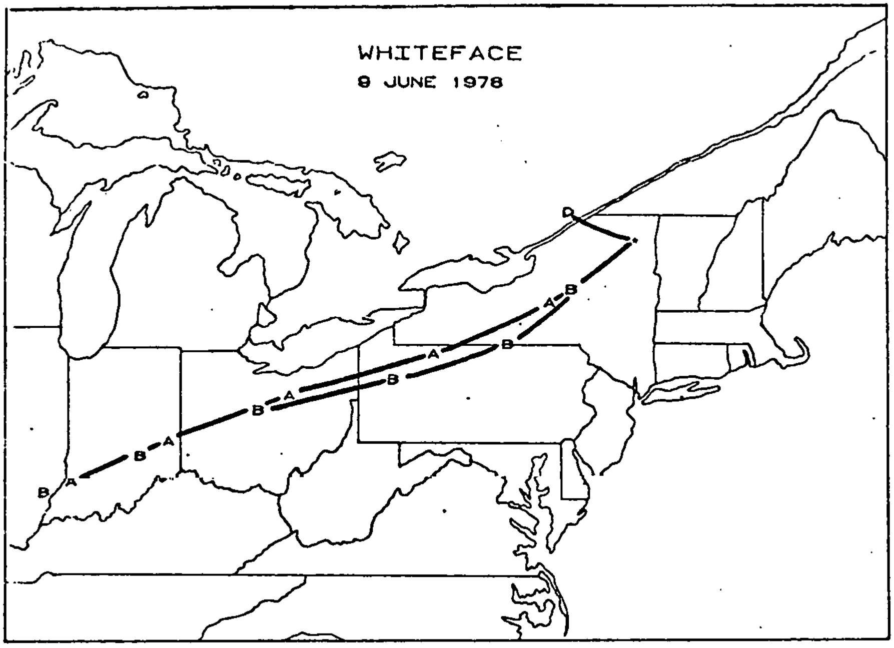
MAP3S Event - 8 June 1978

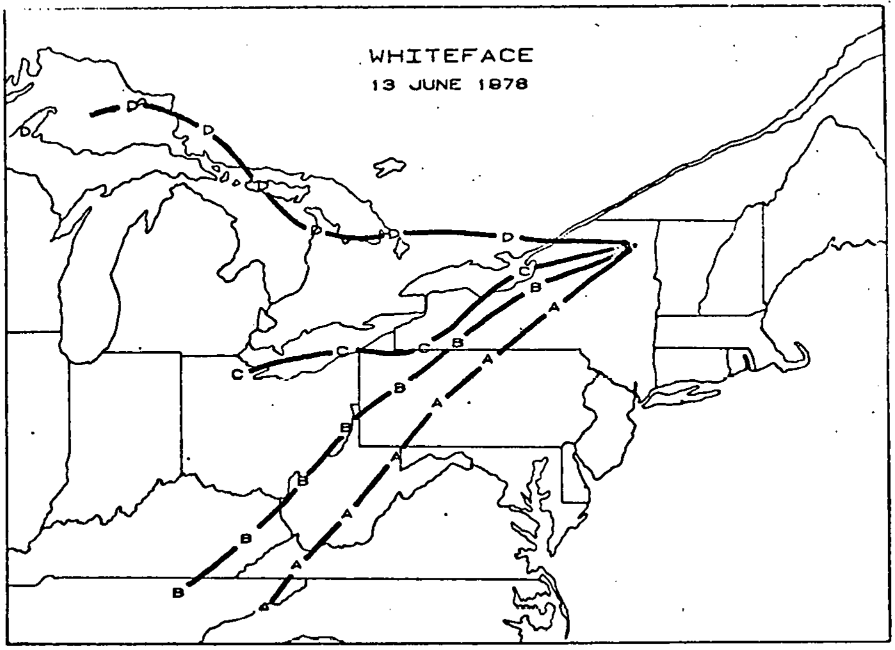
	$[H^+]_L$	$[SO_4^=]$	$[NO_3^-]$	$[NH_4^+]$
Concentration (μmole/liter)	56	28	24	9.3
Deposition (mg/m²)	0.63	30	16	1.9

Sample volume - 554 ml

$[H^+]_L + [NH_4^+]/2[SO_4^=] + [NO_3^-] = 0.82$

Figure 40





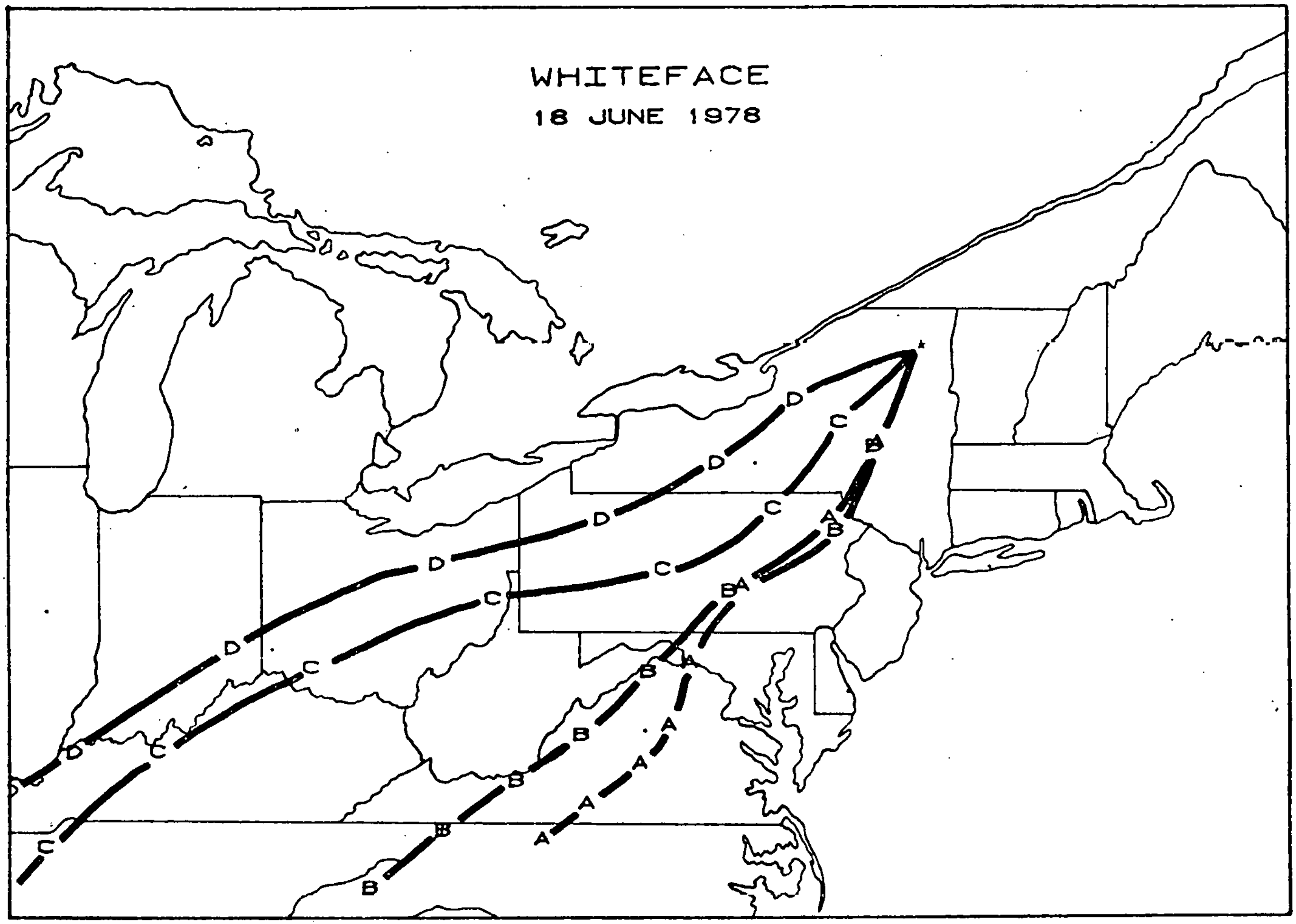
MAP3S Event - 15 June 1978

	$[H^+]_L$	$[SO_4^=]$	$[NO_3^-]$	$[NH_4^+]$
Concentration (μmole/liter)	32	18	11	9.5
Deposition (mg/m^2)	0.80	43	16	4.3

Sample volume - 1227 ml

$[H^+]_L + [NH_4^+]/2[SO_4^=] + [NO_3^-] = 0.88$

Figure 41



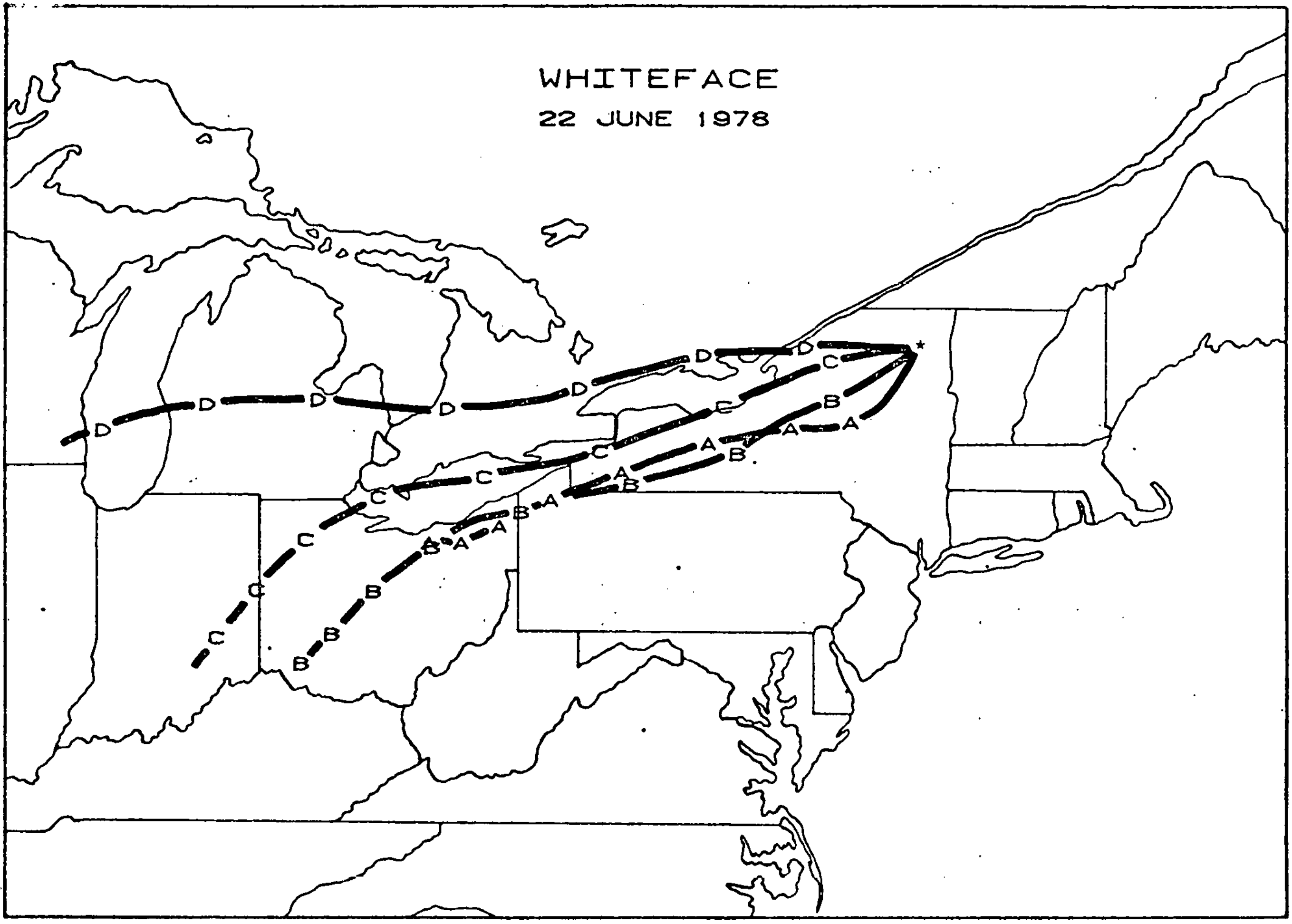
MAP3S Event - 19 June 1978

	$[H^+]_L$	$[SO_4^=]$	$[NO_3^-]$	$[NH_4^+]$
Concentration (μmole/liter)	93	54	43	39
Deposition (mg/m^2)	0.68	31	15	4.2

Sample volume - 291 ml

$[H^+]_L + [NH_4^+]/2[SO_4^=] + [NO_3^-] = 0.87$

Figure 42



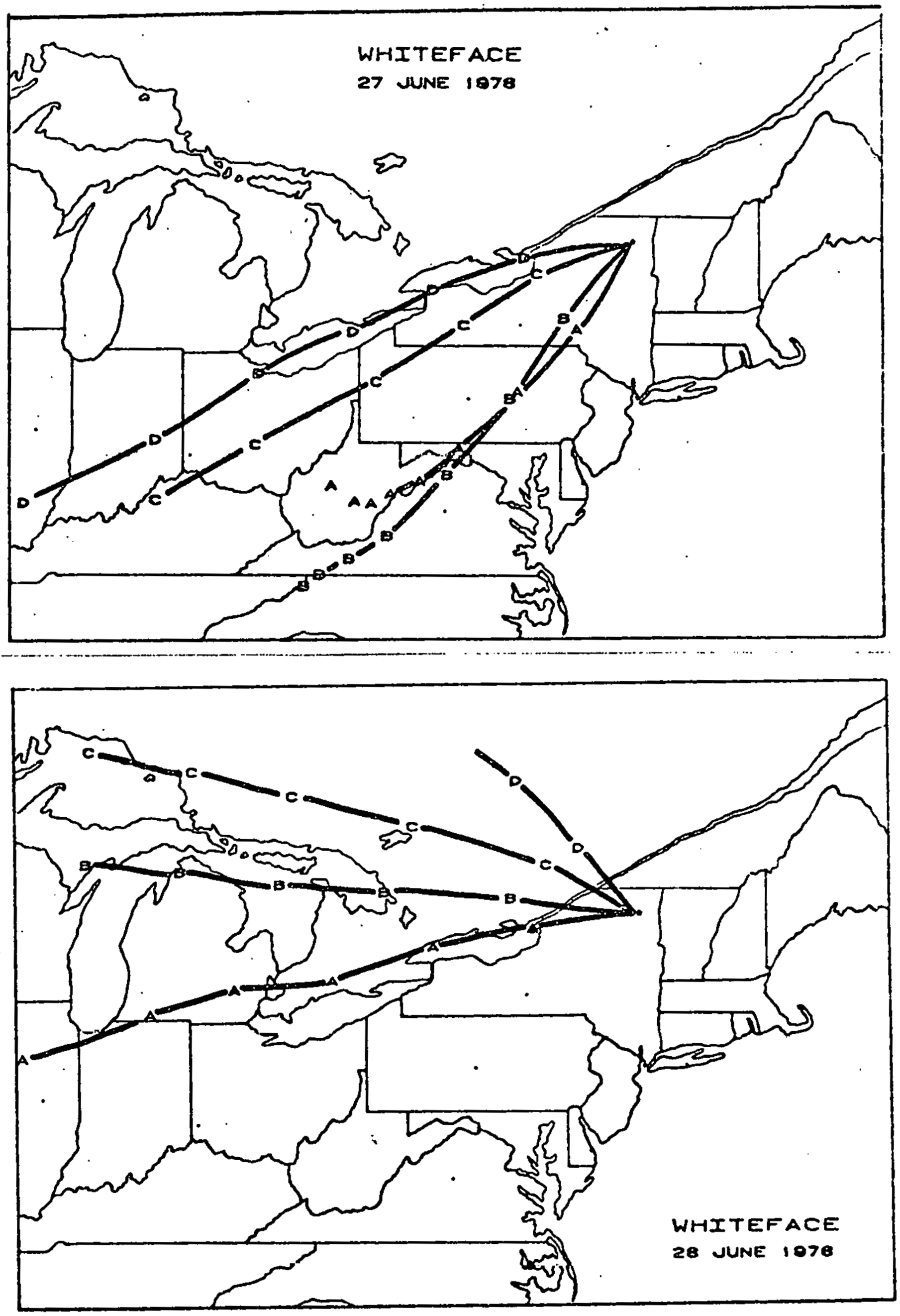
MAP3S Event - 22 June 1978

	$[H^+]_L$	$[SO_4^=]$	$[NO_3^-]$	$[NH_4^+]$
Concentration (µmole/liter)	85	43	25	26
Deposition (mg/m^2)	1.30	63	23	7.2

Sample volume - 751 ml

$[H^+]_L + [NH_4^+]/2[SO_4^=] + [NO_3^-] = 1.00$

Figure 43



MAP3S Event - 28 June 1978

	$[H^+]_L$	$[SO_4^=]$	$[NO_3^-]$	$[NH_4^+]$
Concentration (μmole/liter)	68	35	24	23
Deposition (mg/m^2)	0.96	48	20	5.9

Sample volume - 695 ml

$[H^+]_L + [NH_4^+]/2[SO_4^=] + [NO_3^-] = 0.97$

Figure 44

2.9 The January 1978 "Intensive"

As noted earlier, there exists a seasonal variation in the concentration and deposition of many ions in the northeastern United States. With the exception of nitrate, the major ions exhibited a distinct summer maximum. In this context, case study comparisons between different seasons may be misleading if no consideration is given to air mass trajectories. It was found useful to examine concentration and deposition during the winter months since the trajectories arriving at Whiteface were more evenly balanced between the northern and southwestern sectors. The dominant storms during January 1978 were from rapidly intensifying coastal storms which were responsible for the northerly component of many of the individual events. Figure 45 shows the percentage of occurrence of three hour trajectory endpoints per square degree latitude and longitude for January and July 1978. While not an absolute measure of the passage of a trajectory over a particular point, it does nevertheless provide insight into the seasonal climatology of air masses arriving in the Adirondacks. The higher frequency of occurrence for trajectories passing over the Midwest/Ohio Valley area (allegedly high emission areas), coupled with the increased solar radiation for the summer months, may lead to the summer maximum in ion concentration and ion deposition.

Therefore, in order to examine variability within the winter season, precipitation chemistry for the major ions was matched with corresponding air mass trajectories for January 1978, as shown in Figures 46 through 50. Figure 51 gives the six hour precipitation amounts, MAP3S collection and other general classification of each event. The concentrations are relatively low for each event, with January 13 and 19 being comparable to the extremely

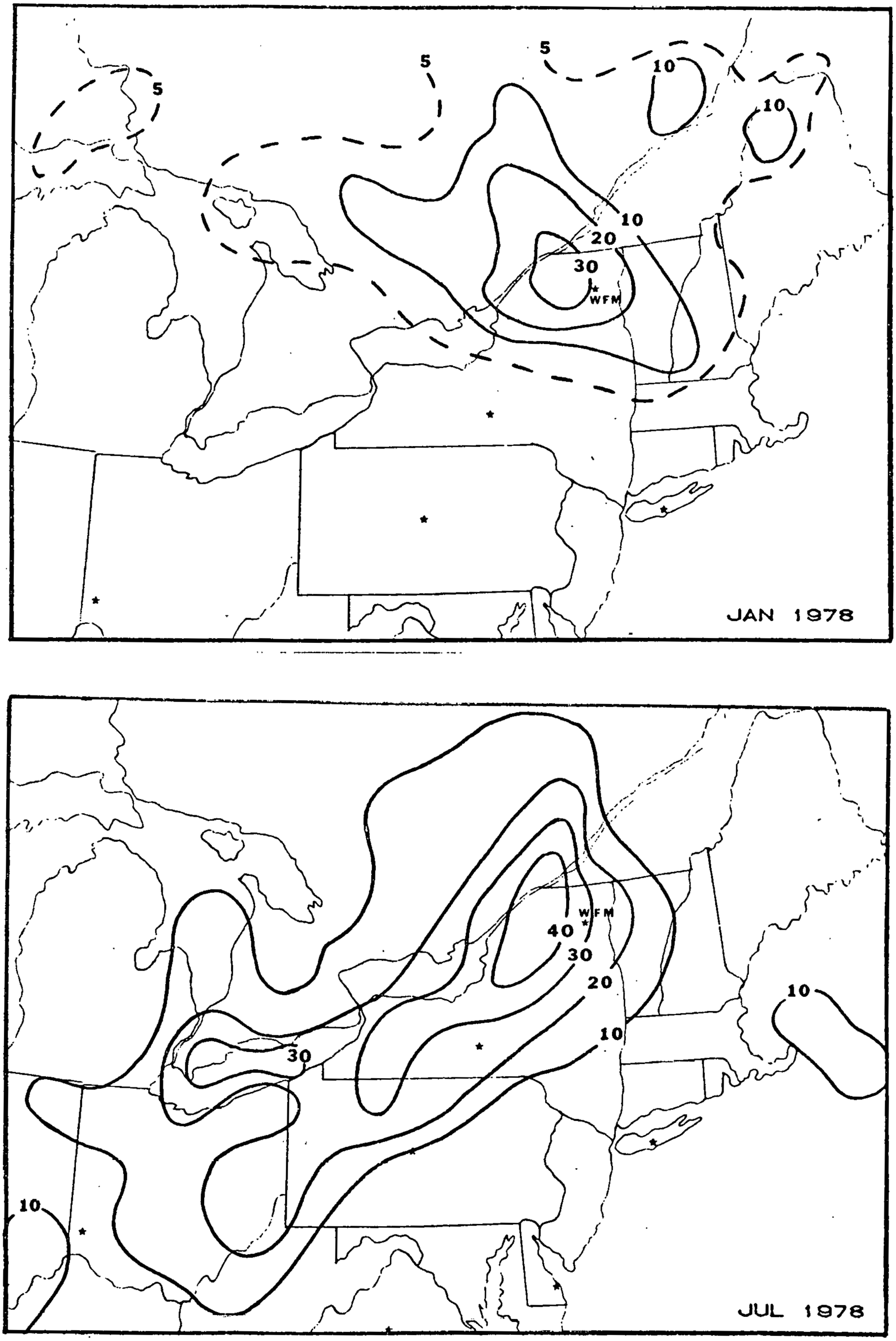
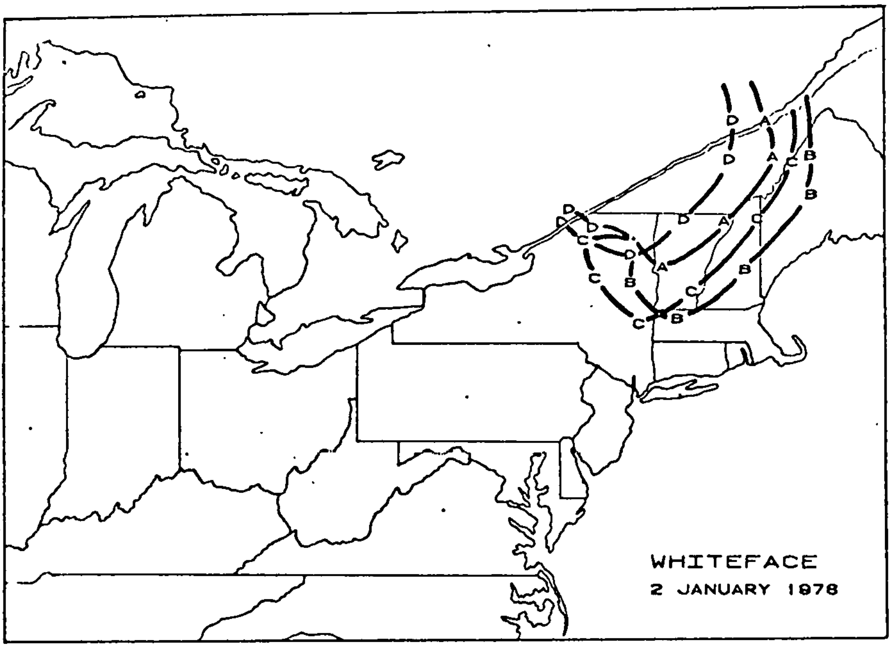
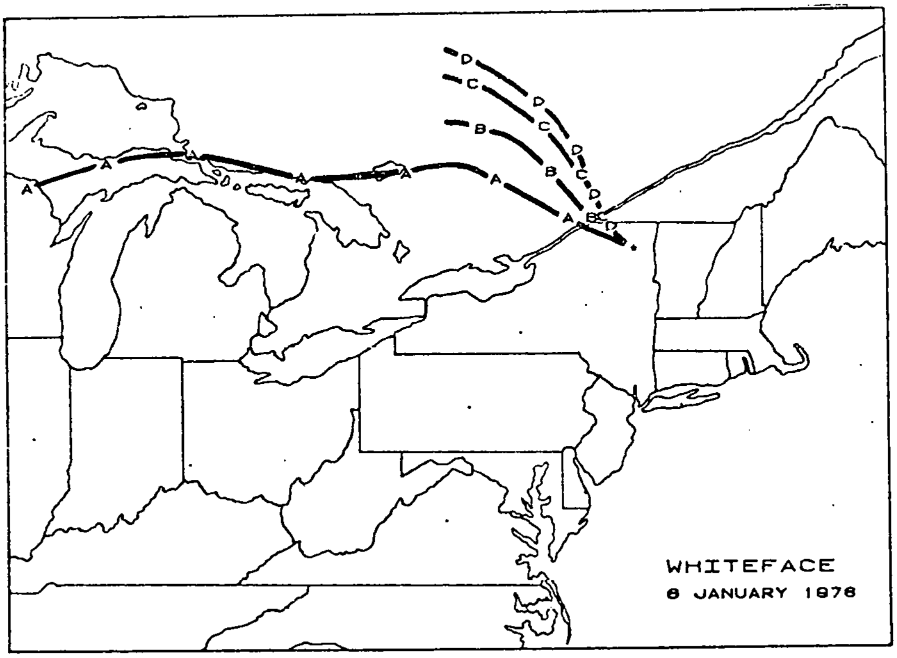


Figure 45. Three hour trajectory endpoint percent of occurrence per square longitude and latitude for Whiteface, January and July 1978





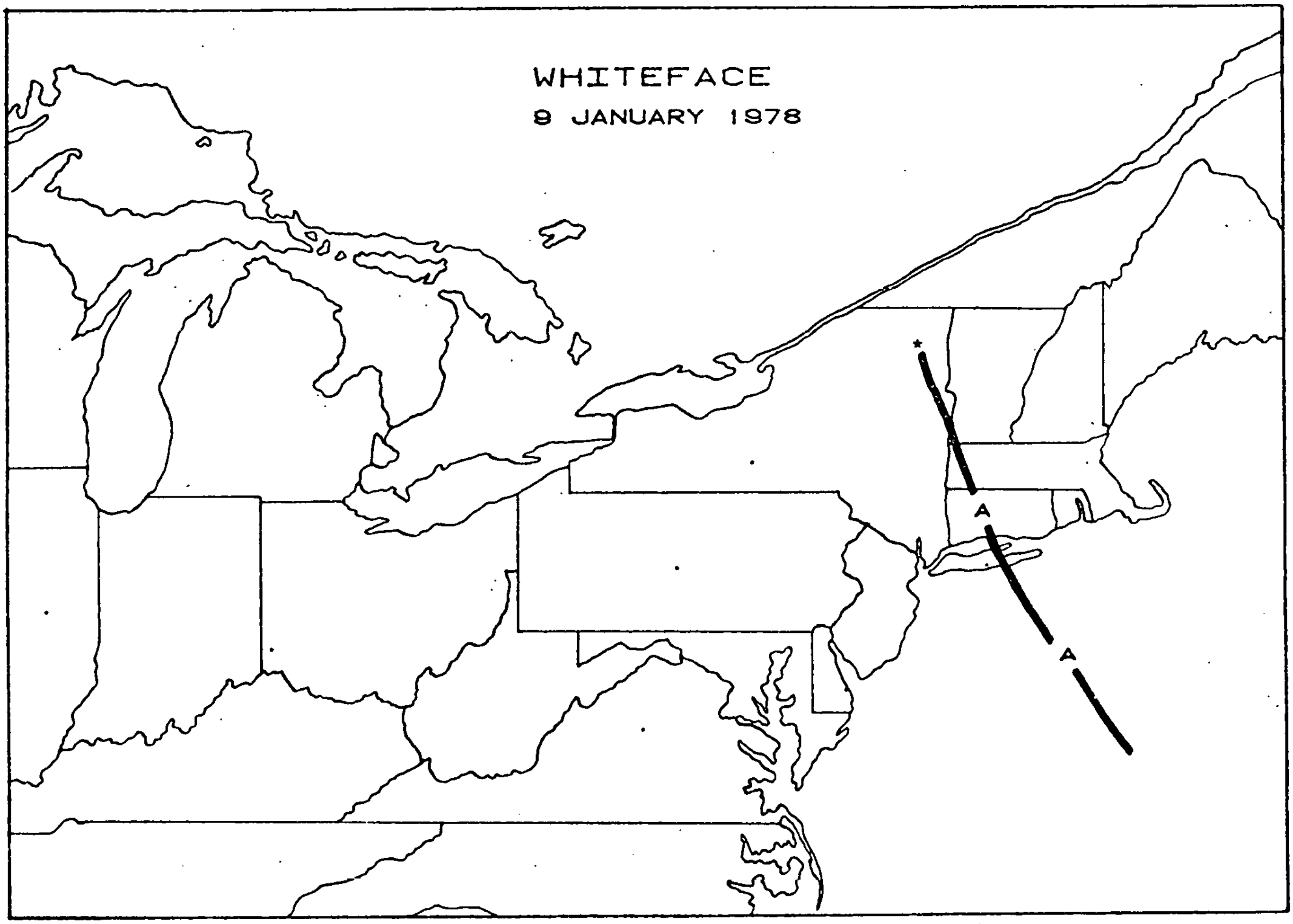
MAP3S Event - 7 January 1978

	$[H^+]_L$	$[SO_4^=]$	$[NO_3^-]$	$[NH_4^+]$
Concentration (μmole/liter)	110	15	91	20
Deposition (mg/m^2)	0.81	11	42	2.6

Sample volume - 260 ml

$[H^+]_L + [NH_4^+]/2[SO_4^=] + [NO_3^-] = 1.07$

Figure 46



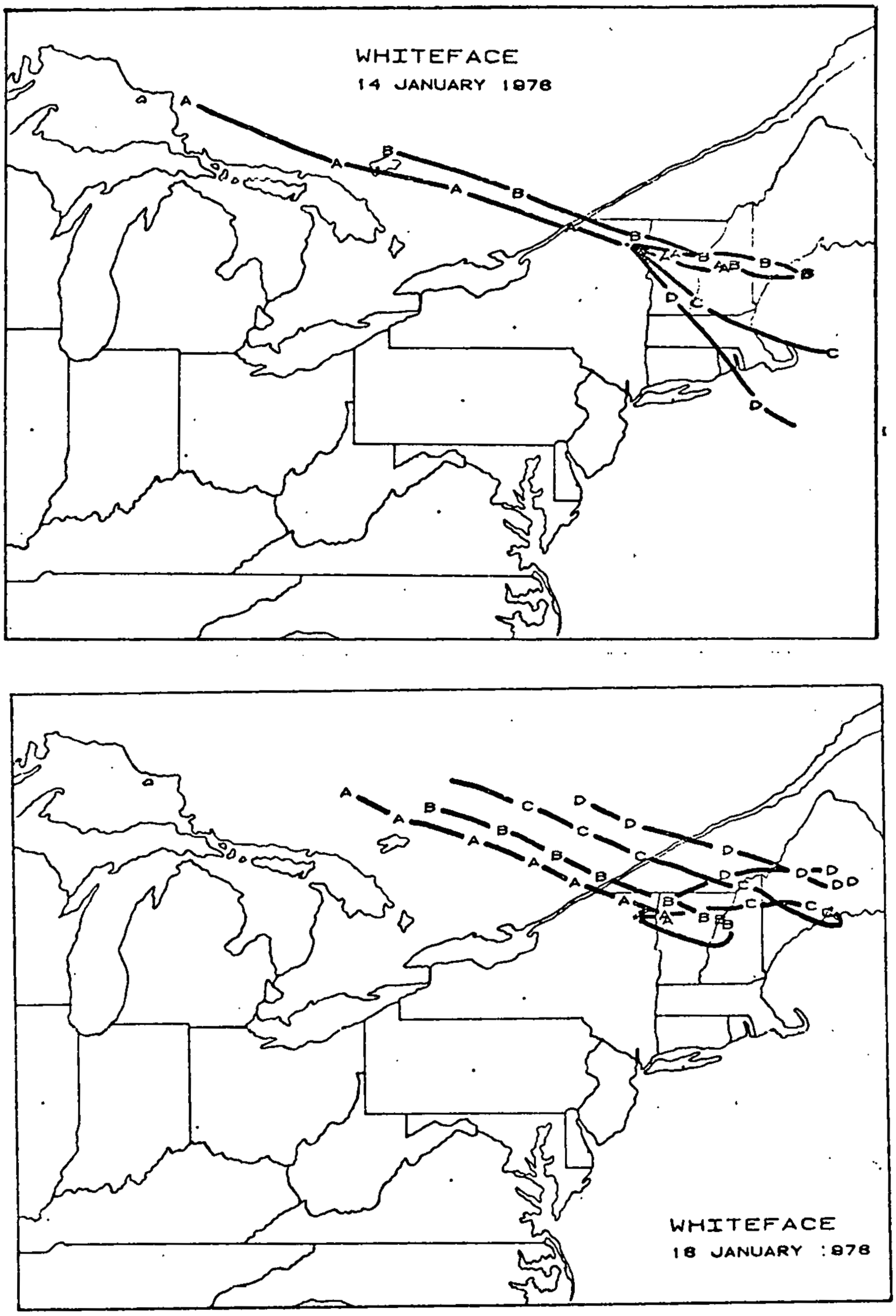
MAP3S Event - 13 January 1978

	$[H^+]_L$	$[SO_4^=]$	$[NO_3^-]$	$[NH_4^+]$
Concentration (μmole/liter)	14	4.7	5.8	0.4
Deposition (mg/m^2)	0.44	17.5	11.4	0.3

Sample volume - 1550 ml

$[H^+]_L + [NH_4^+]/2[SO_4^=] + [NO_3^-] = 0.95$

Figure 47



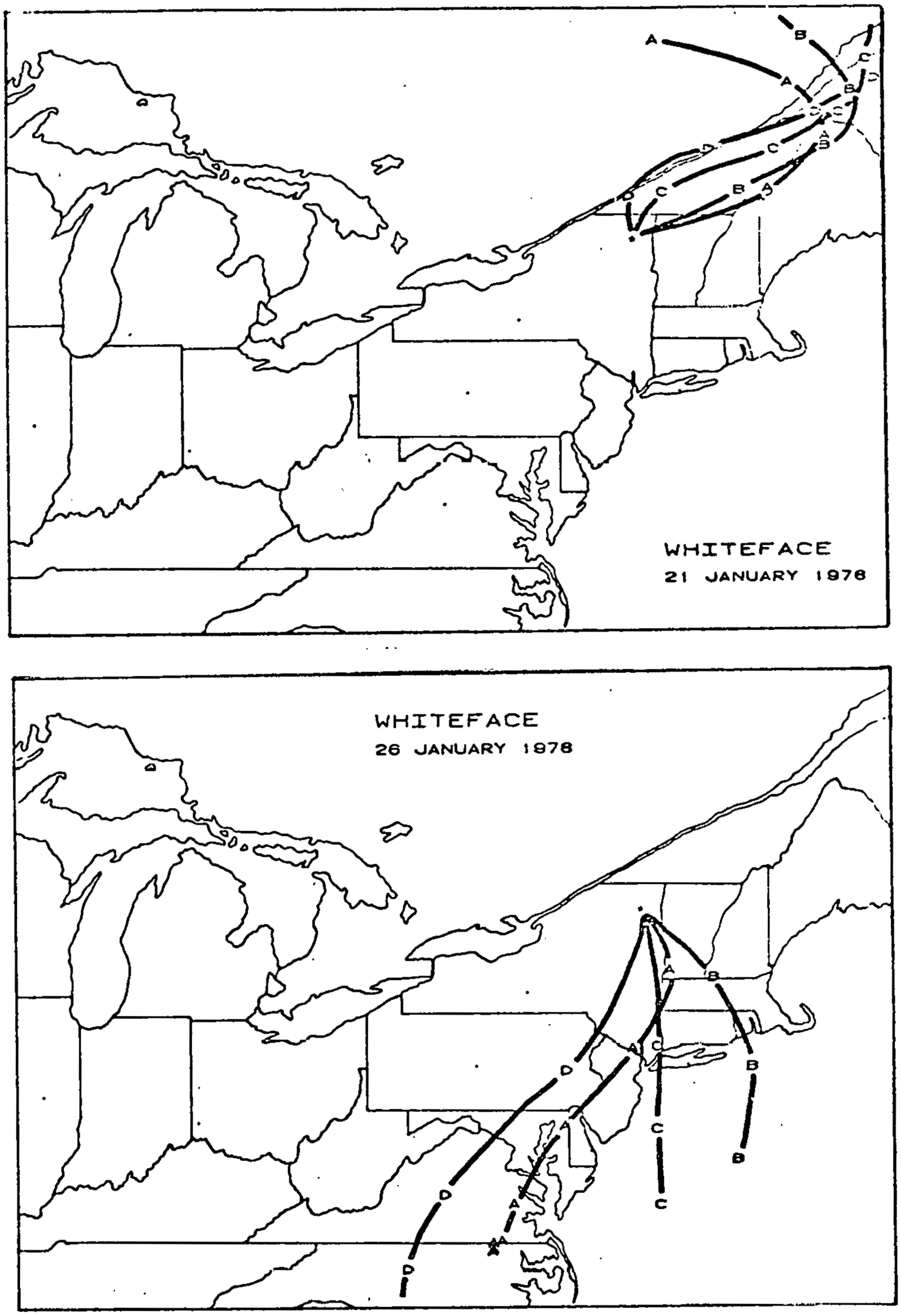
MAP3S Event - 19 January 1978

	$[H^+]_L$	$[SO_4^-]$	$[NO_3^-]$	$[NH_4^+]$
Concentration (μmole/liter)	13	1.9	2.2	0.4
Deposition (mg/m^2)	0.39	6.7	6.1	0.2

Sample volume - 1470 ml

$[H^+]_L + [NH_4^+]/2[SO_4^=] + [NO_3^-] = 2.23$

Figure 48



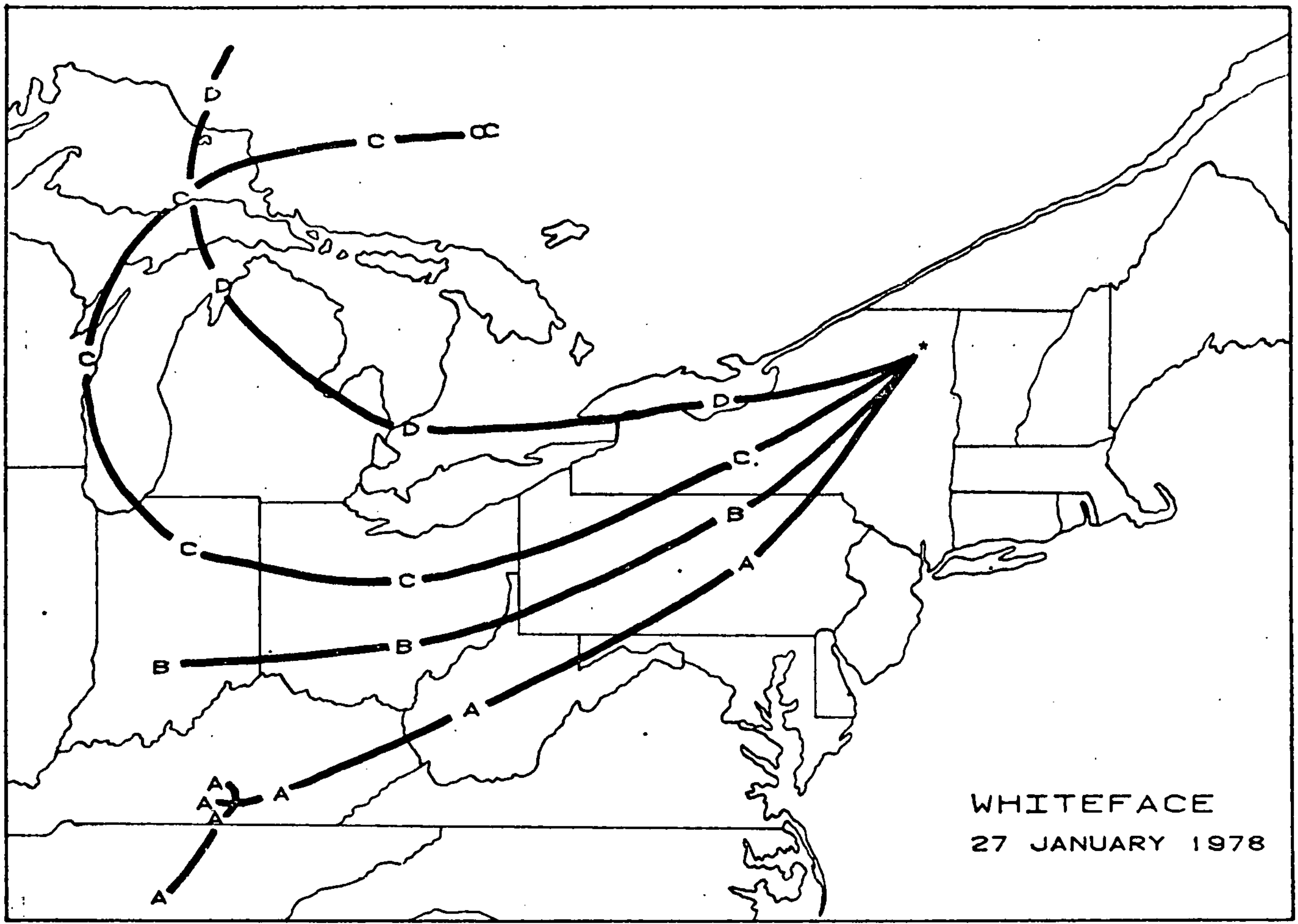
MAP3S Event - 26 January 1978

	$[H^+]_L$	$[SO_4^=]$	$[NO_3^-]$	$[NH_4^+]$
Concentration (μmole/liter)	30	8.4	12	1.1
Deposition (mg/m^2)	0.89	29.5	26	0.6

Sample volume - 1460 ml

$[H^+]_L + [NH_4^+]/2[SO_4^=] + [NO_3^-] = 1.08$

Figure 49



MAP3S Event - 31 January 1978

	$[H^+]_L$	$[SO_4^=]$	$[NO_3^-]$	$[NH_4^+]$
Concentration (μmole/liter)	41	37	27	19
Deposition (mg/m²)	0.20	21	10	1.6

Sample volume - 235 ml

$[H^+]_L + [NH_4^+]/2[SO_4^=] + [NO_3^-] = 0.59$

Figure 50

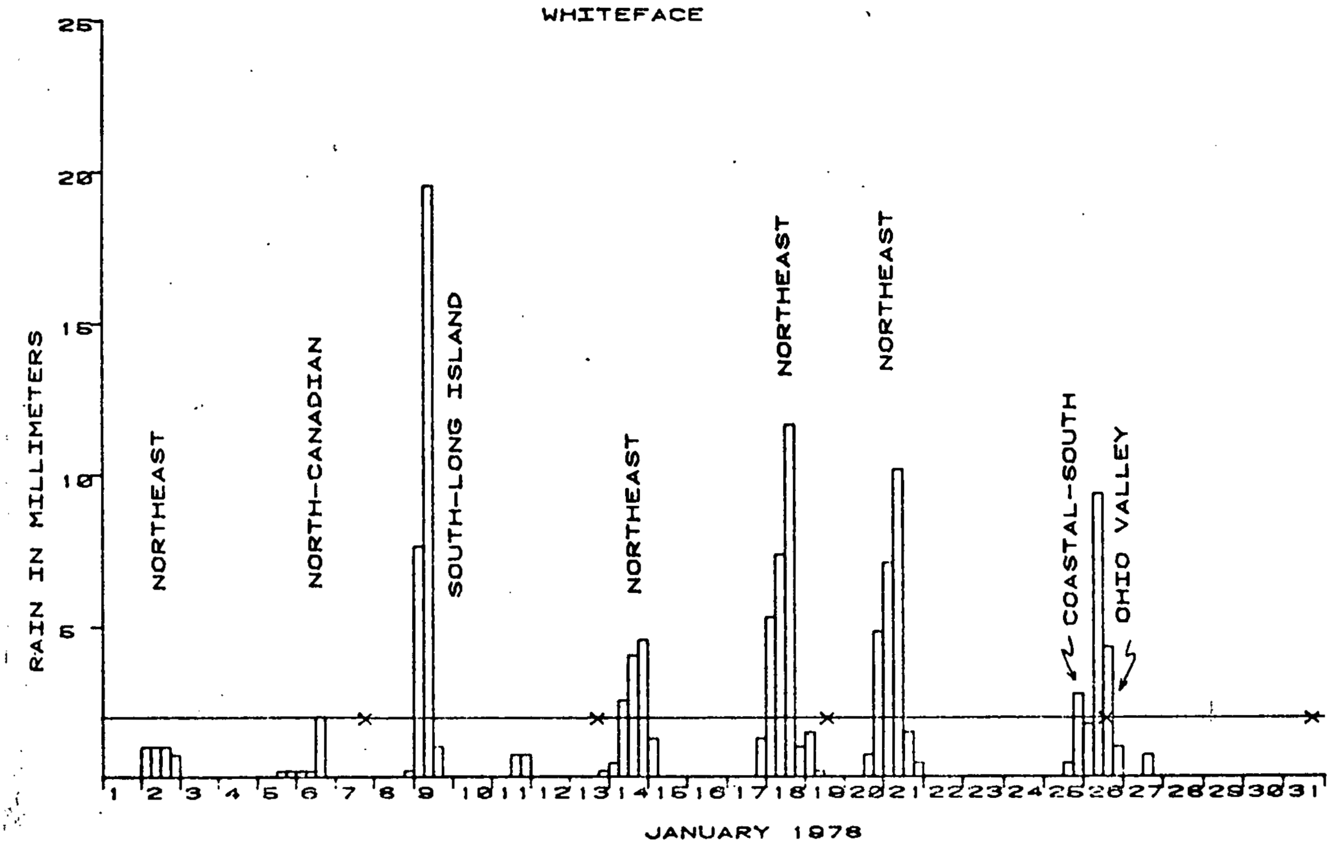


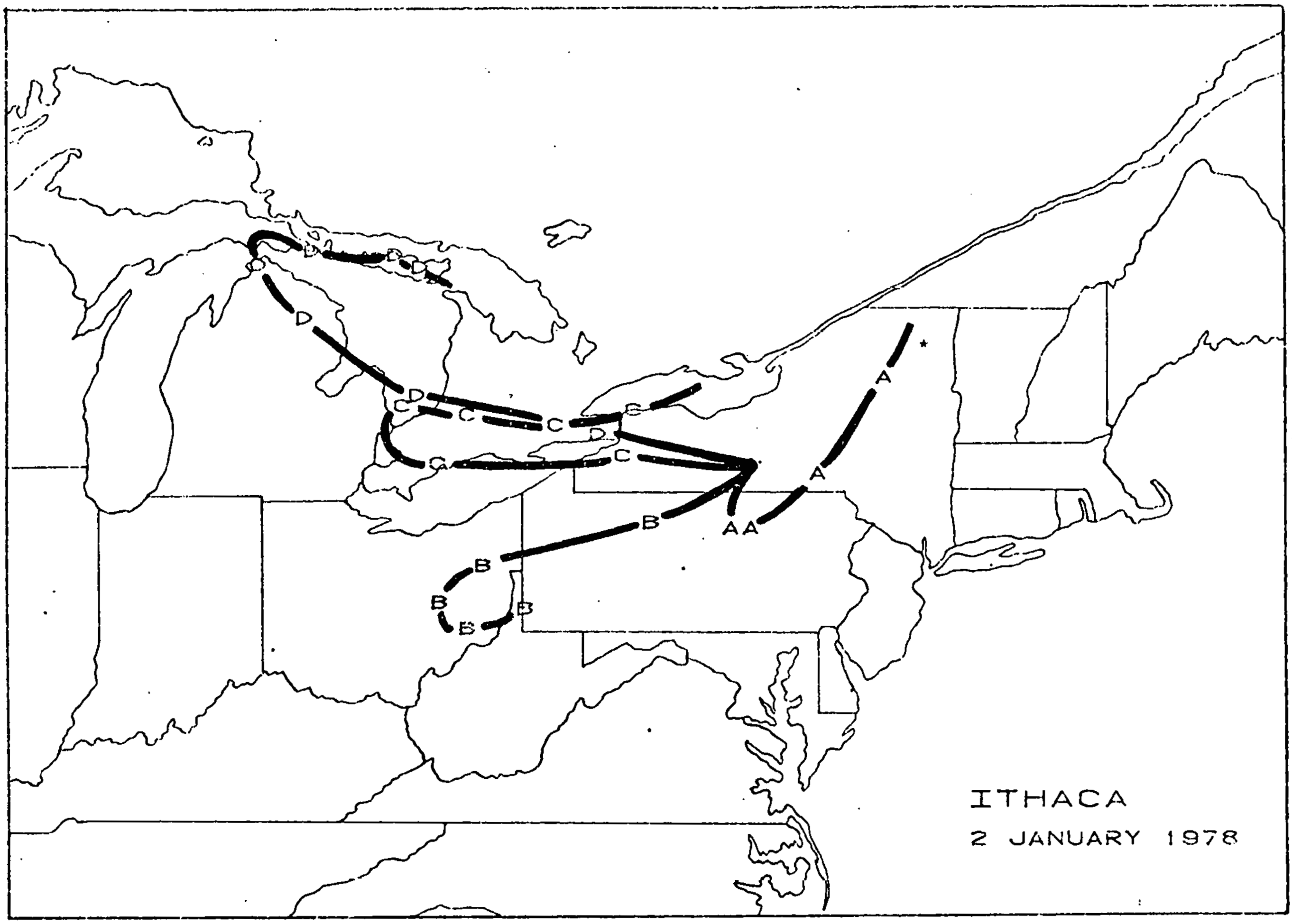
Figure 51. January 1978 six hour precipitation totals for Whiteface

"clean" precipitation of hurricanes David and Frederic (to be discussed later). This is due in part to the large precipitation amounts which are comparable in magnitude to those measured during the hurricanes.

The depositions, however, are in the normal range. It should be noted that, contrary to the summer season, nitrate deposition is comparable to that of sulfate deposition.

Unfortunately, the January 25, 26, and 27, 1978 events were not separated, although the air trajectories originate from two entirely different regions. Hence, it is impossible to separate for Whiteface Mountain the impact of air masses passing over the Ohio Valley region from that caused by air masses from the Canadian sector. Therefore, in order to achieve this goal, the Ithaca January 1978 data have been analyzed. Figures 52 through 57 show the trajectories calculated for every precipitation event and ending at Ithaca. Again, the predominant flow is from the Great Lakes to northeastern Canada sector and the very low concentration values seem to reflect this situation. The deposition values for January 1978 at Ithaca are again moderate as was the case for Whiteface Mountain. An ideal comparison can be made between "Canadian" air mass (January 22, Figure 56) and "Ohio Valley" air mass (January 27, Figure 57). The amount of total precipitation was about the same, so that no "dilution" bias exists:

	Concentration		
	$L[H]^+$ (μmole/L)	$SO_4^=$ (μmole/L)	NO_3^- (μmole/L)
Canadian air Jan. 22 at ITH	14	2.8	4.2
Ohio Valley air Jan. 27 at ITH	45	22	22



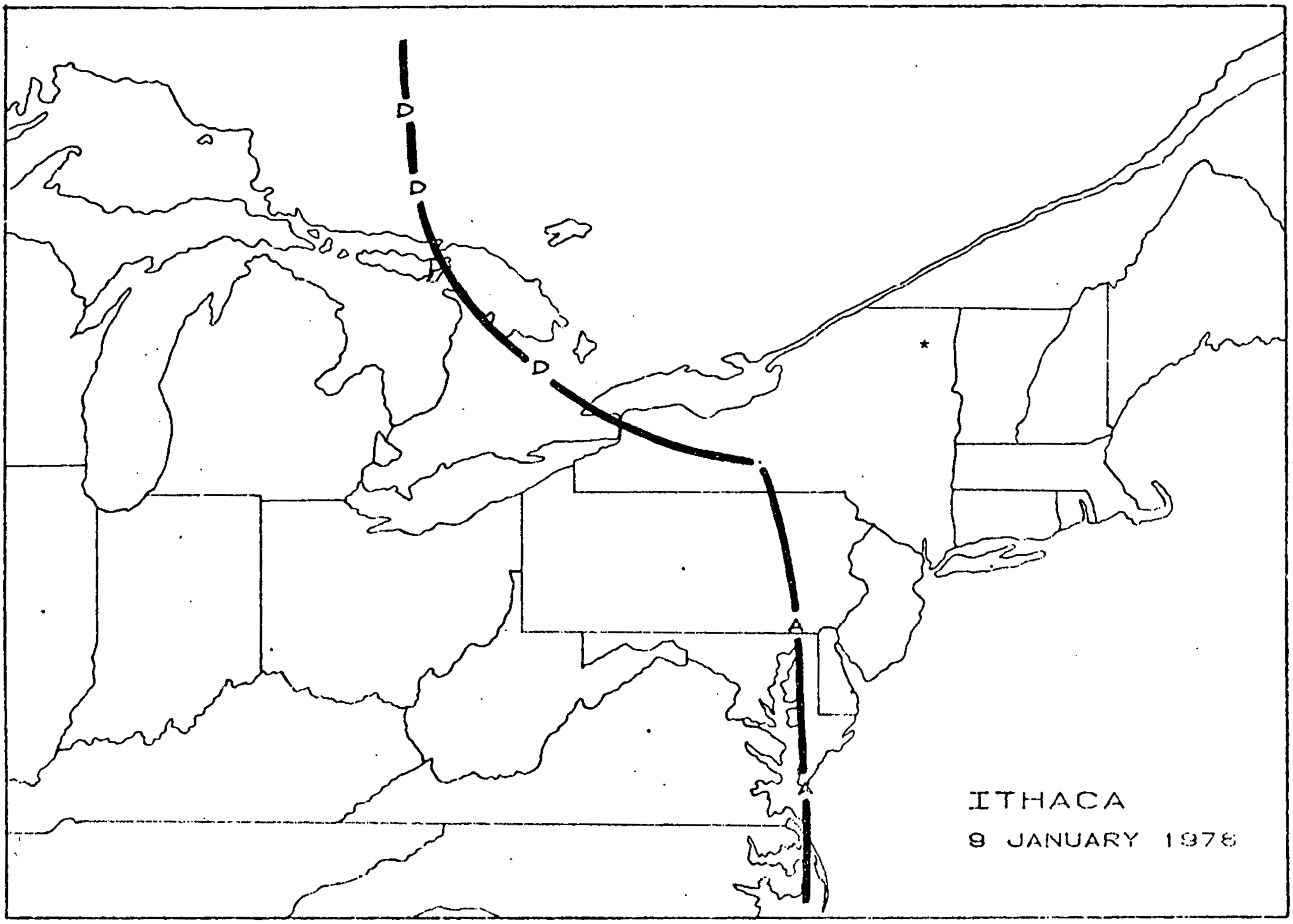
MAP3S Event - 3 January 1978

	$[H^+]_L$	$[SO_4^=]$	$[NO_3^-]$	$[NH_4^+]$
Concentration (μmole/liter)	66	19	55	9.2
Deposition (mg/m^2)	0.34	9.7	18	0.9

Sample volume - 260 ml

$[H^+]_L + [NH_4^+]/2[SO_4^=] + [NO_3^-] = 0.81$

Figure 52



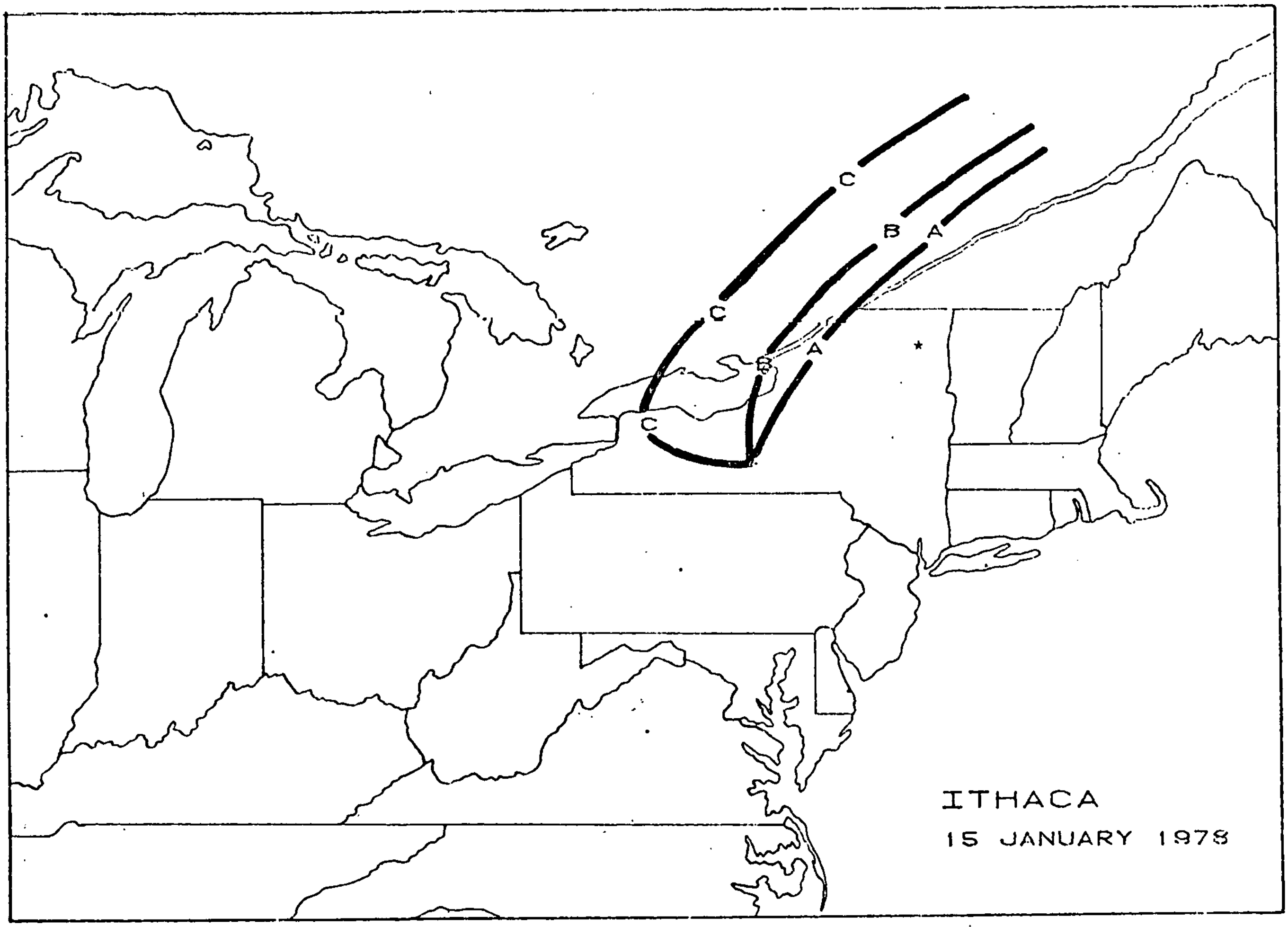
MAP3S Event - 11 January 1978

	$[H^+]_L$	$[SO_4^=]$	$[NO_3^-]$	$[NH_4^+]$
Concentration (μmole/liter)	37	13	15	2.2
Deposition (mg/m^2)	1.50	50	38	1.6

Sample volume - 1980 ml

$[H^+]_L + [NH_4^+]/2[SO_4^=] + [NO_3^-] = 0.96$

Figure 53



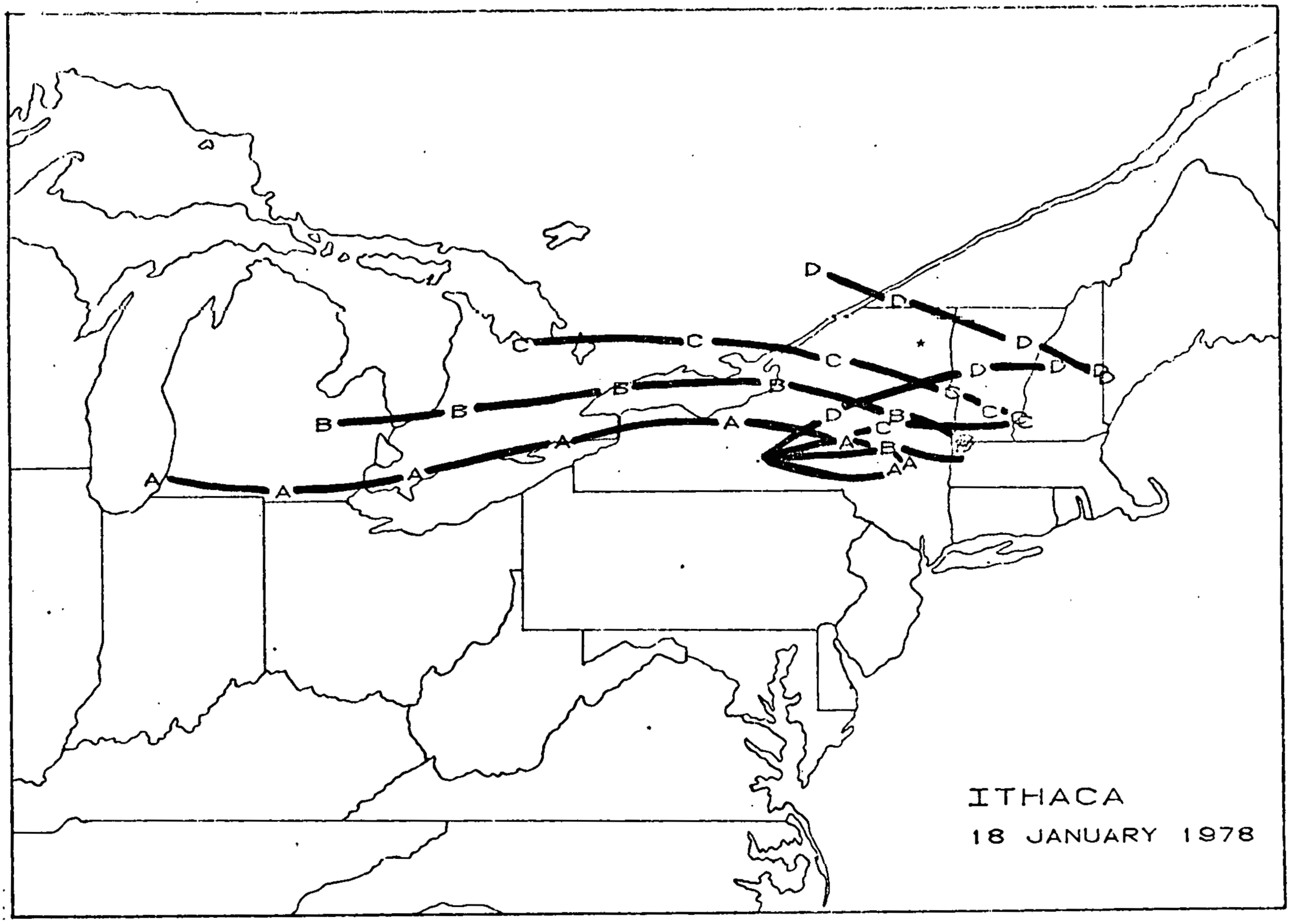
MAP3S Event - 15 January 1978

	$[H^+]_L$	$[SO_4^=]$	$[NO_3^-]$	$[NH_4^+]$
Concentration (μmole/liter)	16	5.3	20	4.1
Deposition (mg/m^2)	0.41	9.2	22	-

Sample volume - 890 ml

$[H^+]_L + [NH_4^+]/2[SO_4^=] + [NO_3^-] = 0.66$

Figure 54



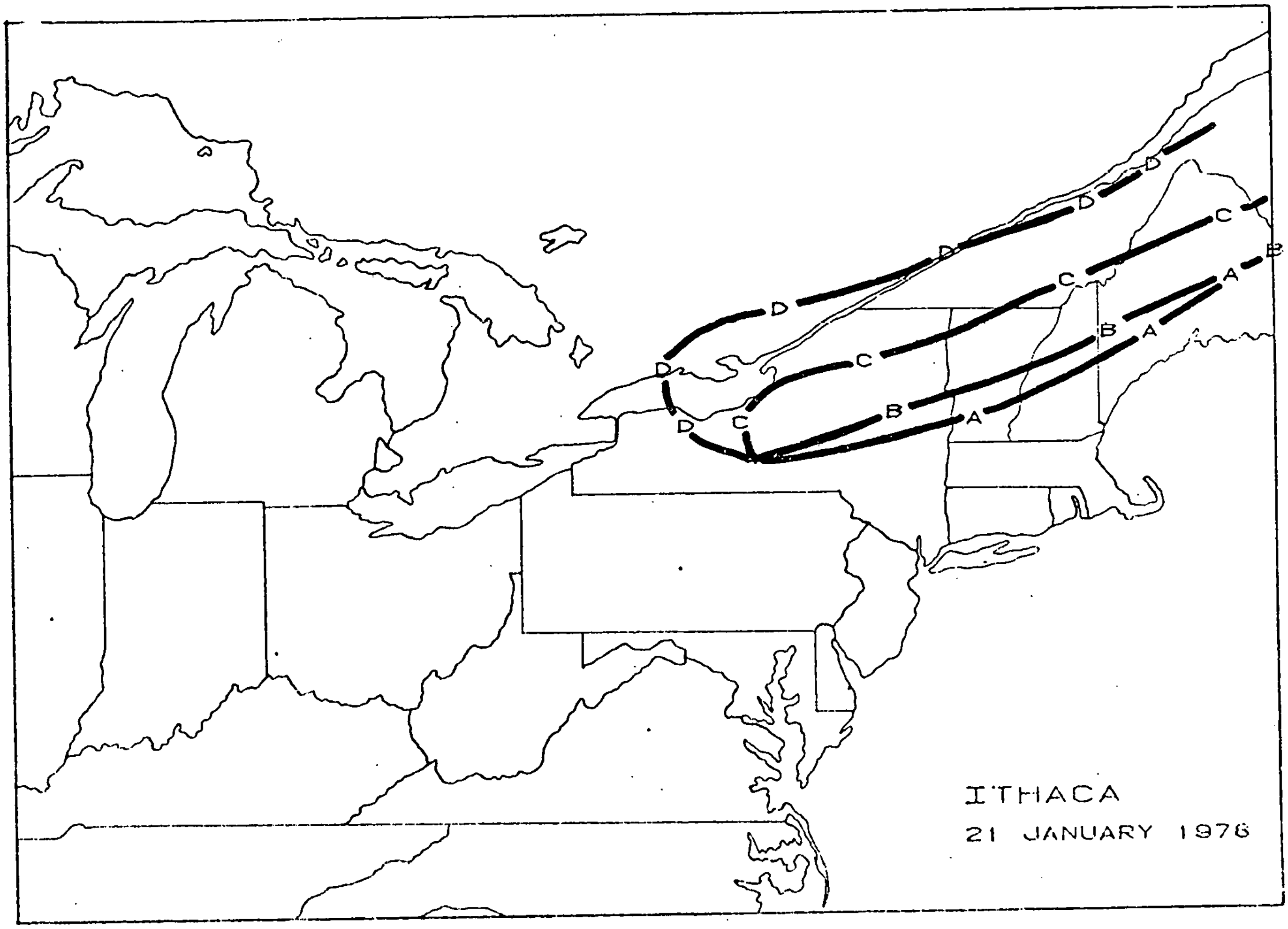
MAP3S Event - 19 January 1978

	$[H^+]_L$	$[SO_4^=]$	$[NO_3^-]$	$[NH_4^+]$
Concentration (μmole/liter)	20	2.9	12	2.2
Deposition (mg/m^2)	0.54	7.9	21.1	0.3

Sample volume - 1390 ml

$[H^+]_L + [NH_4^+]/2[SO_4^=] + [NO_3^-] = 1.25$

Figure 55



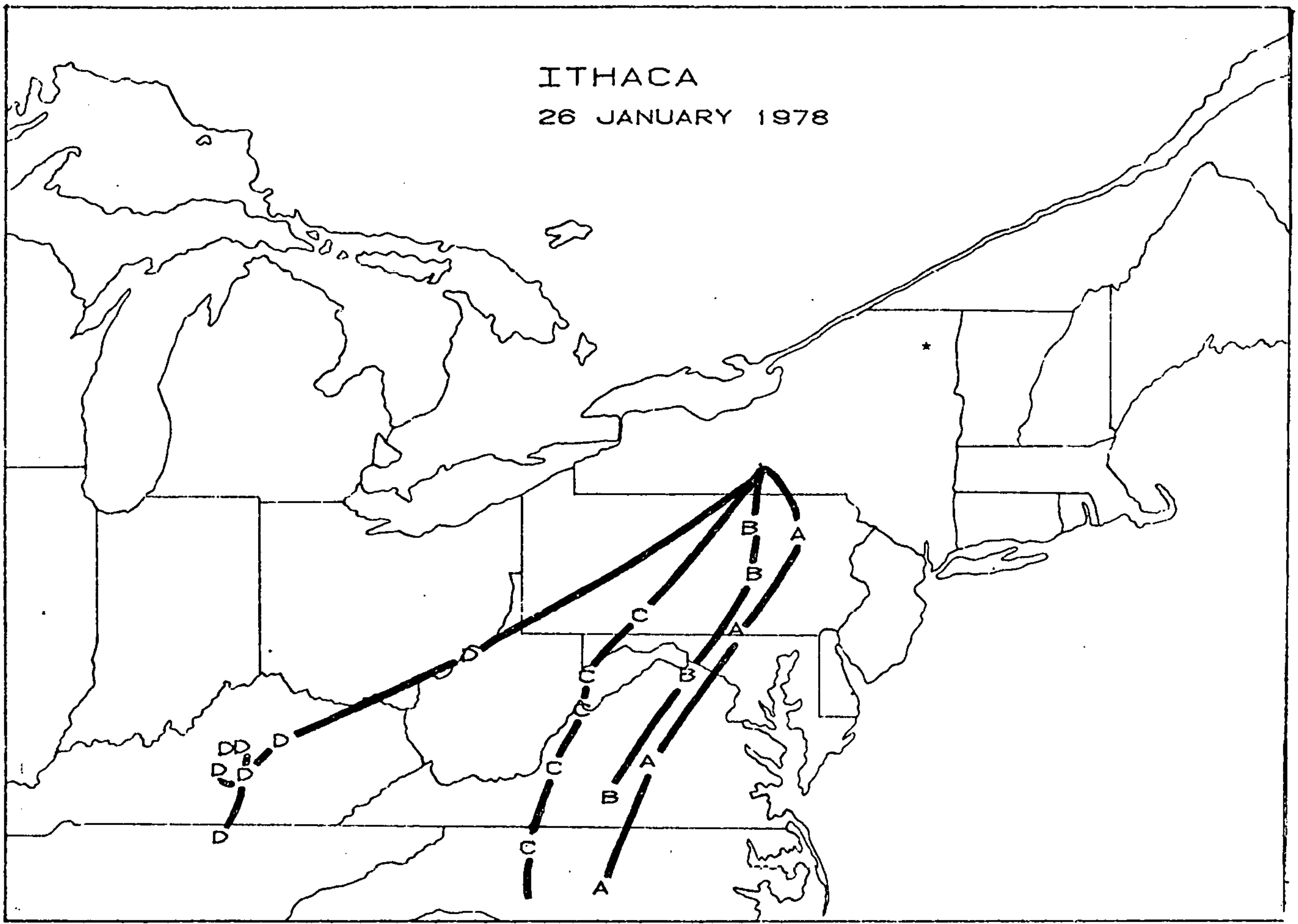
MAP3S Event - 22 January 1978

	$[H^+]_L$	$[SO_4^=]$	$[NO_3^-]$	$[NH_4^+]$
Concentration (μmole/liter)	14	2.8	4.2	0.5
Deposition (mg/m^2)	0.17	4.2	4.1	-

Sample volume - 770 ml

$[H^+]_L + [NH_4^+]/2[SO_4^=] + [NO_3^-] = 1.48$

Figure 56



MAP3S Event - 27 January 1978

	$[H^+]_L$	$[SO_4^=]$	$[NO_3^-]$	$[NH_4^+]$
Concentration (μmole/liter)	45	22	22	1.4
Deposition (mg/m^2)	0.51	23	15	0.3

Sample volume - 540 ml

$[H^+]_L + [NH_4^+]/2[SO_4^=] + [NO_3^-] = 0.70$

Figure 57

Event deposition values are as indicated in Figures 56 and 57 with the 27 January case contributing roughly four to five times that of the 22nd. However, individual case studies must not be taken out of context and their relative contribution to total wet deposition must always be considered. When the case of 27 January is compared with wet deposition for the entire month, the following picture emerges:

Ithaca January 1978 Deposition

	$SO_4^=$ (mg/m^2)	NO_3^- (mg/m^2)	L[H^+] (mg/m^2)
All events except Ohio Valley	81.4 total or 16 per event	113.4 total or 23 per event	2.79 total or 0.6 per event
January 27-28 Ohio Valley	23.3 per event or 33%	15 per event or 8%	0.51 per event or 6%

Obviously, considerable more data are needed to arrive at a general conclusion, but the emerging picture seems to be such that most of the wintertime deposition in the northeastern part of the United States is due to air masses from the north northwest to northeast sector. This is in spite of the findings that the concentration of pollution-related ions in precipitation is very low.

A final remark seems to be appropriate in regard to "deposition." As is seen in Figure 15a, the average precipitation at WFM (solid line) is higher in winter (snow) by almost a factor of two than in summer (rain). Most of the winter snow is caused by air masses from the 270-90° sector. Even though this precipitation shows lower concentration than "summer" rain from the 180-270° sector, the amount of ions deposited is still appreciable. Furthermore, the impact of rain, if any, is almost immediate in the form of runoff. The impact of snow, if any, can be accumulative and delayed.

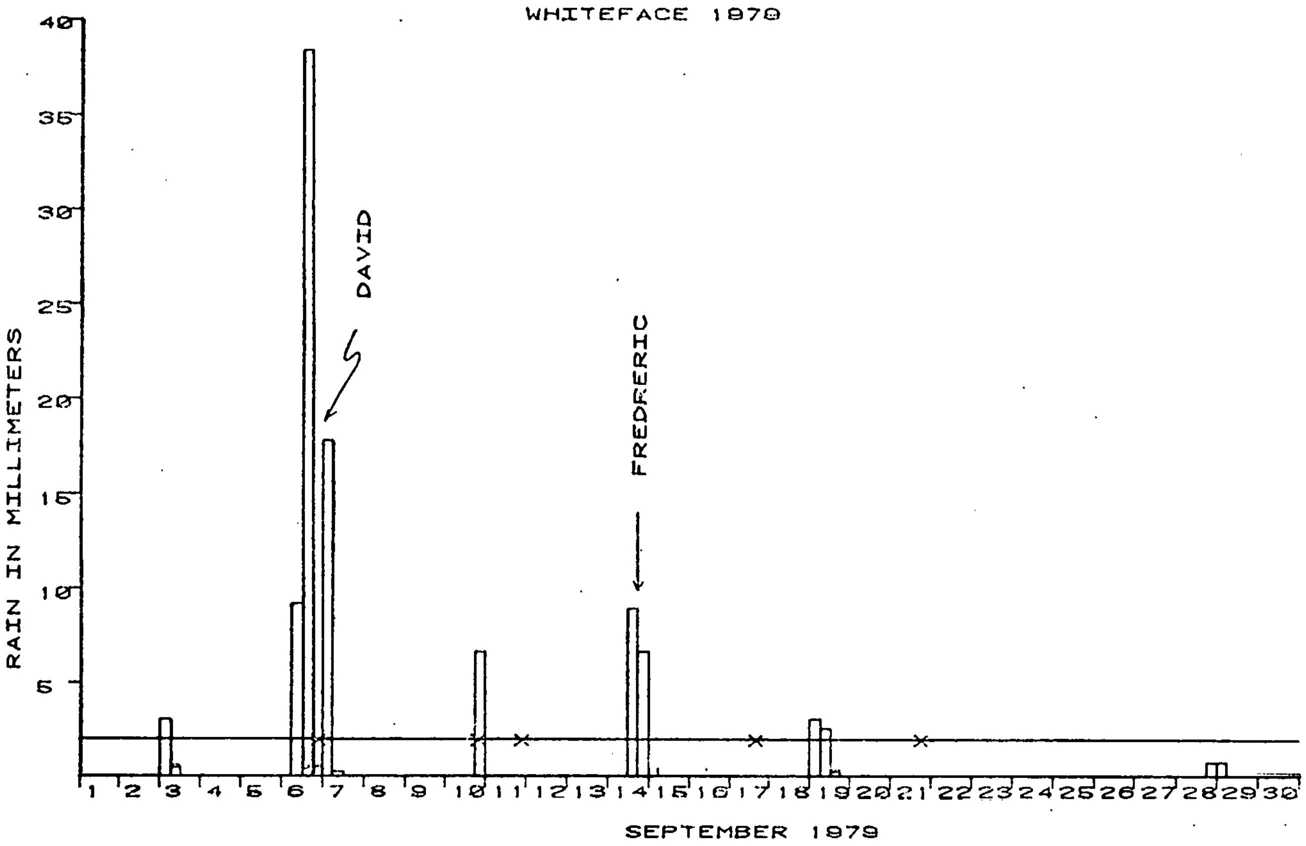
2.10 Impact of Hurricanes David and Frederic on Concentration and Deposition at MAP3S Stations

Two major hurricane events of September 1979 provide a unique opportunity to compare typical MAP3S measurements to those where intense washout processes had been at work. The marine origin of the hurricane, coupled with the diluting effect of massive amounts of rainfall, should make the ion concentrations in precipitation the lowest possible in pollutants, particularly $SO_4^=$, NO_3^-, and H^+. Hurricane David, 6-7 September 1979, and Frederic, 14-15 September 1979, provide such a data set, since the effects of these two systems were felt throughout the northeastern United States.

Figure 58 shows the six hour rainfall totals for September 1979 at Whiteface. The extreme amounts delivered by David over the two day period provide such an ultimately clean environment.

Figures 59 and 60 show the trajectories produced by the ARL-ATAD model for the two events. Both analyses show a strong southerly component, followed by a marked shift to the north northwest. These figures are in good agreement with 850 mb analysis of Falconer and Kadlecek (1980).

Table 16 provides an overview of regional concentration and total wet deposition for these two major storm systems. The day indicated in column one of Table 16 is not necessarily the day when rainfall occurred, but rather the date of MAP3S collection. Values of pH, or free hydrogen ion concentration, from this table suggest a revision might be necessary in the classical definition of the "normal" pH of 5.6. To obtain this theoretical hydrogen ion concentration, it is assumed that only CO_2 contributes to the acidity of precipitation. Concentrations of approximately 2.5 μmole/liter are needed for the sample to have a pH of 5.6. However, no usable samples were obtained throughout the network that reached this hypothetical concentration.


WHITEFACE 1979
RAIN IN MILLIMETERS
40
35
30
25
20
15
10
5
DAVID
FREDRERIC
1
2
3
4
5
6
7
8
9
10
11
12
13
14
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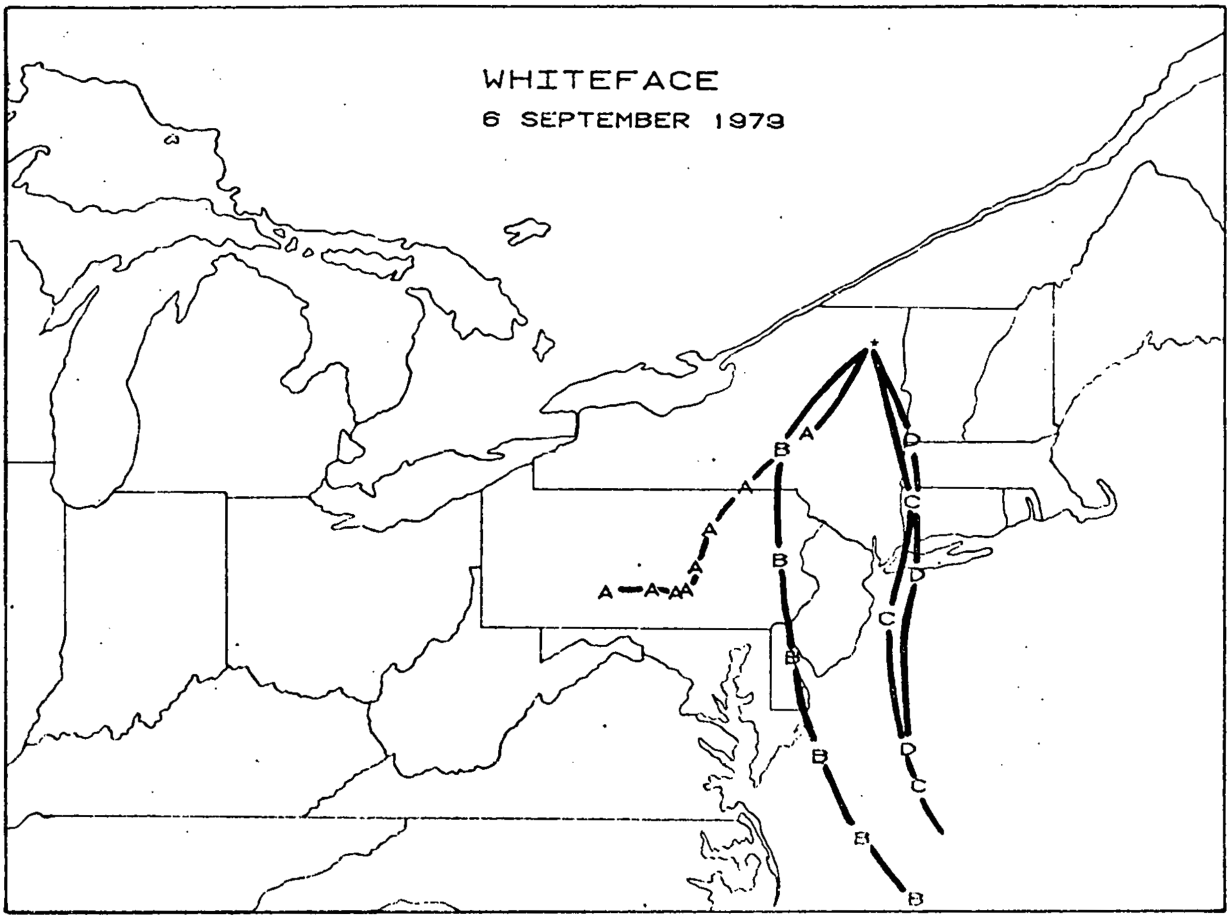
29
30
SEPTEMBER 1979

Figure 58

a)



b)

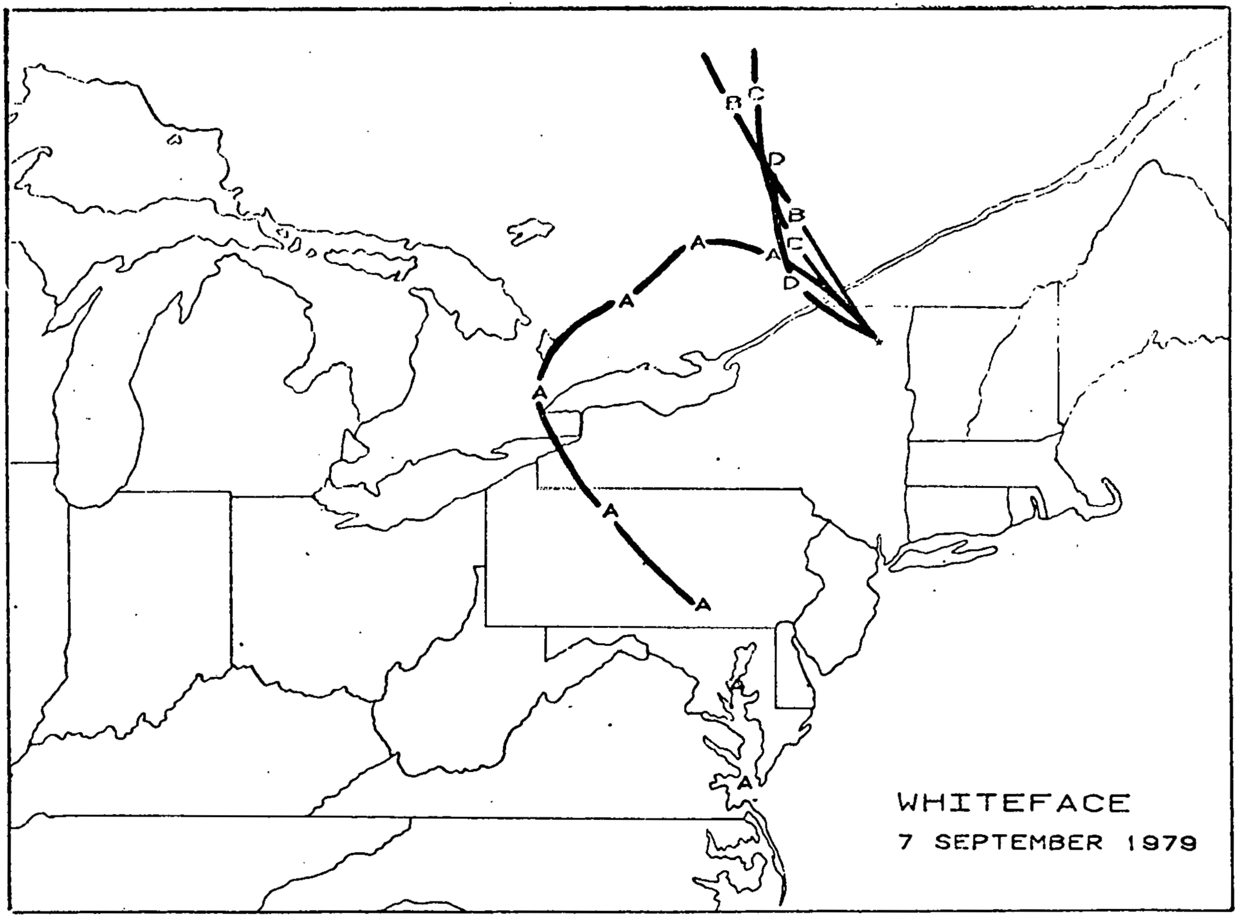
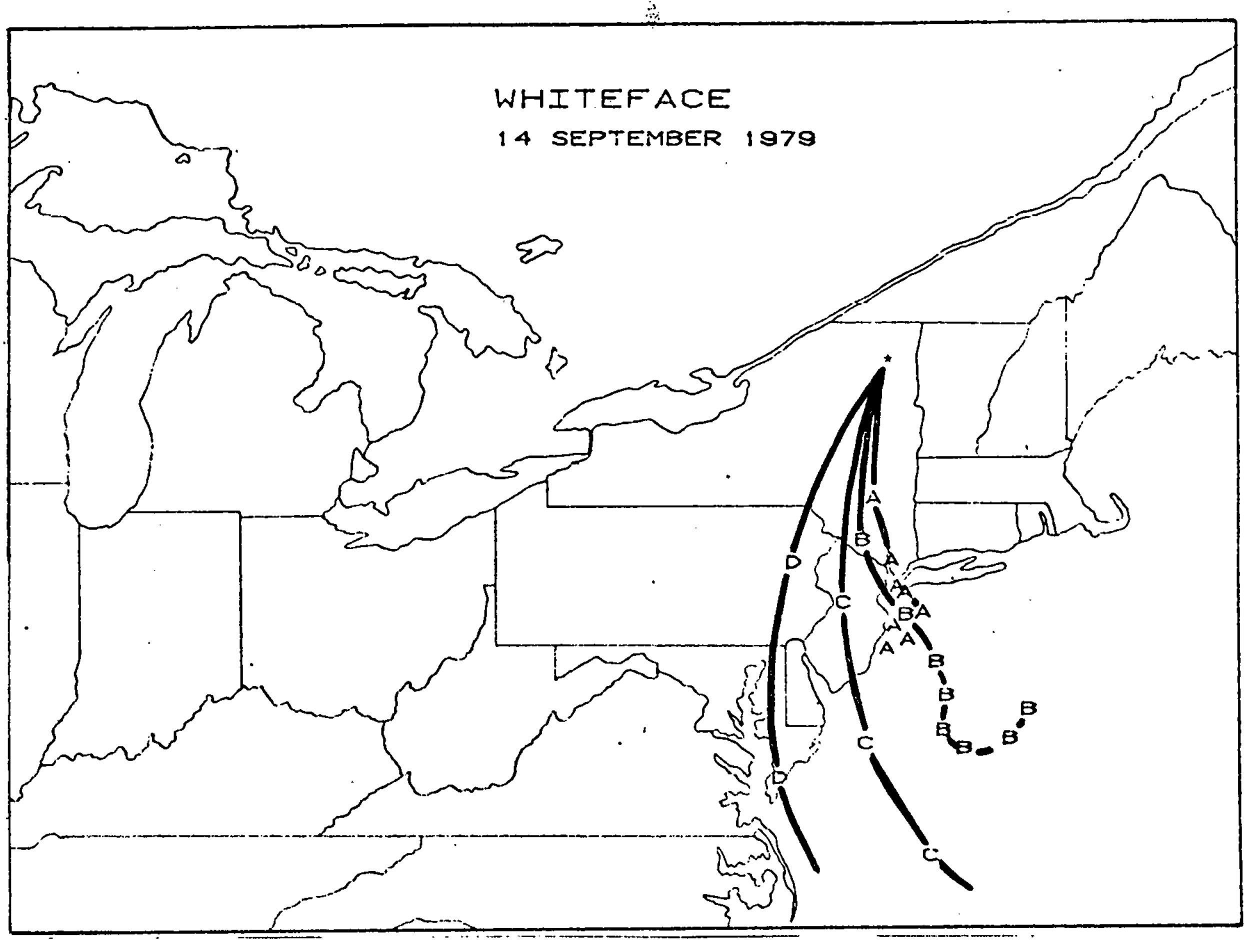


Figure 59. Trajectories for Hurricane David, a) 6 September, and b) 7 September, 1979.

a)



b)

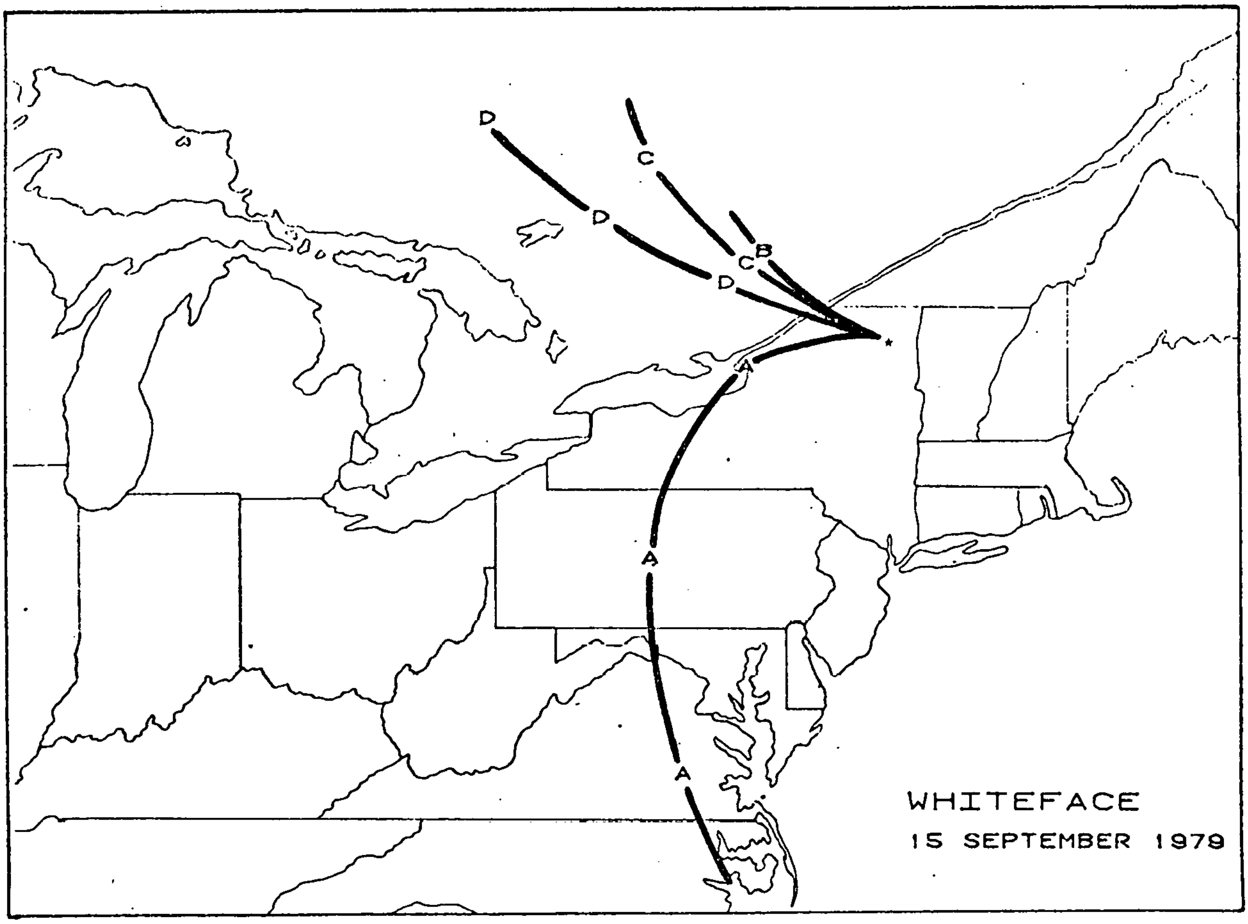


Figure 60. Trajectories for Hurricane David, a) 14 September, and b) 15 September 1979.

TABLE 16

PRECIPITATION CHEMISTRY OF HURRICANES DAVID AND FREDERICK - SEPTEMBER 1979

DAY	P.T. (HRS)	S.V. (ML)	F[H] (UM/L) Mg/m2*	L[H] (UM/L) Mg/m2*	COND. UMH/CM	[SO4] (UM/L) Mg/m2*	[NH4] (UM/L) Mg/m2*	[NO3] (UM/L) Mg/m2*	[CL] (UM/L) Mg/m2*	[NA] (UM/L) Mg/m2*	[K] (UM/L) Mg/m2*	[CA] (UM/L) Mg/m2*	[MG] (UM/L) Mg/m2*
BROOKHAVEN, NY													
6	9.1	444	38 0.34*	18 0.16*	81	39 33.92*	10 1.63*	15 8.43*	540 173.48*	450 93.73*	8.5 3.01*	16 5.81*	43 9.47*
15	1.5	73	2.9										
ITHACA, NY													
3	3	930	78 1.48*	79 1.49*	32	33 60.13*	16 5.48*	16 18.82*	3.6 2.42*	.86 0.38*	.64 10.47*	1.2 0.91*	
7	20	3160	6 0.387*	8.5 0.58*	4	3.7 22.91*	2.2 2.56*	2.5 9.97*	.13 10.29*	1.2 1.78*	1.2 3.03*	.67 2.12*	
15	4	1080	26	45	14	15 31.74*	6.3 2.5*	11 15.03*	2.3 1.80*	1.6 0.81*	.77 0.66*	1.5 1.33*	.49 0.26*
LEWES, DE													
4	.3	6											
6	16	2083	8.1 0.344*	10 0.425*	23	13 53.05*	2.6 1.99*	4.1 10.81*	150 226.1*	110 107.5*	2.5 4.16*	5.4 9.20*	15 15.5*
15	1	482	13 0.128*	11 0.108*	8	8 7.55*	6.3 1.12*	5.1 3.11*	12 4.18*	12 2.71*	1.1 0.42*	.87 0.34*	2.1 0.5*
PENN STATE, PA													
3	5	2166	49 2.65*	48 2.60*	23	28 118.82*	17 13.56*	14 38.37*	3.9 6.11*	1.1 1.12*	.98 1.69*	1.6 2.83*	
6	12.7	2141	11 0.48*	15 0.66*	6	5.4 22.65*	1.3 1.02*	4.4 11.92*	2.4 3.72*	9.4 9.44*	7 11.96*	.95 1.66*	
7	1	37		229 0.18*	130	150 10.87*	100 1.36*	190 8.90*	25 0.57*	11 0.19*	9.1 0.27*	50 1.51*	16 0.29*
15	4.3	448	31 0.28*	32 0.29*	16	14 12.29*	7.4 1.22*	11 6.24*	4.1 1.33*	4.1 0.86*	1.9 0.68*	1.6 0.59*	.62 0.14*
VIRGINIA													
4	7	2000	76 3.1*	100 4.08*	40	34 133.22*	13 9.57*	22 55.68*	8.9 12.88*	2.2 2.06*	1.4 2.23*	.77 1.26*	
7	2.5	4800	8.1 0.97*	13 1.27*	6	4.4 41.4*	2.3 4.06*	3.6 21.87*	4.4 15.28*	4.4 9.91	.37 1.42*	.9 3.53*	.53 1.26*
8	.5	72	126 0.18*	135 0.19*	69	100 14.11*	67 1.78*	45 4.10*	12 0.63*	10 0.34*	9.3 0.55*	15 0.88*	4.1 0.15*
15	17	709		40 0.58*	21	22 30.56*	15 3.92*	13 11.66*	21 10.77*	19 5.32*	1.2 0.58*	1.8 1.04*	2.2 0.77*
WHITEFACE MT., NY													
6		3595	22 1.61*	14 1.03*	8	8.1 57.05*	5.2 6.88*	6.1 27.75*	6.2 16.13*	1.9 3.20*	1.3 3.73*	2.5 7.35*	0.7 1.25*
10		1419	15 0.43*	45 1.3*	19	25 69.5*	12 6.27*	5.5 9.88*	16 16.43*	0.7 0.47*	0.7 0.79*	0.5 0.71*	<d.l.
17		1151	21 0.49*	15 0.35*	6	5.4 12.17*	0.85 0.36*	4.7 6.85*	3.2 2.66*	0.32 0.44*	<d.l.	0.5 0.47*	<d.l.

The 7 September event for Ithaca most closely approximates this value with a concentration of 6 μmole/liter resulting in a pH of 5.2. The fact that a pH of 5.6 may not be appropriate to describe a relevant and representative "background" hydrogen ion concentration in "clean" precipitation has been suggested by other authors making measurements at various remote locations. The MAP3S measurements during an ultimately "clean" event of a hurricane tend to further substantiate the hypothesis that the "natural" pH of precipitation in the northeastern United States, and probably other places, cannot be explained on the basis of CO_2 alone.

With the exception of Brookhaven and Lewes, both coastal sites, the measurements of Table 16 suggest several important conclusions for the September 6 event. In particular, there exists a regional uniformity of very low concentration values throughout the MAP3S network for all major ions in precipitation, in particular for the pollution-related ions of H^+, $SO_4^=$, and NO_3^-. The concentration and deposition of David at several MAP3S stations could be summarized as follows:

Concentration (in [μmole/L]) and Deposition (in [mg/m^2]) for Hurricane David (the deposition values are listed in parenthesis)

	$[SO_4^=]$	$[NO_3^-]$	$L[H^+]$	$[Na^+]$
WFM	8 (57)	6 (28)	14 (1)	2
ITH	4 (23)	3 (10)	9 (0.6)	1
PEN	5 (23)	4 (12)	15 (0.7)	1
VIR	4 (41)	4 (22)	13 (1.3)	3
LEW	13 (53)	4 (11)	10 (0.4)	110
BRO	39 (34)	15 (8)	18 (0.2)	450

The two coastal sites BRO and LEW show higher concentration values for sulfates commensurate with very high concentration values for sodium and all other marine-related ions.

The following order can be established in regard to the concentration values for David in comparison with other values observed during the entire year of 1979 for the stated ions.

	$[SO_4^=]$	$[NO_3^-]$	$F[H^+]$	$[Na^+]$
WFM	6th lowest	2nd lowest	2nd lowest	low
ITH	2nd lowest	2nd lowest	lowest	low
PEN	2nd lowest	3rd lowest	lowest	low
VIR	lowest	2nd lowest	lowest	low
LEW	14 out of 49	2nd lowest	lowest	very high
BRO	30 out of 41	16 out of 41	12 out of 67	highest value for 1979

The deposition values resulting from hurricane David are slightly below or slightly above the respective mean deposition values for the entire year, while the concentration (μmole/L) of pollutant-related material ($SO_4^=$, NO_3^-, H^+) was one of the lowest in precipitation recorded for the entire year 1979. The resulting deposition (mg/m^2) can be classified as producing about average values:

	$(SO_4^=)_{David}/(SO_4^=)_{Mean}$	$(NO_3^-)_{David}/(NO_3^-)_{Mean}$	$L[H^+]_{David}/L[H^+]_{Mean}$
WFM	57/42	28/25	1/1.0
ITH	23/42	10/23	0.6/1.1
PEN	23/42	12/26	0.7/1.0
VIR	41/36	22/20	1.3/1.0

The impact of hurricane Frederic on the precipitation chemistry of the MAP3S stations was mixed. There is no uniform pattern, partly because of the different storm trajectory from September 14 to September 15.

Concentration (in [μmole/L]) and Deposition (in [mg/m^2]) for Hurricane Frederic (the deposition values are listed in parenthesis)

	$[SO_4^=]$	$[NO_3^-]$	$L[H^+]$	$[Na^+]$
WFM	5(12)	5(7)	15(0.4)	1
Mean deposition for 79	(42)	(25)	(1.0)	
ITH	15(31)	11(15)	45(1.0)	1
Mean deposition for 79	(42)	(23)	(1.1)	
PEN	14(13)	11(6)	32(0.3)	4
Mean deposition for 79	(42)	(26)	(1.0)	
VIR	22(31)	13(12)	40(0.6)	19
Mean deposition for 79	(36)	(20)	(1.0)	
LEW	8(8)	5(3)	11(0.1)	12
BRO	N.D.	N.D.	N.D.	N.D.

The ranking of concentration values for hurricane Frederic is presented below:

	$[SO_4^=]$	$[NO_3^-]$	$L[H^+]$
WFM	2nd lowest	lowest	3rd lowest
ITH	9 out of 53	4th lowest	4th lowest
PEN	11 out of 66	3rd lowest	7th lowest
VIR	22 out of 52	13 out of 52	9 out of 50
LEW	4th lowest	4th lowest	4th lowest

The deposition of pollutant-related material ($SO_4^=$, NO_3^-, H^+) resulting from Frederic was below average for all MAP3S stations that reported a precipitation event.

The two hurricane case studies indicate that extensive and prolonged precipitation indeed yields very low concentration values; for some stations, they constituted one of the lowest annual values for pollutant-related materials. While depositions under those circumstances can be considered as average, they do not yield very low values. In particular, they did not constitute a "deposition episode," in spite of high total precipitation.

2.11 Significant Event Analysis

It has been proposed that massive amounts of pollutants delivered in precipitation over a relatively short period of time could be more detrimental than large cumulative totals over one or more months. This study will not try to resolve this question, but rather examine case studies which have the potential for significant deposition.

A significant event will be defined here as one whose value exceeds the annual mean by one standard deviation. Frequency plots were generated for concentration and deposition to determine mean values as well as significant events. From Tables 14 and 15 one can calculate a regional average (represented by the sum of all significant events for all four stations over a three-year period) for the percentage of significant deposition events:

	$[SO_4^=]$	$[NO_3^-]$	$[H^+]$
% of significant events for region	12%	12%	13%

It follows that over the entire region, about 12% of the precipitation events deposit sulfate, nitrate and hydrogen ions in excess of one standard deviation beyond the mean.

Table 17 summarizes these deposition results with the ratio of the significant event to the annual total, the percentage of the total, and the date of collection for the four basic MAP3S stations. Over the three-year period 1977-1979, there were an average of 62 collection events per year for the four stations. No particular pattern emerges as far as their geographic distributions are concerned, i.e., all stations can experience equally high values at some time over the three-year period. Most of the time, deposition episodes for sulfur and hydrogen ions occur simultaneously. The overall summary, i.e., the regional average for all stations and for the three-year period 1977-79, shows that the maximum event concentration for such a deposition episode is between 8-10% of the annual total deposition (from Table 17):

	$\frac{(SO_4^=)\text{max.}}{(SO_4^=)\text{annual}}$	$\frac{(NO_3^-)\text{max.}}{(NO_3^-)\text{total}}$	$\frac{(H^+)\text{max.}}{(H^+)\text{total}}$
All station average per year (mg/m^2)	218/2262	109/1366	4.42/50.3
Percent of annual	9.6%	8.0%	8.8%

It should be noted that an event may extend over several days in some cases and the date of occurrence is actually the date of MAP3S collection.

It is particularly interesting that the maximum event deposition dates for the various ions are not necessarily the same for each station. That is, mechanisms other than the dominant influence of precipitation volume appear to be at work during some events leading to "deposition episodes." Elevated concentration levels would be the logical source for these maximized events. Also many of the events did not occur in the summer months when atmospheric loading with photochemically-induced secondary pollutants is usually highest.

TABLE 17

Significant Deposition Events
(maximum annual deposition)

Station	Year	$(SO_4^=)_{max}$ / $(SO_4^=)_{annual}$ [mg/m^2]	Percent of annual	Date when max. occurred	$(NO_3^-)_{max}$ / $(NO_3^-)_{annual}$ [mg/m^2]	Percent of annual	Date when max. occurred	$(H)_L$ max / $(H)_L$ annual [mg/m^2]	Percent of annual	Date when max. occurred
WFM	1977	132/2333	5.7	9-14	96/1495	6.4	10-18	3.086/46.5	6.6	9-14
	1978	262/1908	13.7	8-30	115/1091	10.5	8-30	5.991/41.2	14.5	8-30
	1979	234/1908	12.3	10-9	80/1346	5.9	10-9	3.919/47.1	8.3	10-9
ITHACA	1977	216/2233	9.7	7-20	122/1336	9.1	10-17	4.285/41.5	10.3	4-29
	1978	159/2351	6.8	8-10	80/1401	5.7	3-1	2.767/49.3	5.6	8-10
	1979	253/2429	10.4	7-24	88/1346	6.5	10-6	5.117/62.0	8.3	7-24
PENN STATE	1977	174/2698	6.4	9-27	98/1716	5.7	9-27	3.954/53.7	7.4	9-27
	1978	220/2448	9.0	6-4	97/1583	6.1	6-4	5.219/56.6	9.2	6-4
	1979	336/3188	10.5	11-4	219/1983	11.0	11-4	4.138/75	5.5	2-27
VIRGINIA	1977	323/1744	18.5	5-31	143/897	15.9	5-31	6.661/31.5	21.1	5-31
	1978	185/2284	8.1	8-28	114/1273	9.0	7-5	3.821/55.7	6.9	7-5
	1979	135/1620	8.4	8-19	60/913	6.6	2-13	4.081/44.0	9.3	9-4
All station average/year		219/2262			109/1366			4.42/50.3		
Percent of annual			9.7			8.0			8.8	

As an extension of these data, Table 18 provides a more detailed look at the variables for these events, including precipitation time. It is immediately obvious that the large values of sample volume is one of the dominant factors influencing "deposition episodes" since all but two events had sample volumes of over 1000 ml. It also suggests that there must be an optimum combination of the concentration values for various ions as well as amount of precipitation delivered. Large values in precipitation, such as occurred during hurricanes David and Frederic, with below average or very low ion concentrations, do not constitute a deposition episode.

It can be concluded that deposition episodes do indeed occur at all stations with large amounts of pollutants delivered in a relatively short time span. No particular pattern emerges as far as their geographic distributions are concerned. Finally, there appears to be no preferred season for the occurrence of these episodes, since they rely on the optimum combination of concentration and precipitation amounts.

TABLE 18

			Ion concentration (μmole/L) coinciding with maximum event deposition			Maximum event deposition (mg/m^2) for 1977, 78, 79, respectively ("Deposition Episodes")			
Station	Date of Maximum Event Deposition	Sample Volume (ml)	L[H^+]	[$SO_4^=$]	[NO_3^-]	$SO_4^=$	NO_3^-	H^+	Precip. Time (Hrs.)
WFM	14 Sep. 77	2100	72	32	35	132	-	3.09	45
	18 Oct. 77	4850	33	9	23	-	96	-	48
	30 Aug. 78	1631	180	82	56	262	115	5.99	22
	9 Oct. 79	4267	45	28	15	234	80	3.92	34
ITH	29 Apr. 77	2100	100	45	32	-	-	4.28	68
	20 Jul. 77	670	350	230	63	216	-	-	12
	17 Oct. 77	2690	71	29	39	-	122	-	37
	1 Mar. 78	110	190	46	190	-	80	-	10
	10 Aug. 78	1130	120	72	25	159	-	2.77	9
	24 Jul. 79	1990	126	65	25	253	-	5.12	5
	6 Oct. 79	2900	78	32	24	-	88	-	15
PEN	27 Sep. 77	2691	72	33	29	174	98	3.95	19.3
	4 Jun. 78	1023	250	110	75	220	97	5.22	5
	27 Feb. 79	2122	96	27	37	-	-	4.14	38.3
	4 Nov. 79	1929	48	89	90	336	219	-	13.5
VIR	31 May 77	1920	170	86	59	323	143	6.66	12
	5 Jul. 78	1076	174	74	84	-	114	3.82	58
	28 Aug. 78	2100	76	45	14	185	-	-	2.3
	13 Feb. 79	1600	45	4	30	-	60	-	10.5
	19 Aug. 79	1145	110	98	67	136	-	-	12.5
	4 Sep. 79	2000	100	34	22	-	-	4.08	7

CHAPTER 3

DISCUSSION AND SUMMARY

Attempts have been made to illustrate concentration and wet deposition of pollutant material at selected stations within the northeastern United States and to characterize as many events as possible with respect to air mass origin. Further attempts have been made to develop a regional pattern for the deposition of dominant ions.

Cumulative totals as well as monthly and yearly variations in concentration and deposition were demonstrated for inland stations covering a sizable regional domain. Of particular interest is the analysis of concentration and ion deposition data for possible regional gradients in either of the above parameters.

Table 13 shows that for the six month summer season, 1978, the hydrogen ion deposition as determined in the laboratory L[H], the sulfate deposition $[SO_4^=]$, and the nitrate deposition $[NO_3^-]$ are of the same order (within ±10%) for the stations Whiteface Mountain, Ithaca, Penn State and Virginia. The deposition of the soil component $[Ca^{++}]$ is almost identical (within ±2%) at all of the above stations. The Illinois station shows a lower $L[H^+]$ deposition and a higher $[Ca^{++}]$ deposition, indicating a higher neutralizing dust component in the rain than was present at the above four stations. But the sulfate and nitrate deposition at Illinois, again, is of the same order as was found for the other four stations. Therefore, based on summer data, a steep gradient in deposition of pollutant-related ions cannot be detected for the above five stations covering a vast area from midwest to northeastern United States.

The concept of a rather uniform pattern of deposition for the entire northeast merits additional examination. The evidence gathered by this wet deposition study does not explicitly support "traditional" hypothesis of pollution-related material released into the atmosphere in the "Midwest/Ohio Valley" being transported directly to the northeastern sector of the United States, where it is deposited by wet (and dry) deposition. While it is possible to trace, over a distance of several hundreds of miles, primary pollutants from their emission source(s) to their ultimate sink at the ground (for example SO_2 or NO_x), it is increasingly more difficult to achieve this goal for secondary pollutants (for example sulfate aerosol or nitric acid vapor). As far as pollution-related ions in precipitation are concerned (for example $SO_4^=$ and NO_3^-, or H^+), this task of establishing a credible and defensible source-receptor relationship is even more challenging. The problem appears to be an extremely complex one consisting of homogeneous and heterogeneous transformation processes and mixing on all meteorological scales.

In order to solidify this concept of a relatively uniform wet deposition pattern, inter-station comparisons must be made. As mentioned earlier, this procedure may not apply for individual events on short time scales, but is applicable for yearly totals provided certain assumptions are made. The critical factor in these comparisons is the normalization of the deposition totals to a specified precipitation amount. As shown by partial correlation coefficients, there is a strict dependence of ion deposition on the amount of precipitation. Therefore, high deposition values at a particular location could be due mainly to enhanced precipitation, rather than to a high concentration of ions in precipitation.

Before normalizing the total deposition, an assumption of a linear relationship between ion deposition and precipitation volume is necessary. Figure 61 provides a reasonable basis to test this assumption by showing the linear correlation of $[SO_4^=]$ deposition and precipitation depth (cm) for the four basic MAP3S stations. While not an absolute correlation, the coefficient of better than 0.60 suggests that linear normalization techniques are applicable.

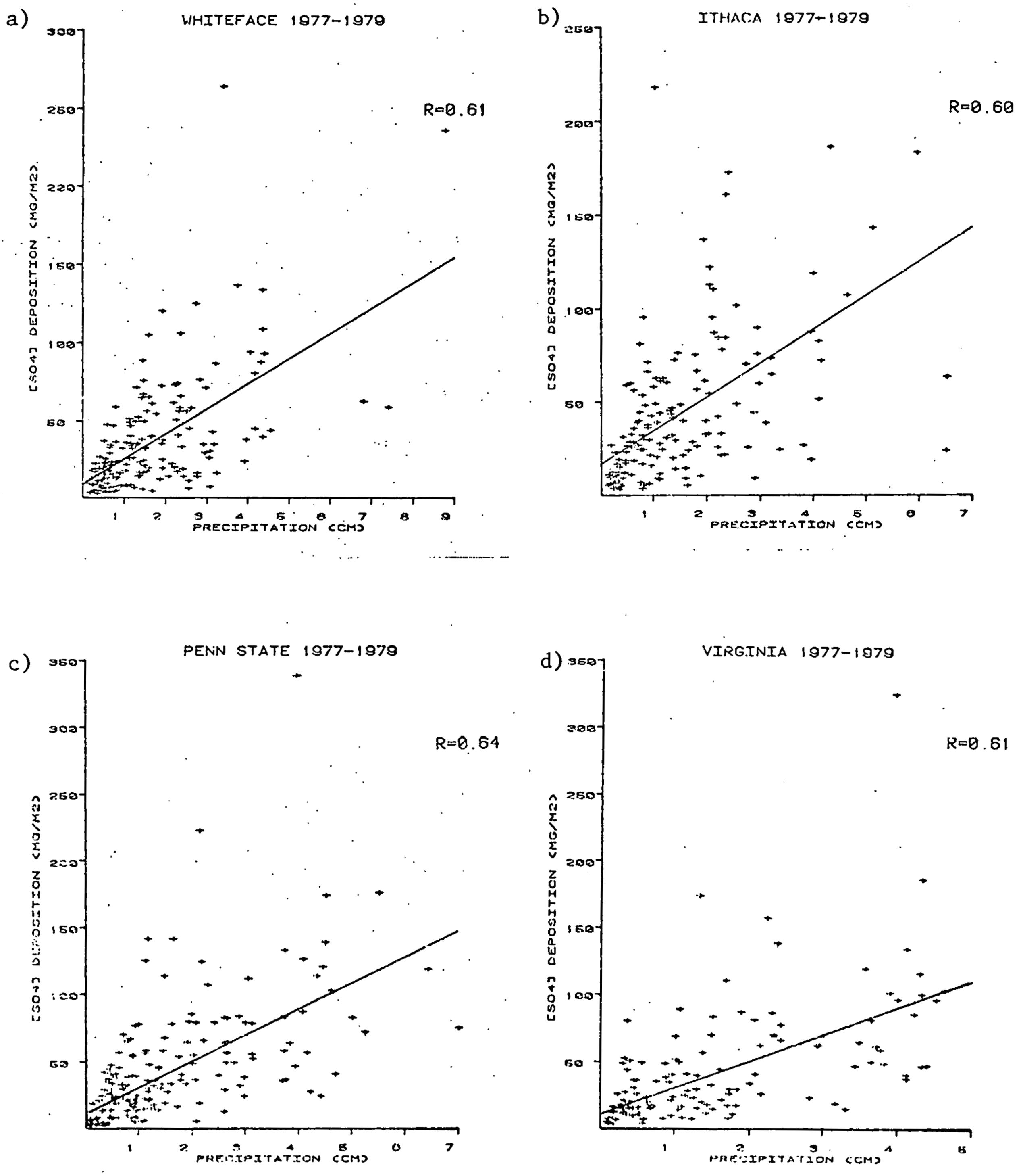


Figure 61. Sulfate deposition vs. precipitation, 1977-79, for a) Whiteface, b) Ithaca, c) Penn State, and d) Virginia

Deposition totals of sulfate the nitrate for 1979 and the two-year period 1978-79 can then be normalized to determine if a significant regional gradient in ion deposition does in fact exist. Figure 62 shows the measured deposition and precipitation volume and normalized values for 1979, while Figure 63 contains the same information for the two-year period 1978-79. Due to lack of data, Oxford, Ohio, was not included in this two-year analysis. Both figures clearly demonstrate that a steep gradient in ion deposition from midwest to northeast does not exist, as was mentioned several times earlier. The normalized regional average for ion deposition per cm of precipitation derived from the two-year 1978-79 data set presented in Figure 63 amounts to:

$[SO_4^{=}]$ = 26.21 ± 3.33 (or ±12.7%) $[mg \cdot m^{-2}]$ per year and per cm of precipitation

$[NO_3^{-}]$ = 15.28 ± 1.73 (or ±11.3%) $[mg \cdot m^{-2}]$ per year and per cm of precipitation

The influence of total precipitation volume on ion deposition was demonstrated earlier. If it is indeed legitimate to normalize ion deposition as was done here - by defining an ion deposition per cm of precipitation - then a surprising result emerges: the Illinois MAP3S site has the highest sulfate deposition of any station considered here. Speculations might be raised as to the possible sources that might contribute to this sulfate deposition. However, our approach here will focus solely on gaining information on the origin of air masses that delivered precipitation to the Illinois site

As was the case for Whiteface, the ARL-ATAD trajectory model was applied to the Illinois MAP3S precipitation chemistry data to determine the trajectory directions for prominent ion concentration and deposition. Figures 64 and 67 show the concentration and deposition of pollution-related ions for

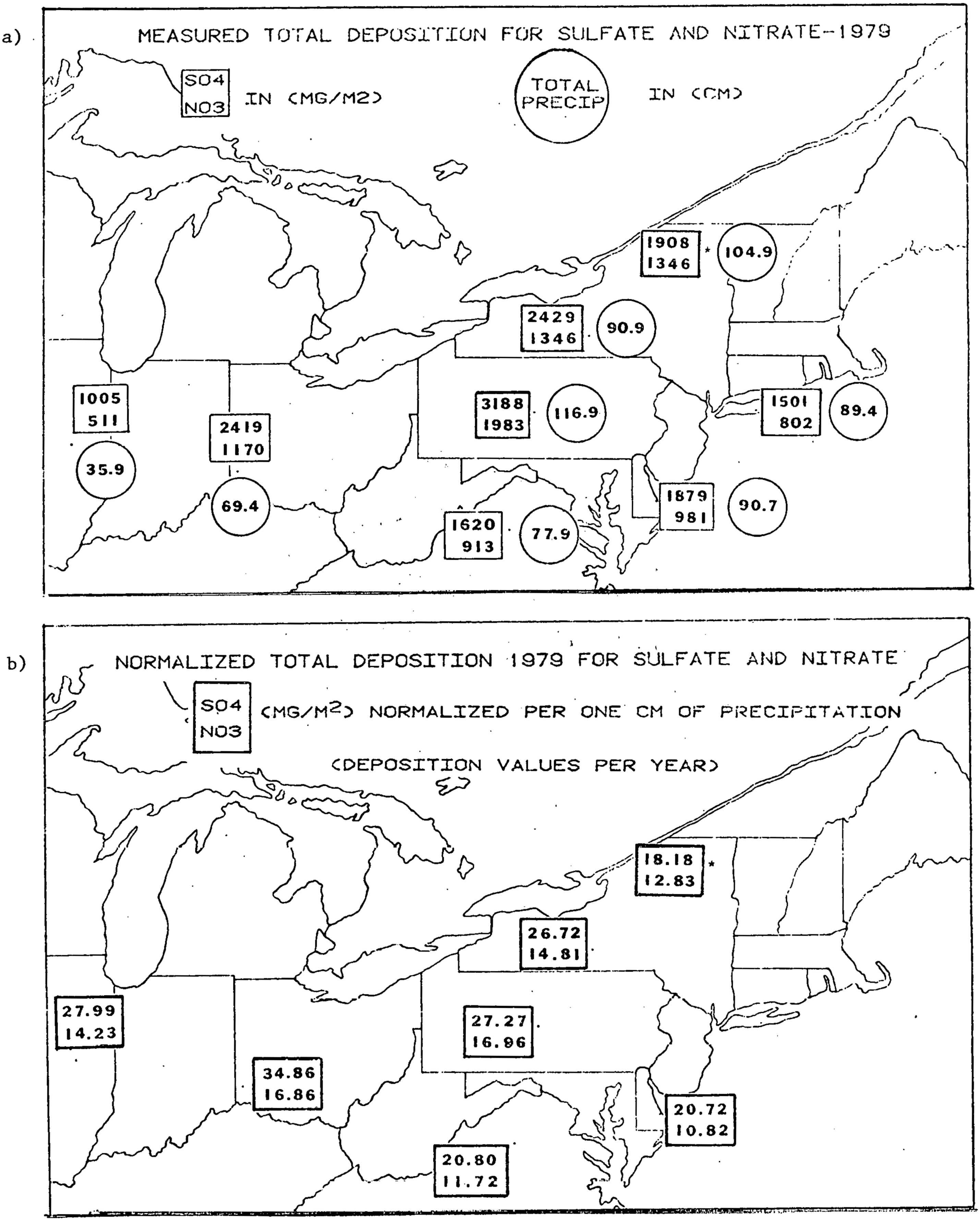


Figure 62. a) Measured, and b) Normalized sulfate and nitrate deposition, 1979

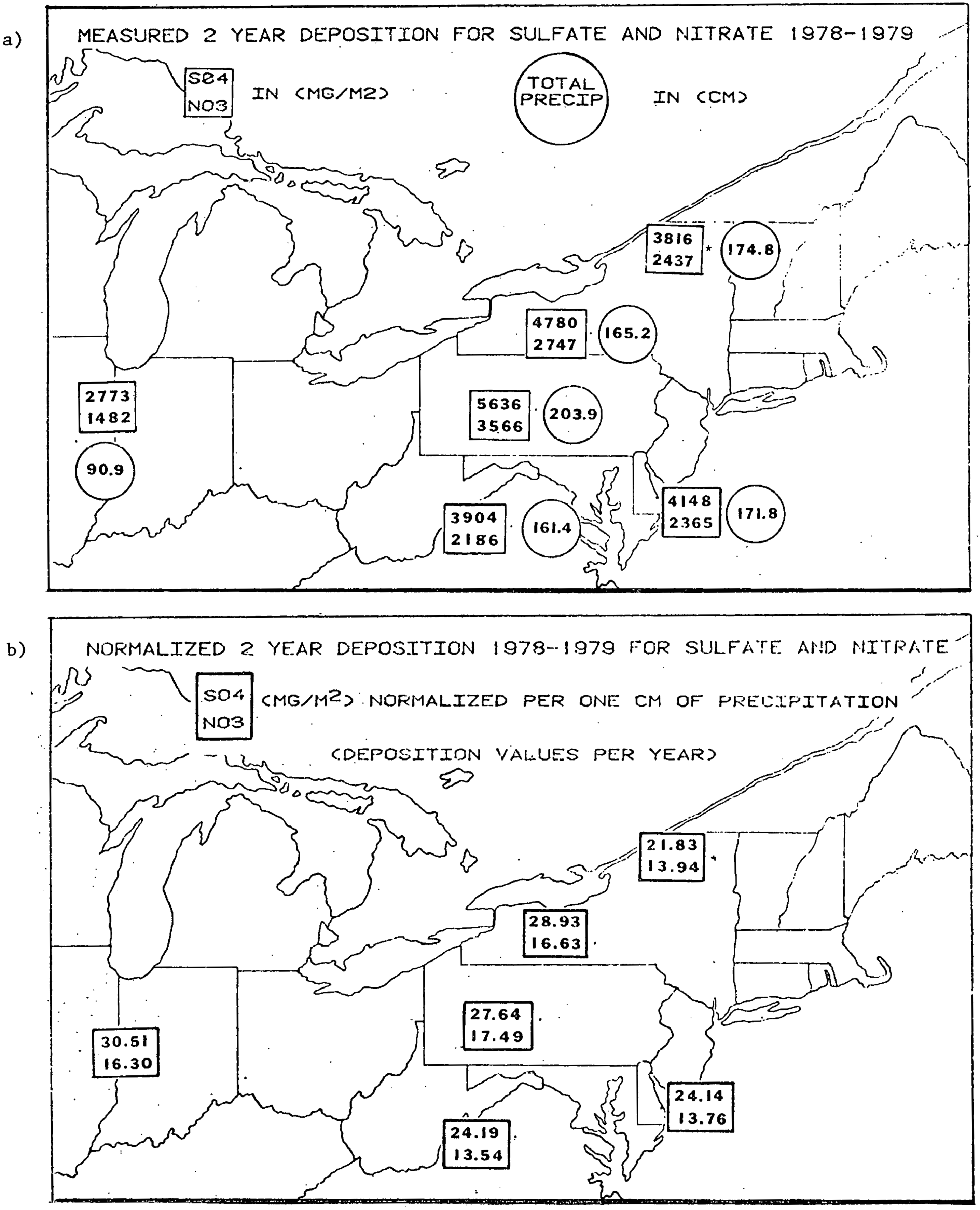


Figure 63. a) Measured, and b) Normalized sulfate and nitrate deposition for 1978-79

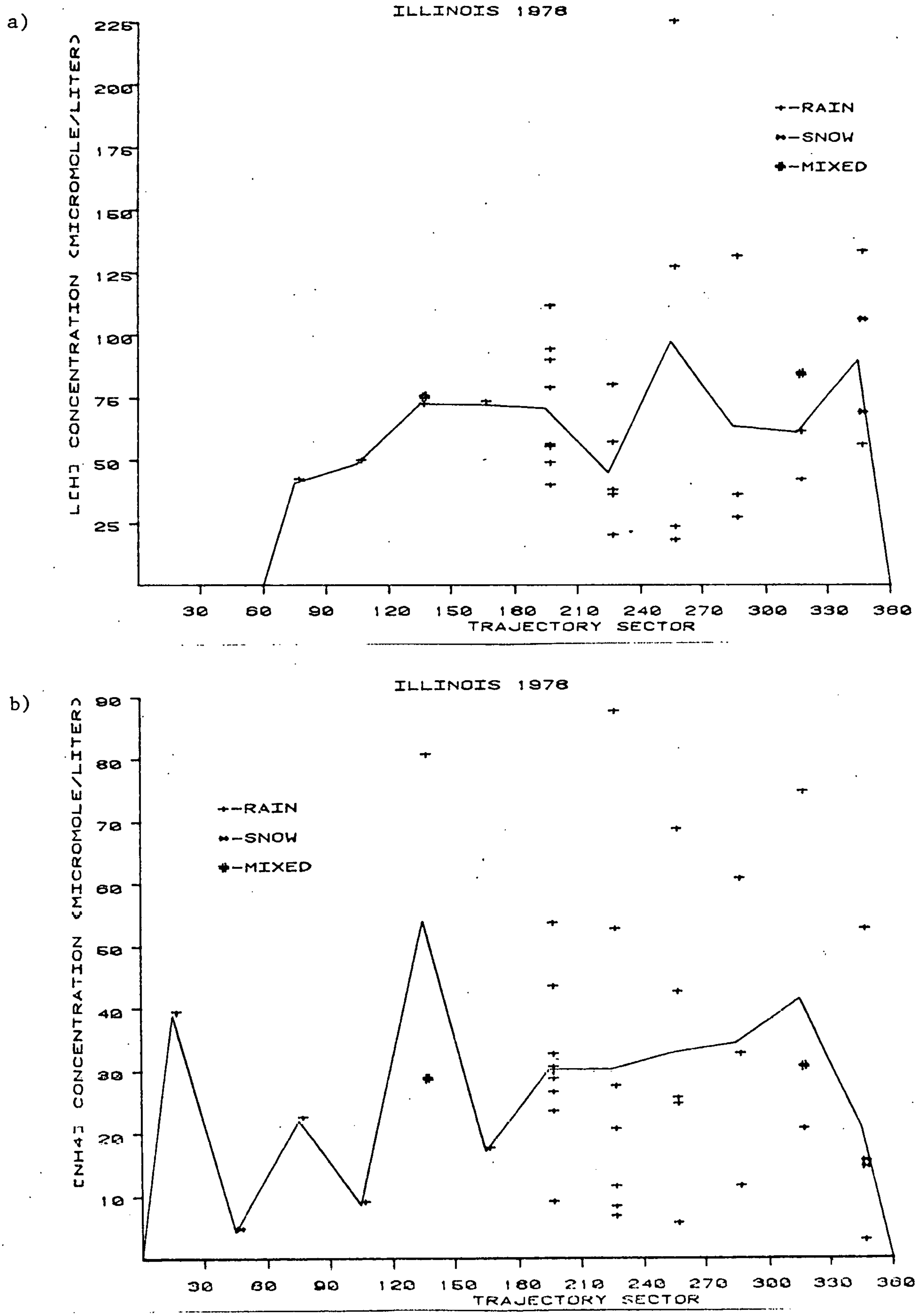


Figure 64. a) Free hydrogen ion, and b) Ammonium ion concentration per 30° trajectory sector for Illinois, 1978.

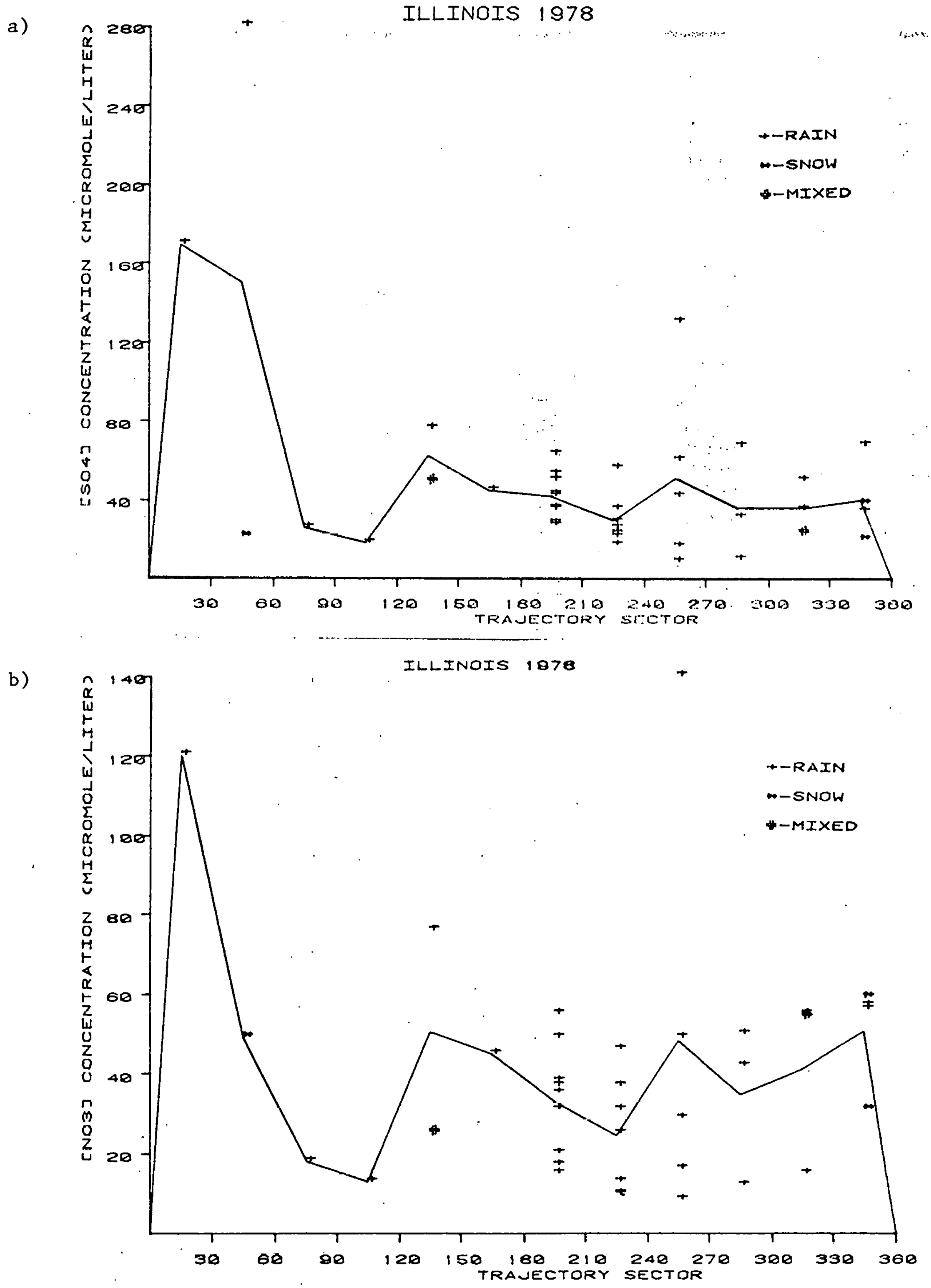


Figure 65. a) Sulfate, and b) Nitrate concentration per 30° trajectory sector for Illinois, 1978.

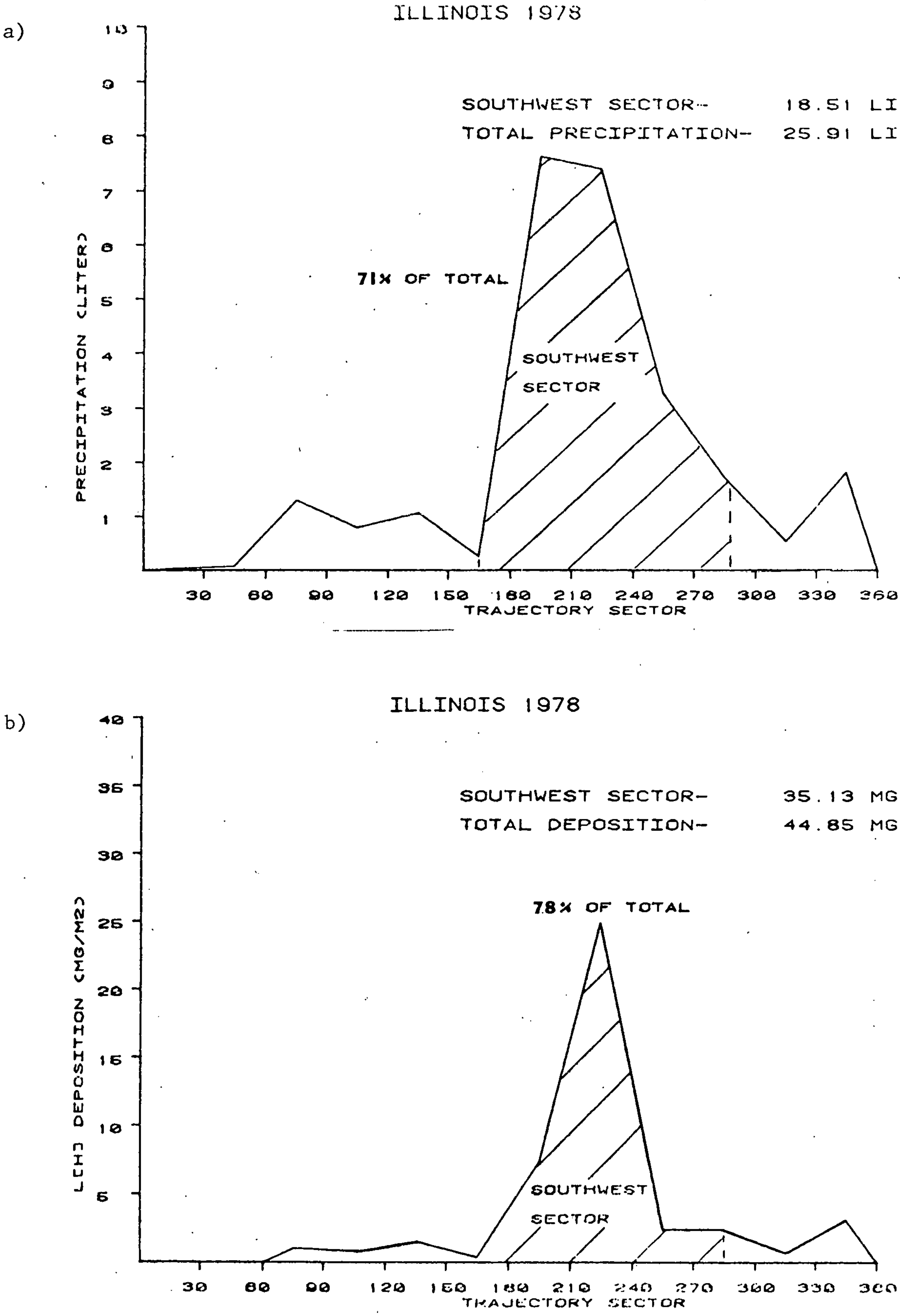


Figure 66. a) Precipitation, and b) Free hydrogen ion deposition per 30° trajectory sector for Illinois, 1978

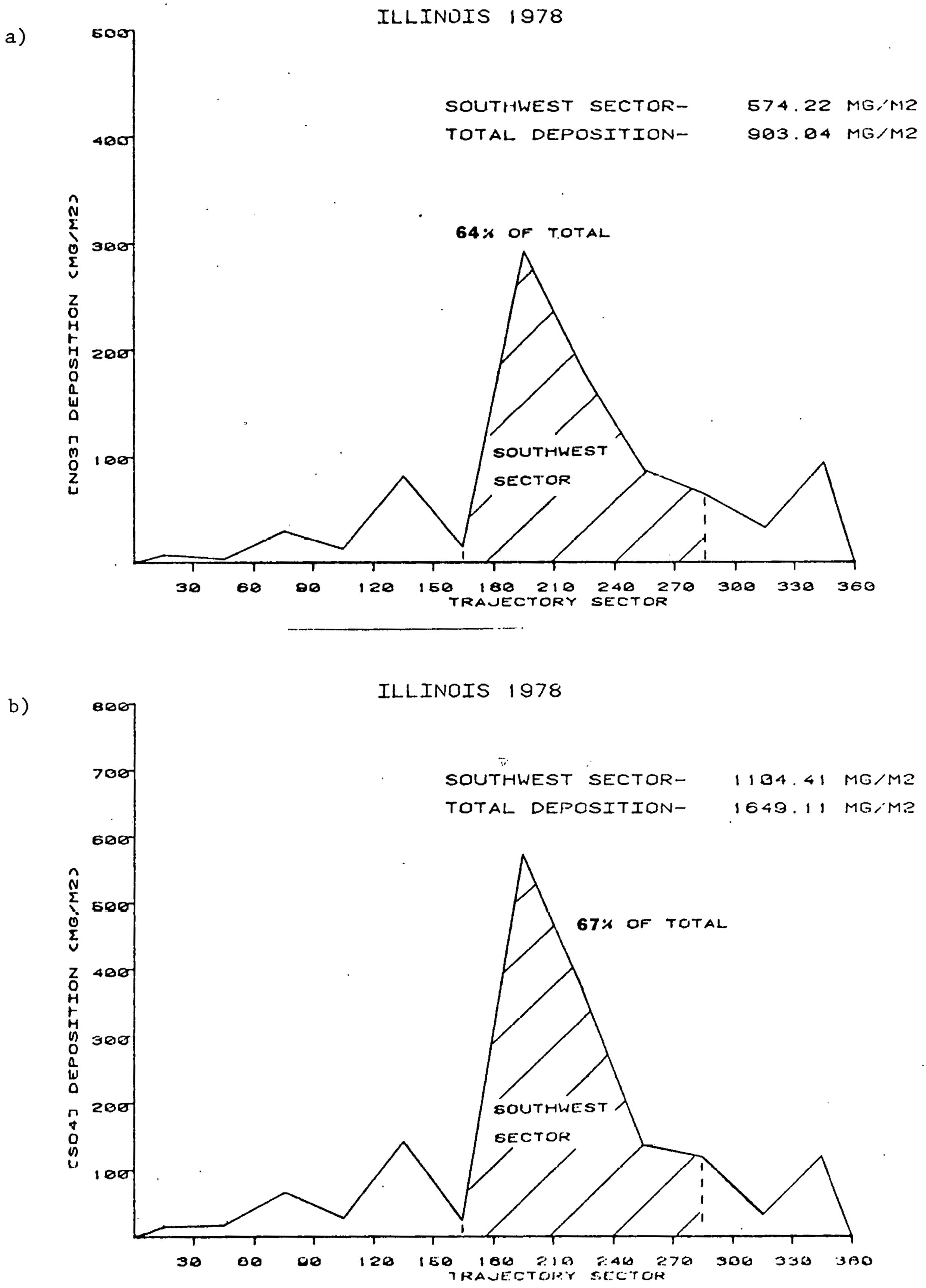


Figure 67. a) Sulfate, and b) Nitrate deposition per 30° trajectory sector for Illinois, 1978

February through December 1978. Clearly, the dominant influence is from the southwest, as was found for Whiteface Mountain and the other MAP3S stations. This again is not surprising since the same prevailing flow patterns are established prior to precipitation at Illinois and Whiteface.

In summary, it follows that on the basis of annual deposition patterns or on the basis of an annual concentration parameter, it appears that "acid rain" is a regional phenomenon characteristic to the entire area covered by the network. There is no strong annual geographical gradient for the deposition of pollution-related ions from which one could draw conclusions about the origin of acid rain or from which one could reasonably identify a source region. From the assessment of 1978 annual concentration and deposition averages, there emerges the tentative conclusion that there exists a "regional superbowl" for acid rain. This does not imply that the precursor material to acid rain is similarly distributed. It simply says that in the northeastern region of the United States all meteorological, physical and chemical processes that affect the accumulation of pollution-related ions ($[SO_4^=]$, $[NO_3^-]$ and $[H^+]$) in rain eventually result in a rather homogeneous annual deposition of these materials over the entire area.

Trajectory sector analyses were used to illustrate that differences in ion concentration and ion deposition between events do occur as a function of air mass origin. Separate discrete events that passed over the "Midwest/Ohio Valley" region were found to exhibit generally higher values in ion concentration than their Canadian counterparts. However, ion deposition was found to be a much stronger function of precipitation volume. This process was occasionally inconclusive, since some MAP3S collection events might actually consist of several smaller scale precipitation events as the trajectories traverse a wide range of approach angles. However, 80% to 90%

of the events and total deposition could be classified using this trajectory classification approach. It is conceivable that a more consistent pattern will emerge as more parameters are taken into consideration, in particular, those that relate to transport and chemical transformations. The documentation of simple air trajectories, receptor concentration, and deposition values on an event basis are necessary, but not sufficient for characterizing source-receptor relationships in regard to acid rain. If the concept of a "regional superbowl" is indeed applicable, then trajectory analysis should extend beyond two days and encompass mesoscale weather patterns.

Trajectory sector analysis may be coupled with emission data to further summarize the deposition differential at a particular location. The emission data covering the continental United States east of the Mississippi River, the states of Iowa, Minnesota, Arkansas, Missouri and Louisiana are (in tons/year):

Particles	SO_x	NO_x	SO_x/NO_x ratio
5.98×10^6	2.16×10^7	8.21×10^6	2.63

For the "Midwest/Ohio Valley" region, covering Indiana, Illinois, Ohio, Kentucky, West Virginia and Pennsylvania alone, the annual emissions are (in tons/year):

	1.09×10^7	3.76×10^6	2.90

For the Canadian provinces of Nova Scotia, Newfoundland, Quebec, Ontario, Prince Edward Island and New Brunswick, the annual emissions are (in tons/year):

2.81×10^5	3.01×10^6	1.57×10^5	19.2

The emissions in the "Midwest/Ohio Valley" region versus the "Canadian/Great Lakes" area are higher by a factor of 3.6 for sulfur components and 24 for nitrogen components.

One might expect to see significant differences in precipitation chemistry as air masses from different regions arrive at a receptor site. Ninety percent of the precipitation events during 1978 were catagorized by means of air mass trajectories corresponding with the event.

Whiteface Mountain (1978)

Midwest/Ohio Valley (160°-280° sector)	56% of the annual precipitation delivering:
	62% of the annual $[H^+]$ deposition
	64% of the annual $[SO_4^=]$ deposition, and
	65% of the annual $[NO_3^-]$ deposition
Canadian/Great Lakes (280°-30° sector)	26% of the annual precipitation delivering:
	31% of the annual $[H^+]$ deposition
	31% of the annual $[SO_4^=]$ deposition, and
	28% of the annual $[NO_3^-]$ deposition

Illinois

(160°-280° sector)	71% of the annual precipitation delivering:
	78% of the annual $[H^+]$ deposition
	67% of the annual $[SO_4^=]$ deposition, and
	64% of the annual $[NO_3^-]$ deposition

It is quite apparent that the precipitation volume, more than any other single factor, determines the amount of deposition for the three pollution-related ions, $[H^+]$, $[SO_4^=]$ and $[NO_3^-]$. The deposition of ions from "Midwest/ Ohio Valley" air and "Great Lakes/Canadian" air does not reflect the very significant differences in emissions that are located in these two regions. The Illinois results further substantiate the above conclusion.

As postulated in Chapter 2, there exists no simple, straightforward relationship between emission source(s) for acid precipitation, precursor gas(es) and receptors of "acid rain," i.e., $[H^+]$, $[SO_4^=]$ and $[NO_3^-]$ ions. The chemical transformation pathway(s) seem to be complex and insensitive to the analysis presented here and based upon available meteorological and chemical information.

Normally, trajectory analysis of individual events will lead to some basic source-receptor relationships. Vital information is still missing on the overall transport/transformation processes that take place in the atmosphere relevant to the formation and deposition of "acid rain."

The concept of a "superbowl" does explain some of the results in that the final product, i.e., "acid rain," is rather evenly distributed over a very large region. It would indicate that intense mixing on a mesoscale, coupled with unknown rate-controlling steps for the formation and deposition of "acidic material" are as important, or more important, than the simplified air mass trajectories currently in use for establishing source-receptor relationships. In summary, the known source regions for precursor gases to "acid rain" cannot yet be unequivocally linked to receptors with the meteorological, physical and chemical information available today.

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