

## Statistical Analysis of Precipitation Chemistry Measurements over the Eastern United States. Part I: Seasonal and Regional Patterns and Correlations

R. M. ENDLICH, B. P. EYNON, R. J. FERREK,\* A. D. VALDES AND C. MAXWELL\*\*

*SRI International, Menlo Park, California*

(Manuscript received 26 December 1986, in final form 1 December 1987)

### ABSTRACT

This paper describes the behavior of the chemical constituents in precipitation, including their typical concentrations and ranges, regional patterns, and seasonal changes. Daily precipitation measurements for the period 1978 through 1983 over the eastern United States were examined for 34 sites. The sites were operated by the Electric Power Research Institute and Utility Acid Precipitation Study Program (known as EPRI-UAPSP), the Multistate Atmospheric Power Production Pollution Study (MAP3S), and the Wisconsin Acid Deposition Monitoring Program (WADMP). Data from these three networks were combined into a single, uniform archive of daily rainfall records containing precipitation amounts, pH, and constituent concentrations. Various statistical analyses were made to determine the predominant characteristics of the data. In Part I of this series of papers, a seasonal analysis is made of the concentrations of hydrogen ion, sulfate, nitrate, and ammonium, and regional differences are described. Also, the statistical relationships of hydrogen ion concentrations to the other principal constituents are discussed. Other aspects of the study are given in Parts II through IV of the series. Part II uses an objective statistical interpolation method (Kriging) to evaluate the spatial patterns of constituents and their trends during the period of record. Part III discusses the ionic balance among the constituents, and Part IV describes the variations in concentrations that are attributable to meteorological factors.

### 1. Introduction

The nature, amounts, and sources of chemical constituents associated with the acidity of precipitation in the eastern United States are matters of wide public concern (National Research Council 1983). Several years of daily precipitation chemistry measurements have been collected in the recent past. These data can be used to examine the amounts and variabilities of the constituents of precipitation, which must be understood prior to assessing the influence of emissions on precipitation chemistry. To provide a basis for an improved understanding of governing factors, this study investigates regional patterns of analyte concentrations and depositions, annual and seasonal changes in analytes, and the relationships among analytes. The analysis methods are statistical and depend on substantial numbers of observations. The computations were done mainly with the SAS computer package (SAS Institute 1985) on the Stanford University IBM 3083 computer.

In a recent analysis of the historical trends of precipitation acidity and emissions (Hidy et al. 1984) the uncertain quality of past data was a major limitation on the analysis, and the need for newer, improved measurements was emphasized. Such measurements of the chemical constituents in precipitation have been made daily by several networks at sampling locations in the eastern United States. The data most uniform in quality and coincident in time are from three networks. The MAP3S (Multistate Atmospheric Power Production Pollution Study) data are from nine sampling locations during the period 1976 through 1983. An analysis of these data for the period 1976–80 has been published by the MAP3S/RAINE Research Community (1982). (For brevity, we will refer to this paper as M/R.) The combined Electric Power Research Institute and Utility Acid Precipitation Study Program (EPRI-UAPSP) data used in this paper stem from sampling at 6 to 20 locations between 1979 and 1983. These UAPSP data form the core of the present study. In addition, data from measurements starting in 1982 made by the Wisconsin Acid Deposition Measuring Program (WADMP) in accordance with MAP3S protocols have been included.

Various investigations can be based on data of this kind, but it is, naturally, not possible to account for the processes which occurred in the atmosphere and produced the chemical makeup of any individual precipitation sample. This paper (Part I of the series) is

\* Current address is the Department of Atmospheric Sciences, University of Washington, Seattle, WA 98195.

\*\* Current address is VeBar, Inc.-ESM Operations, Columbia, MD 21045.

Corresponding author address: Mr. Roy Endlich, SRI International, 333 Ravenswood Ave., Menlo Park, CA 94025.

focused on the seasonal patterns of precipitation constituents, and on the empirical relationships among the constituents. Other parts of the statistical analyses are somewhat distinct, and have been separated into three topics. Part II (Eynon 1988) uses the Kriging methodology to represent the regional patterns and trends of the constituents in an objective manner. Part III (Ferek et al. 1988) discusses chemical balance relationships among the constituents in precipitation samples, and Part IV (Maxwell et al. 1988) describes the variations in precipitation constituents associated with meteorological factors.

## 2. Data sources and quality control

Precipitation chemistry measurements from the three networks—EPRI-UAPSP, MAP3S, and WADMP—were furnished by EPRI. These networks provide data that are similar in quality and in spatial and temporal resolution. All three collected daily samples when precipitation had occurred and made chemical measurements of each sample. The sampling locations included in the present study are shown in Figure 1. The instrumentation at the UAPSP sites included an automatic precipitation sampler, a triple beam balance (for weighing the sample), a weighing bucket rain gauge, digital pH and temperature meters, and a conductivity meter. (Further details are given by Topol and Schwall 1987). At each site a technician gathered the sample between approximately 0800 and 1200 AM (LST) whenever precipitation had occurred during the previous 24 (Mueller et al. 1984). The collectors and

TABLE 1. List of sites making precipitation chemistry measurements.

Network	Site	City	State	Latitude	Longitude
UAPSP	1	Turners Falls	MA	42°35'50"	72°32'55"
	2	Tunkhannock	PA	41°34'30"	75°59'40"
	3	Indian River	DE	38°34'50"	75°14'45"
	4	Zanesville	OH	39°59'02"	82°01'05"
	5	Rockport	IN	37°52'50"	87°07'47"
	6	Giles County	TN	35°17'05"	86°54'11"
	7	Fort Wayne	IN	41°02'39"	85°19'08"
	8	Raleigh	NC	35°43'43"	78°40'48"
	9	Lewisburg	WV	37°50'50"	80°25'00"
	10	Gaylord	MI	44°56'58"	84°38'30"
	11	Clearfield	KY	38°08'10"	83°27'17"
	12	Alamo	TN	35°47'32"	89°08'03"
	13	Winterport	ME	44°37'05"	68°58'30"
	14	Uvalda	GA	32°03'18"	82°28'25"
	15	Selma	AL	32°28'25"	87°05'03"
	16	Clinton	MS	32°21'06"	90°17'15"
	17	Marshall	TX	32°39'58"	94°25'06"
	18	Lancaster	KS	39°34'10"	95°18'17"
	19	Brookings	SD	44°19'54"	96°49'45"
	20	Underhill	VT	44°31'42"	72°52'08"
	21	Big Moose	NY	43°49'03"	74°54'08"
	22	McArthur	OH	39°14'06"	82°28'41"
	23	Yampa	CO	40°10'	106°55'
MAP3S	71	Whiteface	NY	44°24'	73°45'
	72	Ithaca	NY	42°23'	76°43'
	73	Penn State	PA	40°47'	77°57'
	74	Charlottesville	VA	38°03'	78°33'
	75	Champaign	IL	40°03'	88°22'
	76	Brookhaven	NY	40°52'	72°53'
	77	Lewes	DE	38°46'	75°00'
78	Oxford	OH	39°32'	84°44'	
79	Oak Ridge	TN	36°00'	84°12'	
WISCONSIN	91	Round Lake	WI	46°08'	91°34'
	92	Legend Lake	WI	44°32'	88°23'
	93	Lake Geneva	WI	42°21'	88°18'

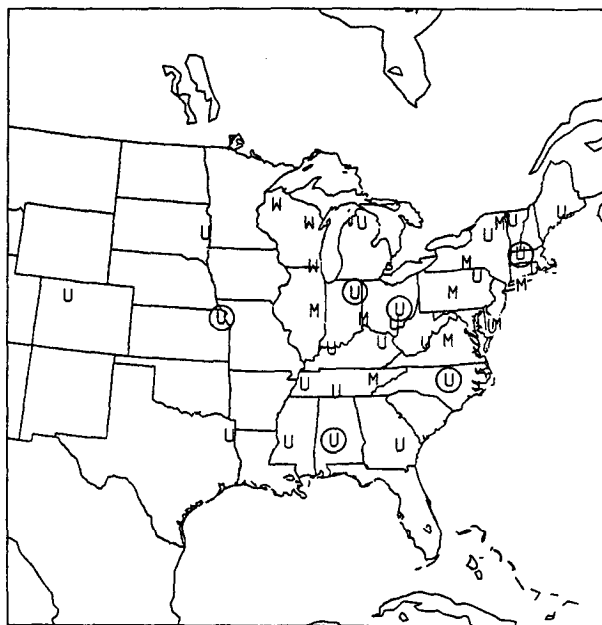


FIG. 1. Locations of sites with precipitation chemistry measurements (U = UAPSP Network, M = MAP3S Network, and W = WADMP Network).

procedures were designed to avoid contamination and sample degradation. Conductivity and pH were measured onsite. Then the daily samples were stored in a refrigerator for up to 7 days. Each week the daily samples were sent in a cold pack to a central chemistry laboratory where they were analyzed. In the laboratory, pH and conductivity were measured with digital meters; sulfate, nitrate, and chloride by ion chromatography; ammonium by colorimetry; sodium, potassium, calcium, and magnesium by atomic absorption spectroscopy; the acidity by titration to pH 8.3.

The reliability of the EPRI-UAPSP data has been examined in several ways (Mueller et al. 1984) including the use of the separate analysis of two collectors at the same site (analyzed separately), dividing precipitation samples from a single collector and making separate measurements, and using reference samples of known concentration. These tests show that the absolute differences between measurements divided by mean concentrations are approximately 5% for sulfate, nitrate, and ammonium; 10% for hydrogen ion, sodium, calcium, magnesium, and chloride; and 20% for

potassium. These accuracy estimates are similar to those reported by M/R (1982).

The three datasets were combined into a single, consistent archive. Table 1 lists the names and locations of the sites, and an identification number of each one. Figure 2 shows the periods for which measurements were available, as provided on the network data tapes. To insure that the data included in the combined data archive were of acceptable quality for statistical analysis, the data were edited to remove highly questionable values. Also, values viewed as suspicious based on flags set of the time of sample collection (e.g., fertilizing, harvesting, or spraying near the collector) were eliminated. Entries were removed from records if there were serious disagreements between field and laboratory pH, field and laboratory conductivity, total anion and cation concentrations, or sample volume and precipitation gauge measurements. (Details of the editing procedure are given in Endlich et al. 1986). The editing procedure affected approximately 6% of the roughly 10 000 data records in the archive. In some records, only one entry (e.g., phosphate concentration) was deleted, while in other records more than one entry was removed. The actual percentages of edited records for each network are 7.8 for the UAPSP dataset, 4.3 for the MAP3S data, and 10.4 for the WADMP data. Also, there were missing entries in the original data due to problems with the precipitation samples or their chemical analysis. The proportion of records at the individual sites with one or more missing entries ranged from approximately 7% to 40%. Thus, in the data archive, missing entries are substantially more numerous than entries removed by editing.

The combined data base was constructed to have one rainfall record for each rainfall day at each site. At a few sites, several collectors were operated simultaneously. In addition, in a few cases multiple rainfall records were recorded for a single day, corresponding to sampling periods of less than 24 h. All records at a site for a given day were combined into a single record.

Meteorological data closest in space and time to each precipitation event were associated with that event and are discussed in Part IV of this series.

### 3. Statistical summaries

#### a. Annual averages and variability

Using the completed archive, data summaries were prepared for the three networks for each site and year, and include means, medians, standard deviations, quartiles, and extreme values for concentrations and deposition per event, plus estimated total deposition of each analyte. Table 2 shows the values for 1982 for Zanesville, Ohio, a typical site in the Ohio Valley, and Table 3 shows the values for Lancaster, Kansas, which is generally upwind from most of the principal pollution sources. Summary tables for each complete monitoring year at each site are given in Endlich et al. (1986). The letter *N* refers to the numbers of observations of a particular variable; the total number of precipitation events is equal to *N* plus the number of missing measurements. Mean values are computed with each precipitation sample given equal weight (i.e., the usual mean), and also by weighting each measured variable by the amount of precipitation associated with that event. For example, the mean sulfate concentra-

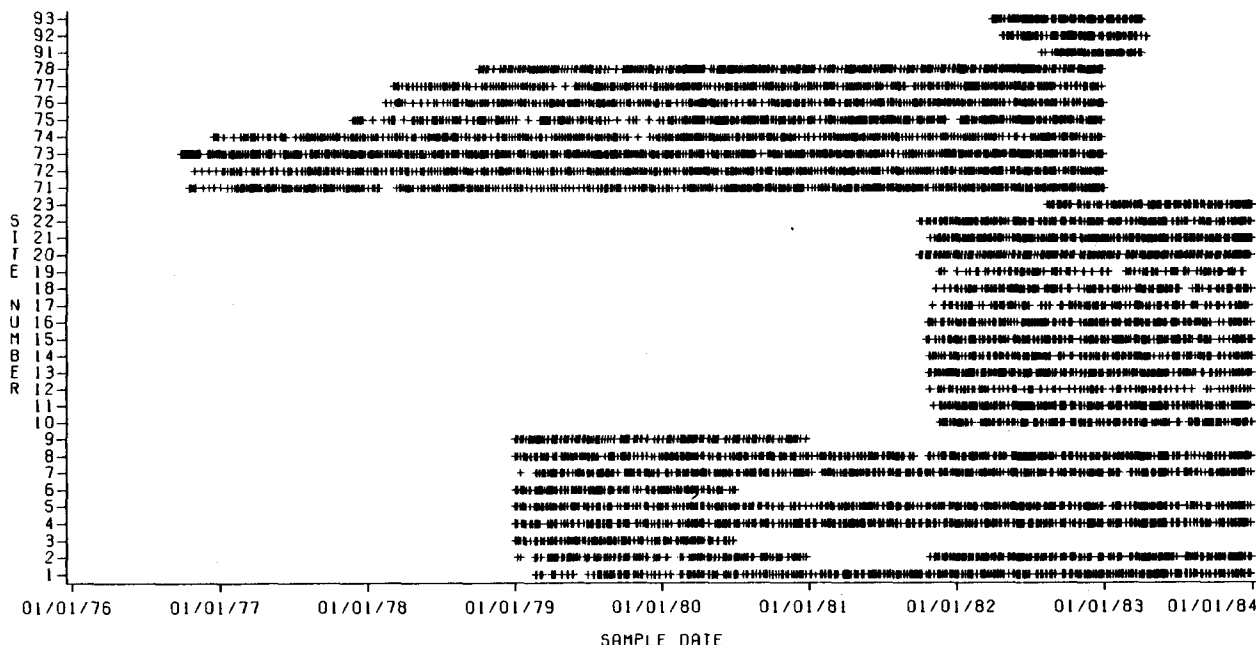


FIG. 2. Calendar of measurements for all sites.

TABLE 2. Annual summary statistics for Zanesville, Ohio—1983.

	Units	N	No. missing	Mean	Weighted mean	Standard deviation	Minimum	1st quartile	Median	3rd quartile	Maximum
PRECIPITATION	CM	108	2	0.925	.	0.991	0.025	0.152	0.508	1.507	4.450
TEMPERATURE	DEG C	109	1	23.358	.	2.277	19.300	21.700	22.400	24.808	29.900
pH-FIELD		87	23	4.181	4.265	0.249	3.530	4.030	4.190	4.327	5.040
pH-LAB		106	4	4.200	4.279	0.251	3.530	4.040	4.217	4.334	4.970
CONDUCTIVITY-FIELD	UMHOS/CM	109	1	39.482	.	23.478	10.000	22.942	32.000	49.500	130.000
CONDUCTIVITY-LAB	UMHOS/CM	107	3	38.954	.	23.499	10.600	22.100	32.100	49.672	140.000
__CONCENTRATION__		.	.	.	.	.	.	.	.	.	.
SULFATE	UMOLES/L	105	5	35.155	27.114	23.780	3.863	18.750	29.410	46.415	122.000
NITRATE	UMOLES/L	105	5	34.463	21.834	25.413	7.842	15.840	26.040	46.045	121.200
AMMONIUM	UMOLES/L	103	7	19.852	14.274	19.451	0.955	5.104	13.640	25.830	112.900
POTASSIUM	UMOLES/L	98	12	0.718	0.553	0.694	0.026	0.247	0.507	0.935	3.343
ALUMINUM	UMOLES/L	0	110	.	.	.	.	.	.	.	.
CALCIUM	UMOLES/L	100	10	6.870	4.121	7.547	0.125	2.208	4.527	8.006	42.500
MAGNESIUM	UMOLES/L	100	10	1.582	0.992	1.797	0.070	0.517	0.955	1.846	10.090
SODIUM	UMOLES/L	99	11	2.986	2.185	4.503	0.000	0.826	1.678	3.914	32.250
PHOSPHATE	UMOLES/L	100	10	0.094	0.073	0.079	0.005	0.057	0.075	0.095	0.423
CHLORIDE	UMOLES/L	105	5	5.574	3.950	4.917	0.553	2.490	4.670	6.404	30.380
TTL. ORGANIC CARBON	UMOLES/L	0	110	.	.	.	.	.	.	.	.
ACIDITY	UMOLES/L	85	25	113.980	99.265	51.319	50.870	81.321	99.760	131.400	337.800
STRONG ACID	UMOLES/L	0	110	.	.	.	.	.	.	.	.
TOTAL ACID	UMOLES/L	0	110	.	.	.	.	.	.	.	.
H <sup>+</sup> -FIELD	UMOLES/L	87	23	77.433	59.247	48.940	9.120	47.118	64.565	93.325	295.121
H <sup>+</sup> -LAB	UMOLES/L	106	4	74.364	58.929	47.090	10.715	46.337	60.679	91.201	295.121
__DEPOSITION/EVENT__		.	.	.	.	.	.	.	.	.	.
SULFATE	MG/M**2	103	7	25.148	.	29.917	0.244	7.026	14.874	30.858	158.087
NITRATE	MG/M**2	103	7	13.079	.	13.077	0.669	4.954	8.754	16.380	76.586
AMMONIUM	MG/M**2	101	9	2.519	.	3.562	0.014	0.493	1.369	2.603	18.304
POTASSIUM	MG/M**2	96	14	0.215	.	0.350	0.002	0.050	0.094	0.190	2.007
ALUMINUM	MG/M**2	0	110	.	.	.	.	.	.	.	.
CALCIUM	MG/M**2	98	12	1.668	.	2.129	0.074	0.443	0.986	1.708	11.254
MAGNESIUM	MG/M**2	98	12	0.241	.	0.337	0.009	0.059	0.132	0.239	1.942
SODIUM	MG/M**2	97	13	0.504	.	0.886	0.000	0.077	0.192	0.428	5.151
PHOSPHATE	MG/M**2	98	12	0.067	.	0.068	0.002	0.016	0.041	0.093	0.302
CHLORIDE	MG/M**2	103	7	1.336	.	1.658	0.060	0.354	0.726	1.584	9.236
TTL. ORGANIC CARBON	MG/M**2	0	110	.	.	.	.	.	.	.	.
H <sup>+</sup> -FIELD	MG/M**2	87	23	0.564	.	0.596	0.007	0.126	0.361	0.722	3.194
H <sup>+</sup> -LAB	MG/M**2	104	6	0.564	.	0.637	0.008	0.122	0.344	0.760	3.528
pH FROM H <sup>+</sup> -FIELD(*)		.	.	.	4.227	.	.	.	.	.	.
pH FROM H <sup>+</sup> -LAB(*)		.	.	.	4.230	.	.	.	.	.	.
__TOTAL DEPOSITION__		.	.	.	.	.	.	.	.	.	.
SULFATE	KG/HA/YR	.	.	28.088	.	.	.	.	.	.	.
NITRATE	KG/HA/YR	.	.	14.855	.	.	.	.	.	.	.
AMMONIUM	KG/HA/YR	.	.	2.842	.	.	.	.	.	.	.
POTASSIUM	KG/HA/YR	.	.	0.243	.	.	.	.	.	.	.
ALUMINUM	KG/HA/YR	.	.	.	.	.	.	.	.	.	.
CALCIUM	KG/HA/YR	.	.	1.940	.	.	.	.	.	.	.
MAGNESIUM	KG/HA/YR	.	.	0.278	.	.	.	.	.	.	.
SODIUM	KG/HA/YR	.	.	0.572	.	.	.	.	.	.	.
PHOSPHATE	KG/HA/YR	.	.	0.075	.	.	.	.	.	.	.
CHLORIDE	KG/HA/YR	.	.	1.502	.	.	.	.	.	.	.
TTL. ORGANIC CARBON	KG/HA/YR	.	.	.	.	.	.	.	.	.	.
H <sup>+</sup> -FIELD	KG/HA/YR	.	.	0.655	.	.	.	.	.	.	.
H <sup>+</sup> -LAB	KG/HA/YR	.	.	0.628	.	.	.	.	.	.	.

tion in Table 2 is 35.15  $\mu\text{moles L}^{-1}$ , while the precipitation-weighted value is 27.11 due to the fact that heavier rains usually have lower analyte concentrations. [The hydrogen ion concentrations are computed from pH measurements by inverting the formula for pH to obtain the relationship  $\text{H}^+ (\mu\text{moles L}^{-1}) = \text{antilog}_{10}(6-\text{pH})$ .] In addition, the mean deposition of each analyte per event in  $\text{mg m}^{-2}$  is given in Tables 2 and 3. (De-

position can be computed only for those events for which both concentrations and precipitation amounts were measured.) Some rainfall records lack concentrations, or precipitation amounts, or both. To avoid underestimation of the total yearly deposition of an analyte in such cases, the mean concentration and the mean precipitation per event for that year and for that site were substituted for the missing values. These total

values in kilograms per hectare per year are shown in the lower parts of the tables.

Mean values for pH computed by three different methods are given in the tables. The mean and weighted mean pH are the arithmetic and precipitation-weighted arithmetic average of the pH values (field and laboratory). The pH means indicated with an (\*) are the negative logarithm (base 10) of the precipitation-

weighted mean hydrogen ion concentration (in moles  $L^{-1}$ ), for hydrogen ion calculated from the individual field and laboratory pH values as described above. The latter method estimates the pH of a physical combination of all of the rainfall collected. These methods for computing representative average values of pH are among those discussed by other investigators, including Stensland and Bowersox (1984) and Liljestrand (1985).

TABLE 3. Annual summary statistics for Lancaster, Kansas—1983.

	Units	N	No. missing	Mean	Weighted mean	Standard deviation	Minimum	1st quartile	Median	3rd quartile	Maximum
PRECIPITATION	CM	69	0	1.255	.	1.245	0.076	0.381	0.889	1.875	7.167
TEMPERATURE	DEG C	64	5	21.494	.	3.396	14.600	19.475	20.800	21.975	34.000
pH-FIELD		57	12	4.896	4.841	0.567	3.810	4.490	4.730	5.155	6.830
pH-LAB		60	9	4.862	4.851	0.526	3.890	4.470	4.698	5.057	6.270
CONDUCTIVITY-FIELD	UMHOS/CM	65	4	16.590	.	12.904	3.600	8.800	13.000	20.000	84.000
CONDUCTIVITY-LAB	UMHOS/CM	61	8	17.471	.	12.236	3.780	11.000	15.000	22.150	85.000
CONCENTRATION		.	.	.	.	.	.	.	.	.	.
SULFATE	UMOLES/L	60	9	20.734	16.018	15.599	2.992	11.275	16.332	25.045	95.530
NITRATE	UMOLES/L	60	9	24.284	17.656	15.430	4.106	14.709	19.555	30.560	96.070
AMMONIUM	UMOLES/L	60	9	28.846	21.217	23.188	2.467	14.804	21.892	35.333	134.600
POTASSIUM	UMOLES/L	61	8	1.144	0.676	1.894	0.038	0.319	0.575	1.192	11.611
ALUMINUM	UMOLES/L	0	69	.	.	.	.	.	.	.	.
CALCIUM	UMOLES/L	60	9	9.468	6.498	9.790	0.432	3.423	6.615	12.162	55.060
MAGNESIUM	UMOLES/L	62	7	1.537	1.039	1.719	0.154	0.559	0.930	1.798	11.020
SODIUM	UMOLES/L	56	13	3.024	2.342	3.754	0.000	0.680	1.724	3.605	16.355
PHOSPHATE	UMOLES/L	61	8	0.100	0.075	0.135	0.007	0.047	0.067	0.098	0.979
CHLORIDE	UMOLES/L	60	9	3.475	2.570	3.405	0.210	1.324	2.315	3.887	15.160
TTL. ORGANIC CARBON	UMOLES/L	0	69	.	.	.	.	.	.	.	.
ACIDITY	UMOLES/L	57	12	56.464	52.532	25.447	25.090	41.005	51.780	66.125	189.200
STRONG ACID	UMOLES/L	0	69	.	.	.	.	.	.	.	.
TOTAL ACID	UMOLES/L	0	69	.	.	.	.	.	.	.	.
H <sup>+</sup> -FIELD	UMOLES/L	57	12	23.117	19.197	25.987	0.148	7.010	18.621	32.359	154.882
H <sup>+</sup> -LAB	UMOLES/L	60	9	22.828	19.641	21.024	0.537	8.760	20.063	33.884	128.825
DEPOSITION/EVENT		.	.	.	.	.	.	.	.	.	.
SULFATE	MG/M**2	60	9	21.409	.	17.502	1.095	7.378	16.493	32.999	92.812
NITRATE	MG/M**2	60	9	15.239	.	11.193	1.401	7.581	13.902	20.882	71.912
AMMONIUM	MG/M**2	60	9	5.317	.	4.203	0.056	1.991	4.523	7.842	22.886
POTASSIUM	MG/M**2	61	8	0.365	.	0.376	0.012	0.129	0.217	0.499	1.905
ALUMINUM	MG/M**2	0	69	.	.	.	.	.	.	.	.
CALCIUM	MG/M**2	60	9	3.618	.	3.359	0.236	1.174	2.673	4.955	14.745
MAGNESIUM	MG/M**2	62	7	0.341	.	0.333	0.014	0.107	0.208	0.409	1.471
SODIUM	MG/M**2	56	13	0.741	.	1.102	0.000	0.133	0.323	0.783	5.342
PHOSPHATE	MG/M**2	61	8	0.098	.	0.098	0.001	0.038	0.064	0.143	0.619
CHLORIDE	MG/M**2	60	9	1.252	.	1.376	0.061	0.390	0.727	1.353	6.993
TTL. ORGANIC CARBON	MG/M**2	0	69	.	.	.	.	.	.	.	.
H <sup>+</sup> -FIELD	MG/M**2	57	12	0.263	.	0.301	0.000	0.052	0.139	0.390	1.444
H <sup>+</sup> -LAB	MG/M**2	60	9	0.273	.	0.305	0.001	0.055	0.143	0.423	1.446
pH FROM H <sup>+</sup> -FIELD(*)		.	.	.	4.717	.	.	.	.	.	.
pH FROM H <sup>+</sup> -LAB(*)		.	.	.	4.707	.	.	.	.	.	.
TOTAL DEPOSITION		.	.	.	.	.	.	.	.	.	.
SULFATE	KG/HA/YR	.	.	15.094	.	.	.	.	.	.	.
NITRATE	KG/HA/YR	.	.	10.845	.	.	.	.	.	.	.
AMMONIUM	KG/HA/YR	.	.	3.777	.	.	.	.	.	.	.
POTASSIUM	KG/HA/YR	.	.	0.267	.	.	.	.	.	.	.
ALUMINUM	KG/HA/YR	.	.	.	.	.	.	.	.	.	.
CALCIUM	KG/HA/YR	.	.	2.599	.	.	.	.	.	.	.
MAGNESIUM	KG/HA/YR	.	.	0.244	.	.	.	.	.	.	.
SODIUM	KG/HA/YR	.	.	0.529	.	.	.	.	.	.	.
PHOSPHATE	KG/HA/YR	.	.	0.070	.	.	.	.	.	.	.
CHLORIDE	KG/HA/YR	.	.	0.889	.	.	.	.	.	.	.
TTL. ORGANIC CARBON	KG/HA/YR	.	.	.	.	.	.	.	.	.	.
H <sup>+</sup> -FIELD	KG/HA/YR	.	.	0.185	.	.	.	.	.	.	.
H <sup>+</sup> -LAB	KG/HA/YR	.	.	0.190	.	.	.	.	.	.	.

The use of consistent computational methods is especially important if one is comparing published means from different investigations, e.g., for determining time trends in analytes.

### b. Seasonal patterns

A set of six geographically representative sites was selected for studying various facets of precipitation chemistry including the seasonal patterns of analyte concentrations. The sites were chosen to span the area of interest, i.e., one from the northeast, one from the west, etc. To insure maximum uniformity of data, all sites were selected from the UAPSP network. Also, sites with relatively long data records were given preference. The sites selected from Table 1 were Turners Falls, Zanesville, Fort Wayne, Raleigh, Selma, and Lancaster. These stations are encircled in Fig. 1.

The changes in seasonal averages of hydrogen ion and in the analyte concentrations for sulfate, nitrate, and ammonium are shown in Figs. 3–6 for the six sites. At each site, the spring, summer, fall, and winter precipitation weighted-mean concentrations using all available data for the season, are shown connected by dotted lines. Spring was defined to include March, April, and May; summer includes June, July, and Au-

gust; fall includes September, October, and November; and winter includes December, January, and February. There were at least 25 rainfall days per season at each site. The vertical bars in the figures indicate 95% confidence intervals for the precipitation-weighted mean concentrations (calculated from formulas given by Cochran 1977). In Figs. 3–6, the values with non-overlapping confidence intervals coincide with those that were statistically different at the 5% confidence level.

At all sites except Lancaster, Kansas, Fig. 3 shows that the highest hydrogen ion concentrations occurred in summer. At Lancaster the annual variability was small, and the highest acidity was in winter. The seasonal patterns of sulfate concentrations (Fig. 4) were very similar to those for hydrogen ion. Nitrate curves (Fig. 5) showed less seasonal variation than hydrogen ion and sulfate. All sites east of the Mississippi showed maximum nitrate concentrations in spring or summer. Ammonium curves (Fig. 6) also peaked in spring or summer. Thus, at the five sites east of the Mississippi, hydrogen ion, sulfate, nitrate, and ammonium showed peaks in either spring or summer. The peak values of sulfate and nitrate may be due to higher levels of oxidants and warmer temperatures during spring and summer which contributed to faster oxidation of sulfate and nitrate to acids.

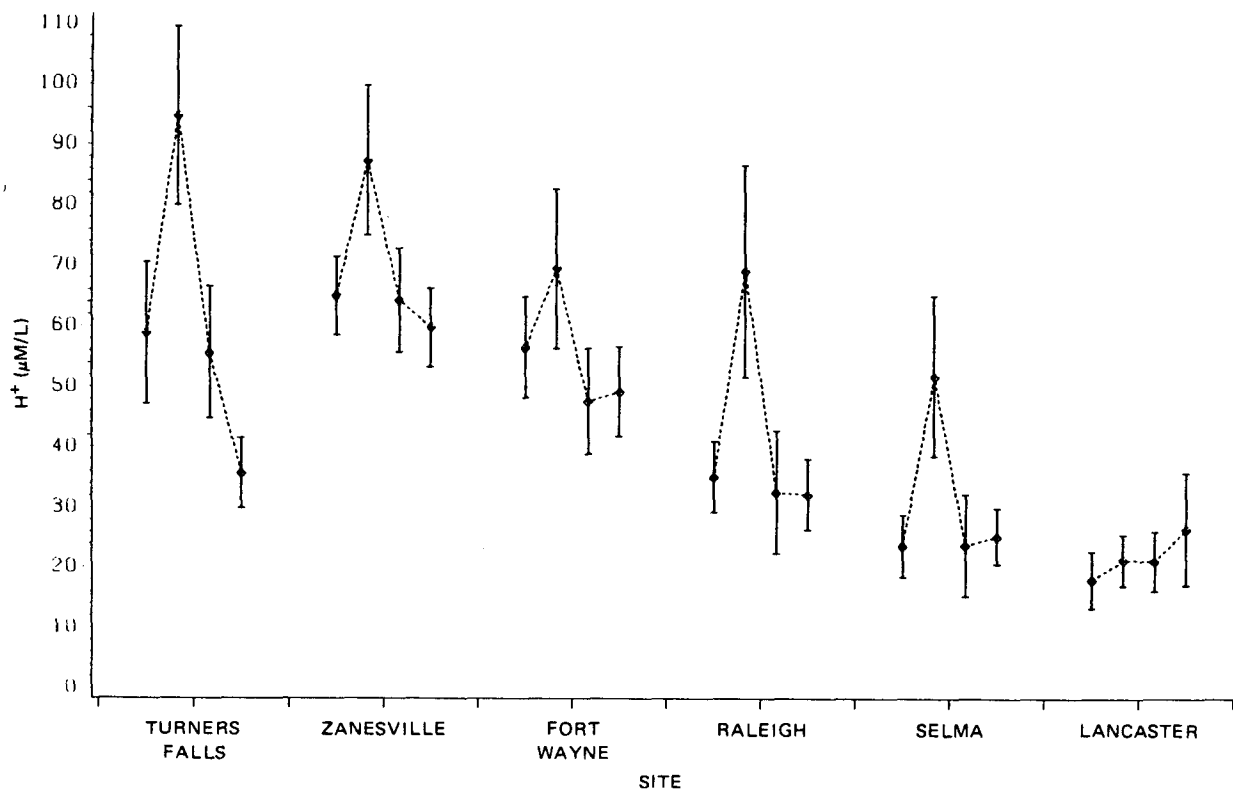


FIG. 3. Seasonal precipitation-weighted mean hydrogen ion concentrations ( $\mu\text{moles L}^{-1}$ ) at six sites. Seasons, in order, are Spring (March–May), Summer (June–August), Fall (September–November), and Winter (December–February). Means are based on all available data. Vertical lines indicate 95% confidence intervals for the precipitation-weighted means.

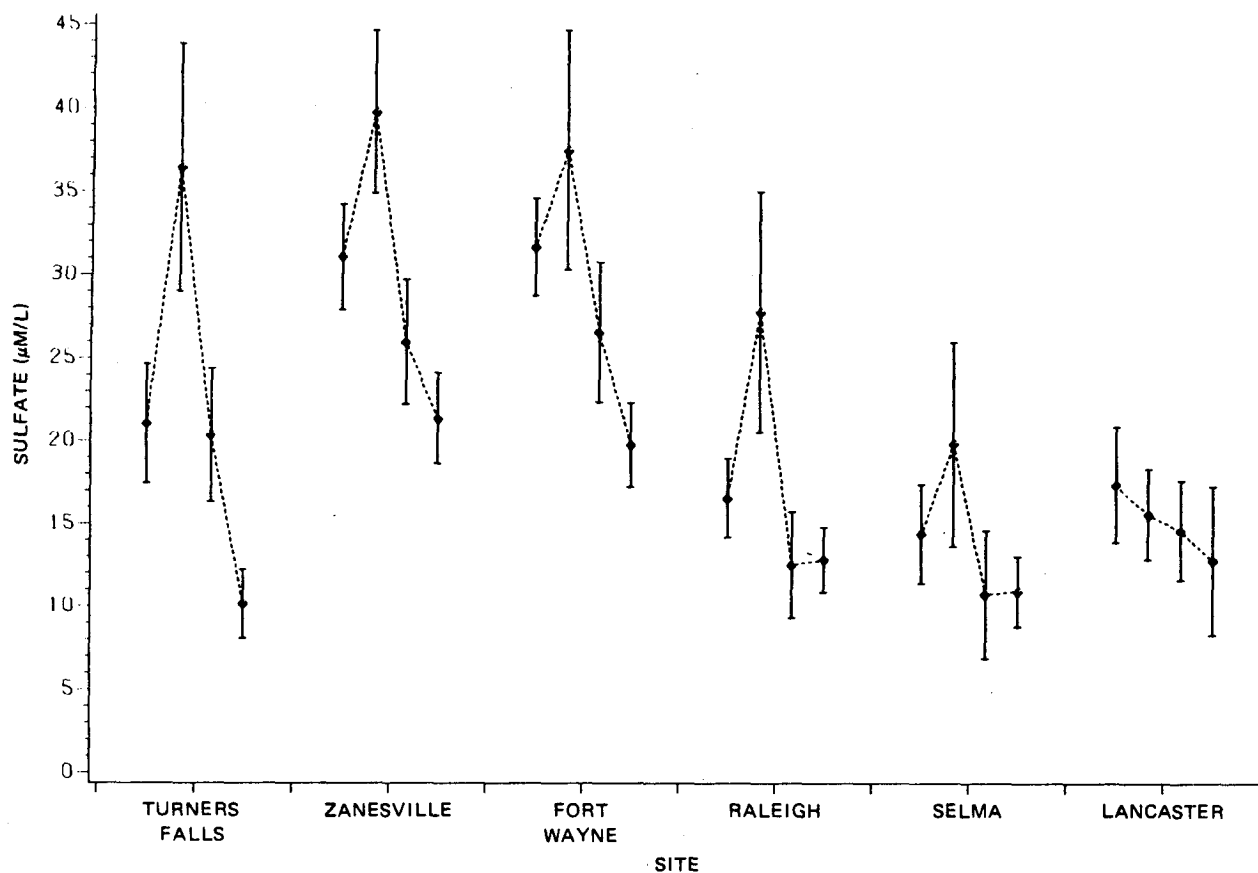


FIG. 4. Seasonal precipitation-weighted mean sulfate concentrations ( $\mu\text{moles L}^{-1}$ ) at six sites. Seasons, in order, are Spring (March–May), Summer (June–August), Fall (September–November), and Winter (December–February). Means are based on all available data. Vertical lines indicate 95% confidence intervals for the precipitation-weighted means.

#### 4. Relationships of acidity to other analytes

##### a. Correlation analysis

The relationships of pH to all other analytes, and the relationships among analytes, can be investigated through correlations based on daily samples. These correlations, calculated from all rainfall days with measured data at the site, are shown in Table 4 for an eastern and a western site (Turners Falls and Lancaster). The correlations are based on over 350 rainfall days at Turners Falls and approximately 150 rainfall days at Lancaster. Hence, all correlations at Turners Falls with absolute value greater than 0.15, and all correlations at Lancaster greater than 0.20, are significantly different from zero at the 0.05 significance level.<sup>1</sup> Overall, these day-to-day correlations are much larger than the correlations of bulk month-to-month depositions reported in Hidy et al. (1984) and Peters et al. (1982). Because analyte concentrations have approx-

imately a lognormal distribution (M/R 1982), correlations were also calculated between the logarithms of the concentration amounts. Very similar correlation patterns were observed to those shown here.

The first part of Table 4 (for Turners Falls), shows that the correlation coefficient for hydrogen ion and sulfate was 0.86; for hydrogen ion and nitrate, 0.84; and for hydrogen ion and ammonium, 0.70. All other hydrogen ion correlations were much lower. Also note that the correlation coefficient between sulfate and nitrate was 0.74; between sulfate and ammonium, 0.83; and between nitrate and ammonium, 0.78. These high positive intercorrelations among sulfate, nitrate, and ammonium ions account for the positive correlation of hydrogen ion with ammonium (a neutralizer), although a negative partial correlation would be obtained for hydrogen ion and ammonium if the effects of sulfate and nitrate were controlled. In comparing the relationships among analytes as shown by these correlation coefficients, it is important to bear in mind that the squares of the correlation coefficients represent the fraction of explained variance. Slightly lower correlation coefficients (not shown) were found at the four other sites of the Mississippi (Zanesville, Fort Wayne,

<sup>1</sup> Significance levels were obtained from the exact test of Pearson correlations performed by SAS PROC CORR (SAS Institute 1985).

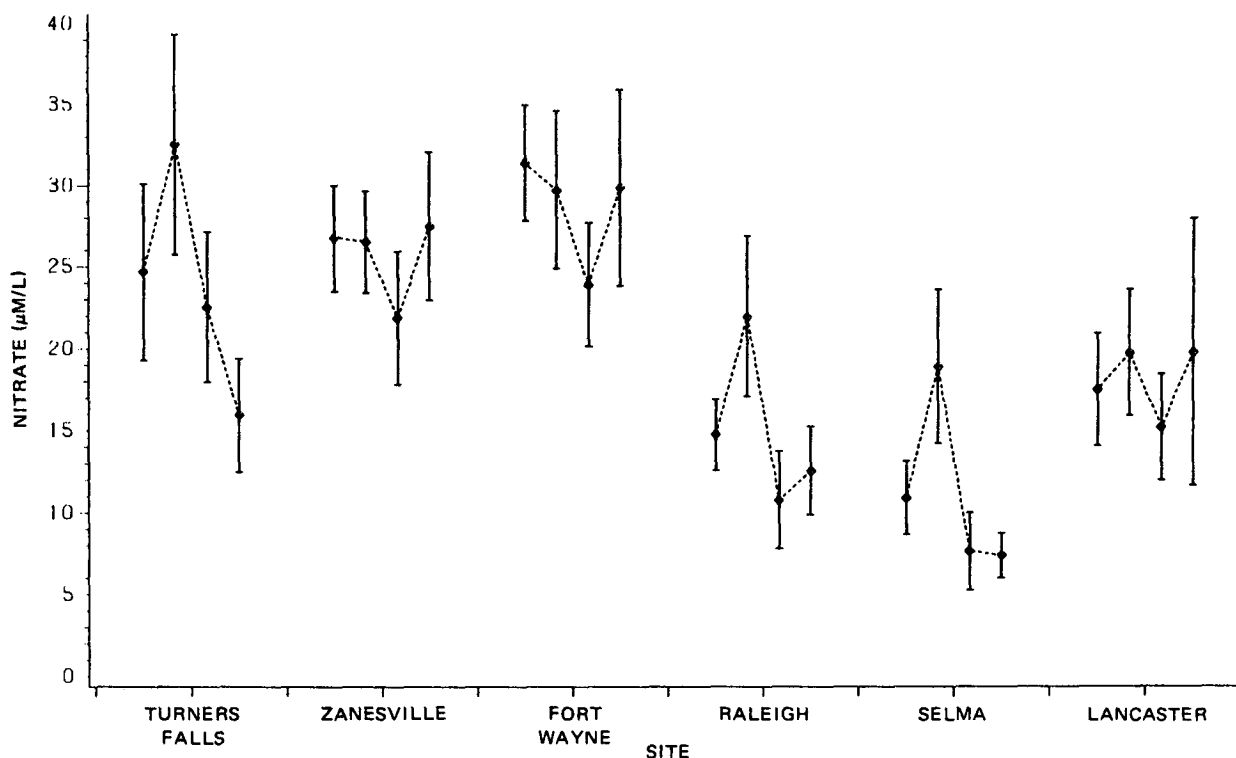


FIG. 5. Seasonal precipitation-weighted mean nitrate concentrations ( $\mu\text{moles L}^{-1}$ ) at six sites. Seasons, in order, are Spring (March–May), Summer (June–August), Fall (September–November), and . . . Winter (December–February). Means are based on all available data. Vertical lines indicate 95% confidence intervals for the precipitation-weighted means.

Raleigh, and Selma). The correlation coefficients for hydrogen ion and calcium or magnesium were greatest (as large as 0.5 and 0.3 respectively) at Turners Falls and Selma. At Lancaster (lower part of Table 4) the correlation coefficients for hydrogen ion and all other ions in the list are much lower than at Turners Falls and other eastern sites, however, the relative ranking of the correlation coefficients of hydrogen ion with sulfate, nitrate, and ammonium is the same as at Turners Falls.

In addition, Table 4 (plus similar tables for the four other sites mentioned above) shows that the correlation coefficients of sulfate and nitrate, and sulfate and ammonium, were 0.67 or greater at all six sites, and the correlation coefficients for nitrate and ammonium were 0.57 or greater at all sites. The relationship of sulfate and nitrate with ammonium is believed to be due to the very efficient absorption of gaseous ammonia by acidic droplets. The correlation coefficients for sodium and chloride ranged from 0.63 at Fort Wayne to 0.98 at Raleigh. The latter site may have been influenced by sea salt transported during oceanic air trajectories. The correlation coefficients for magnesium and chloride ranged from 0.29 at Fort Wayne to 0.83 at Selma. The correlation coefficients for calcium and magnesium, both expected to be soil-derived, ranged from 0.51 at Selma to 0.93 at Lancaster. For calcium and sulfate, the correlation coefficients were rather constant

over the area and ranged from 0.43 at Raleigh to 0.60 at Selma. This may indicate a reaction of sulfur dioxide with calcium carbonate or the presence of non-acidic sulfate (e.g., cement dust) in the precipitation. At all six sites the correlation coefficients for precipitation amount and concentrations of hydrogen ion, sulfate, nitrate, etc., were in the range of 0 to  $-0.4$ . This is expected since heavier rains are generally more dilute.

The correlation coefficients discussed above clearly indicate that for these data the major factors related to precipitation acidity are concentrations of sulfate and nitrate, and the degree to which they are neutralized by ammonia. The absolute correlations are lowest at Lancaster which has the highest mean pH value. Also, the concentrations of the three main constituents are not independent since both sulfate and nitrate are emitted from combustion sources, and the presence of acid is required for droplets to effectively absorb atmospheric ammonia.

#### b. Linear regressions for acidity

In order to understand the relationship of ionic concentrations to acidity, statistical models relating hydrogen ion and ionic concentrations were fitted to the data. There are several techniques that can be used including stepwise regression and principal component analysis. As an initial step, we used simple regression



equations that are of the same form at all sites. The theoretical relationship for ionic balance (given later) is very close to linear, which suggests regression equations of the form

$$H^+ = a_0 + \sum_i a_i C_i. \quad (1)$$

The  $C_i$  are concentrations ( $\mu\text{moles L}^{-1}$ ) of the various analytes, and the  $a_i$  are the appropriate coefficients of each analyte in the regression. Deviations of the fitted coefficients<sup>2</sup> from those of the ion balance yield information about the presence of unmeasured ions and measurement methods. The  $R^2$  of the regression fit measures the association between hydrogen ion and the particular ions in the equation (the fraction of variance explained). Also, the correlation analysis described earlier showed that pH is heavily dependent on sulfate, nitrate, and ammonium. Therefore, four regression equations were fitted to the data from each of the six sites to test the dependence of hydrogen ion on different combinations of analytes. The hydrogen ion concentration calculated from laboratory pH was regressed on 1) sulfate alone; 2) sulfate and nitrate; 3) sulfate, nitrate, and ammonium; and 4) the previous three analytes plus calcium, potassium, magnesium, sodium, and chloride. These are the ions for which data were most consistently available in the network. The increase in effectiveness, as additional analytes are included in the equations, is shown in Table 5. At two sites (Fort Wayne and Lancaster) the relatively small  $R^2$  values and relatively large residual standard errors for regression models 1 and 2 indicate that sulfate alone, or sulfate plus nitrate, are not sufficiently reliable for effective prediction of hydrogen ion concentration. Because sulfate and nitrate concentrations are highly correlated, either of them could be used as the first variable with little change in the results, i.e., nitrate could be used instead of sulfate in the equation using only one variable. The combination of terms for both nitrate and sulfate gives, at most, a modest improvement in explained variance over using one of them alone. When ammonium is added (regression model 3), the  $R^2$  values generally improve, and the equation is most applicable at stations with high mean hydrogen ion concentrations (and least applicable at Lancaster

which has low mean hydrogen ion concentrations). In regression model (4), when all ions are considered, the  $R^2$  values improve to better than 0.9 at all sites, including Lancaster. Also, the residual errors decrease substantially over the third equation. In summary, Table 5 shows that at the sites with highest mean acidity (the five easternmost sites), sulfate, nitrate, and ammonium in combination account for approximately 68% or more of the variability in hydrogen ion, and adding other ions (particularly calcium and magnesium) increases the explained variance to more than 90%. These results are similar to those reported by M/R (1982). In contrast, at Lancaster (a low acidity site), the first three ions explain only 40% of the variance, however, adding other ions increases the explained variance to more than 90%. Thus, at all six sites, simple linear equations using the measured ion concentrations leave less than 10% of the variability in hydrogen ion concentrations unexplained. This residual variability can be attributed in large part to the measurement uncertainties in the analyte concentrations.

A common regression equation was fitted to the data from all six sites with separate intercept terms allowed at each site. These coefficients are listed in Table 6. The intercept terms were found to differ significantly between sites. The intercepts are largest at Turners Falls and Zanesville where pH was lowest.

To test whether the ion coefficients differed from site to site, regression model 4 was also computed with separate regression coefficients for each site. There was considerable variability in the regression coefficients at different sites, however, no globally significant improvement in the predictability of the equation was found by using separate coefficients at each site. The precision of the coefficients at individual sites is also substantially lower than for the combined sites (Table 6), due to the smaller sample sizes at each site alone. Therefore the equation in Table 6 using all eight analytes with common coefficients at all sites and separate intercepts is found to be the most precise of those examined. For application to a new site, it would be advisable to use the coefficients shown in Table 6 along with an intercept term interpolated for the new site from intercept values at the nearest sites listed in the table.

If perfect measurements of ionic concentrations were available and only the eight ionic species were present, the regression equation would be essentially the ionic balance equation

$$H^+ = 2SO_4^- + NO_3^- - NH_4^+ - 2Ca^{++} - K^+ - 2Mg^{++} - Na^+ + Cl^- \quad (2)$$

with integer coefficients and a zero intercept. (For equilibrium samples with concentrations similar to those observed in this study, atmospheric carbonate contributions are expected to be negligible.) In practice, the intercepts in each of the regression equations are

<sup>2</sup> From a statistical standpoint the indications of lognormality in the ionic distributions might suggest a transformation to logarithmic scale, i.e.,

$$\log(H^+) = b_0 + \sum b_i \log_{10}(C_i).$$

However, this is equivalent to the model

$$H^+ = e^{b_0} \pi C_i^{b_i}$$

which does not correspond to the ion balance equation and does not allow testing of hypotheses of interest. The skewness of the marginal distribution of hydrogen ion is not so large as to rule out a normal distribution of the regression error, and the observed effectiveness of the linear regressions confirm that they are the most appropriate form for this investigation.

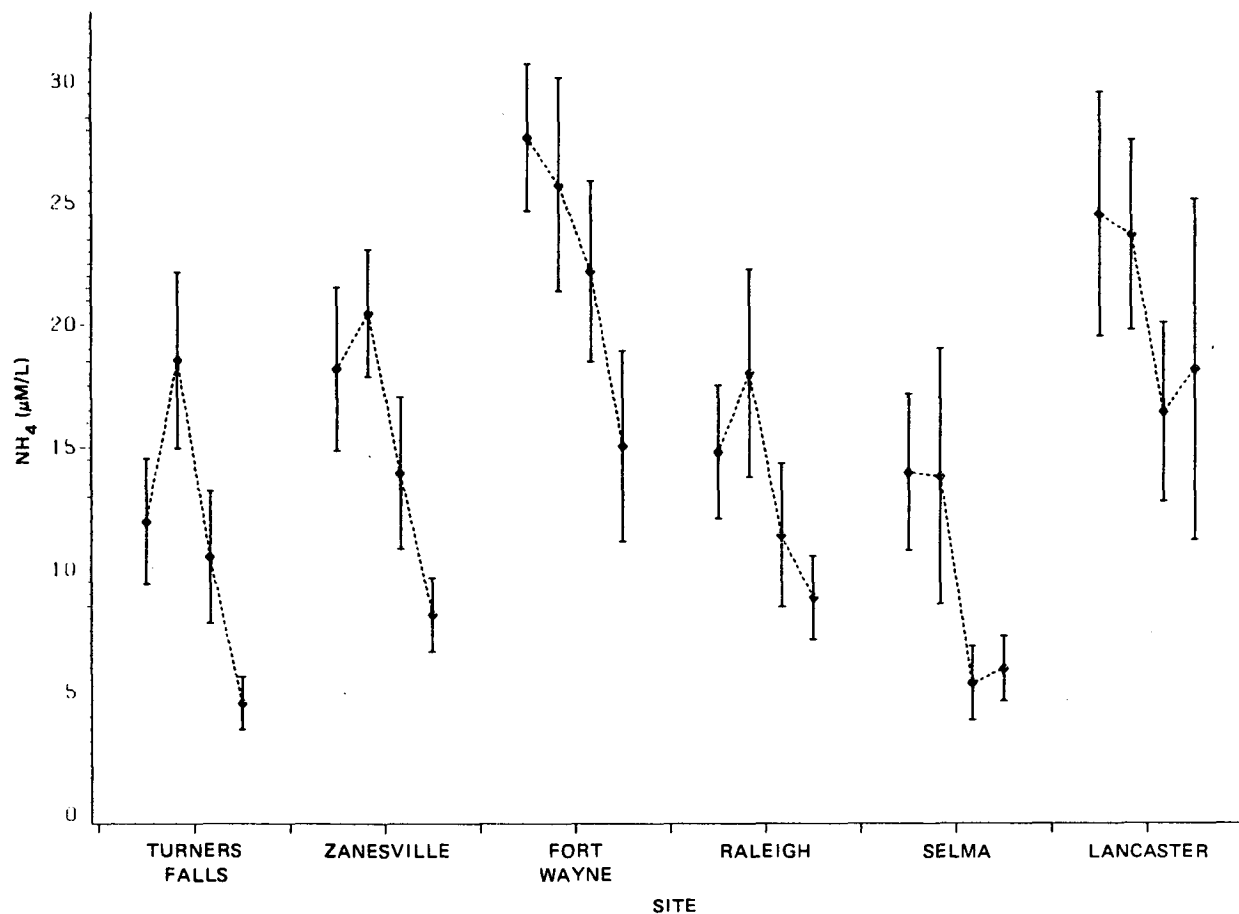


FIG. 6. Seasonal precipitation-weighted mean ammonium concentrations ( $\mu\text{moles L}^{-1}$ ) at six sites. Seasons, in order, are Spring (March-May), Summer (June-August), Fall (September-November), and Winter (December-February). Means are based on all available data. Vertical lines indicate 95% confidence intervals for the precipitation-weighted means.

significantly greater than zero. This result may be due to the presence of unmeasured anions or to the measurement (by atomic absorption methods) of undissociated cations. The analyte coefficients in Table 6 have the same sign, but in some cases are significantly different from the integer values from the ion balance equation. For instance, the sulfate coefficient for the laboratory hydrogen ion is about 10% lower than the theoretical value of 2.0. Similarly, the calculated coefficient for nitrate is about 10% lower than the theoretical value of 1.0. The coefficients for analytes of low concentrations (e.g., magnesium and potassium) are not accurate because the concentrations are near the limits of measurement. The differences from theoretical coefficients may be due to the presence of nonmeasured analytes (e.g., organic compounds) whose concentrations are correlated with the measured analytes.

## 5. Summary

A statistical investigation was made of the regional and seasonal patterns of the chemical constituents in precipitation, the relationships among various consti-

tuents and precipitation acidity, and the representation of acidity by a linear combination of constituent concentrations for the eastern half of the United States. Analysis of the data seasonally showed that in the eastern part of the region the highest hydrogen ion and sulfate concentrations occurred in summer, while nitrate showed smaller seasonal variations. Ammonium concentrations peaked in spring or summer. At a western site (Lancaster, Kansas) the seasonal variations in hydrogen ion and analyte concentrations were small.

The relationships between acidity (hydrogen ion concentration) and the other chemical constituents were investigated. In the regions where acidity was highest, concentrations of sulfate and nitrate were relatively high and ammonium concentrations were also relatively high, but not to the extent that acidity was neutralized. The two predominant cations were hydrogen and ammonium, and the predominant anions were sulfate and nitrate. Together, these four accounted for 75% or more of the total ionic content of the precipitation at each of the six sites. A correlation analysis of the constituents at the six sites showed that the concentrations of hydrogen ions were most highly related

TABLE 4. Correlation coefficients among analytes for two sites.

Turner Falls, MA												
Name	FLDPH	LABPH	H FLD	H LAB	SO <sub>4</sub>	NO <sub>3</sub>	NH <sub>4</sub>	Ca	K	Mg	Na	Cl
FLDPH	1.00	0.91	-0.84	-0.82	-0.75	-0.68	-0.58	-0.30	-0.06	-0.24	-0.02	-0.20
LABPH	0.91	1.00	-0.72	-0.90	-0.77	-0.75	-0.63	-0.33	-0.04	-0.26	-0.04	-0.23
H FLD	-0.84	-0.72	1.00	0.76	0.71	0.62	0.52	0.28	0.06	0.24	-0.04	0.10
H LAB	-0.82	-0.90	0.76	1.00	0.86	0.84	0.70	0.39	0.05	0.31	0.02	0.25
SO <sub>4</sub>	-0.75	-0.77	0.71	0.86	1.00	0.74	0.83	0.49	0.17	0.44	0.28	0.30
NO <sub>3</sub>	-0.68	-0.75	0.62	0.84	0.74	1.00	0.78	0.61	0.18	0.61	0.24	0.42
NH <sub>4</sub>	-0.58	-0.63	0.52	0.70	0.83	0.78	1.00	0.67	0.20	0.60	0.25	0.29
Ca	-0.30	-0.33	0.28	0.39	0.49	0.61	0.67	1.00	0.33	0.85	0.25	0.35
K	-0.06	-0.04	0.06	0.05	0.17	0.18	0.20	0.33	1.00	0.42	0.07	0.11
Mg	-0.24	-0.26	0.24	0.31	0.44	0.61	0.60	0.85	0.42	1.00	0.43	0.68
Na	-0.02	-0.04	-0.04	0.02	0.28	0.24	0.25	0.25	0.07	0.43	1.00	0.68
Cl	-0.20	-0.23	0.10	0.25	0.30	0.42	0.29	0.35	0.11	0.68	0.68	1.00
PRECIP	0.35	0.46	-0.29	-0.40	-0.36	-0.41	-0.37	-0.26	-0.11	-0.20	-0.19	-0.15

Lancaster, KS												
Name	FLDPH	LABPH	H FLD	H LAB	SO <sub>4</sub>	NO <sub>3</sub>	NH <sub>4</sub>	Ca	K	Mg	Na	Cl
FLDPH	1.00	0.94	-0.74	-0.73	-0.26	-0.13	0.00	0.26	0.21	0.24	0.23	0.26
LABPH	0.94	1.00	-0.72	-0.77	-0.25	-0.17	0.05	0.27	0.20	0.26	0.29	0.26
H FLD	-0.74	-0.72	1.00	0.95	0.57	0.38	0.31	-0.12	-0.12	-0.11	-0.12	-0.08
H LAB	-0.73	-0.77	0.95	1.00	0.53	0.37	0.23	-0.14	-0.14	-0.13	-0.16	-0.11
SO <sub>4</sub>	-0.26	-0.25	0.57	0.53	1.00	0.78	0.81	0.57	0.50	0.58	0.35	0.50
NO <sub>3</sub>	-0.13	-0.17	0.38	0.37	0.78	1.00	0.76	0.66	0.50	0.59	0.32	0.61
NH <sub>4</sub>	0.00	0.05	0.31	0.23	0.81	0.76	1.00	0.55	0.46	0.55	0.37	0.53
Ca	0.26	0.27	-0.12	-0.14	0.57	0.66	0.55	1.00	0.78	0.93	0.57	0.64
K	0.21	0.20	-0.12	-0.14	0.50	0.50	0.46	0.78	1.00	0.78	0.53	0.59
Mg	0.24	0.26	-0.11	-0.13	0.58	0.59	0.55	0.93	0.78	1.00	0.68	0.71
Na	0.23	0.29	-0.12	-0.16	0.35	0.32	0.37	0.57	0.53	0.68	1.00	0.90
Cl	0.26	0.26	-0.08	-0.11	0.50	0.61	0.53	0.64	0.59	0.71	0.90	1.00
PRECIP	-0.23	-0.14	0.02	-0.05	-0.33	-0.43	-0.33	-0.32	-0.26	-0.31	-0.17	-0.27

to sulfate concentrations, to a slightly smaller degree with nitrate concentrations, and to a still smaller degree with concentrations of ammonium (the principal neutralizer). The correlation coefficients were highest at the easternmost stations of the network. Analytes other

than the three mentioned above correlated with hydrogen ion only to a minor extent. In addition, there were significant correlations between sulfate and nitrate, between both of these and ammonium, and between calcium and the above analytes.

TABLE 5. Effectiveness of regression equations relating laboratory hydrogen ion concentrations to other analytes.

Site	Fort Wayne, IN	Lancaster, KS	Raleigh, NC	Selma, AL	Turners Falls, MA	Zanesville, OH
<i>Model 1: Sulfate</i>						
<i>N</i>	349	126	312	183	336	405
<i>R-Squared</i>	0.46	0.29	0.80	0.88	0.76	0.72
<i>Mean of Dep Var</i>	60.18	22.02	57.63	47.64	82.97	83.62
<i>Resid Std Err</i>	32.25	16.59	23.25	18.87	30.43	29.97
<i>Model 2: Sulfate, Nitrate</i>						
<i>N</i>	349	126	312	183	336	405
<i>R-Squared</i>	0.46	0.29	0.83	0.90	0.85	0.73
<i>Mean of Dep Var</i>	60.18	22.02	57.63	47.64	82.97	83.62
<i>Resid Std Err</i>	32.29	16.60	21.39	17.61	24.11	29.46
<i>Model 3: Sulfate, Nitrate, Ammonium</i>						
<i>N</i>	349	126	312	183	336	405
<i>R-Squared</i>	0.68	0.40	0.89	0.97	0.86	0.83
<i>Mean of Dep Var</i>	60.18	22.02	57.63	47.64	82.97	83.62
<i>Resid Std Err</i>	24.90	15.29	17.61	10.25	22.98	23.52
<i>Model 4: Sulfate, Nitrate, Ammonium, Calcium, Potassium, Magnesium, Sodium, Chloride</i>						
<i>N</i>	221	97	207	164	205	271
<i>R-Squared</i>	0.92	0.92	0.96	0.98	0.93	0.96
<i>Mean of Dep Var</i>	60.83	23.86	52.06	46.00	81.66	77.03
<i>Resid Std Err</i>	12.83	6.18	9.33	7.39	15.60	11.64

TABLE 6. Regression coefficients and standard errors of estimate for relating hydrogen ion concentrations to other analyte concentrations with separate site intercepts.

Site	Fort Wayne, IN	Lancaster, KS	Raleigh, NC	Selma, AL	Turners Falls, MA	Zanesville, OH
INTERCEPT	6.57	3.74	7.53	7.25	10.01	11.35
	<u>Coefficient</u>	<u>±</u>				
SULFATE	1.77	0.05				
NITRATE	0.91	0.05				
AMMONIUM	-0.71	0.05				
CALCIUM	-1.71	0.17				
POTASSIUM	0.15	0.20				
MAGNESIUM	-1.55	0.46				
SODIUM	-0.69	0.09				
CHLORIDE	0.71	0.09				
N	1171					
R-Squared	0.94					
Mean	61.51					
Resid. Stan. Er.	12.44					

Several linear regression equations that relate hydrogen ion concentrations to combinations of the concentrations of various analytes were tested, and their explained variance was computed. For five sites east of the Mississippi River, sulfate alone and sulfate plus nitrate accounted for 46% to 90% of the variability in hydrogen ion. At these same sites, three analytes (sulfate, nitrate, and ammonium) explained 68% to 97% of the variability in hydrogen ion. At Lancaster (the westernmost of six selected sites), the combination of sulfate and nitrate concentrations accounted for only 29% of the variability in hydrogen ion. Adding ammonium (which is usually the largest single analyte concentration in Lancaster) raised the explained variance to 40%, far below that of the eastern sites. Adding other analytes (calcium, magnesium, sodium, and chloride) to the equations raised the explained variance to more than 90% at all sites. While sulfate, nitrate, and ammonium in combination were able to explain much of the variation of hydrogen ion at the more acidic sites, at the other sites the ability to predict hydrogen ion was much improved if all ions were considered.

**Acknowledgments.** This research was carried out under sponsorship of the Electric Power Research Institute and the Utility Acid Precipitation Study Program (Contract U101-03) with Dr. Peter K. Mueller and Mary Ann Allan as Technical Monitors. Charlene Mueller Boyce of EPRI furnished the data tapes and information about them. Our co-workers Kenneth Nitz, Dr. Chandrakant Bhumralkar, Dr. Bruce Cantrell, and Dr. David Ross contributed to the study.

## REFERENCES

- Cochran, W. G., 1977: *Sampling Techniques*. Third edition, John Wiley & Sons.
- Endlich, R. M., B. P. Eynon, R. Ferek, A. D. Valdes and C. Maxwell, 1986: Statistical analysis of precipitation chemistry data over the eastern United States. UAPSP 112, Utility Acid Precipitation Study Program and Electric Power Research Institute, Palo Alto. Prepared by SRI International, Menlo Park.
- Eynon, B. P., 1988: Statistical analysis of precipitation chemistry measurements over the Eastern United States. Part II: Kriging analysis of regional patterns and trends. *J. Appl. Meteor.*, **27**, 1334-1343.
- , and P. Switzer, 1983: The variability of rainfall acidity. *Canadian Statistics*, **11**, 11-24.
- Ferek, R. J., B. P. Eynon and R. M. Endlich, 1988: Statistical analysis of precipitation chemistry measurements over the Eastern United States. Part III: The ionic balance among chemical constituents. *J. Appl. Meteor.*, **27**, 1344-1351.
- Hidy, G. M., D. A. Hansen, R. C. Hendry, K. Ganesau and K. Collins, 1984: Trends in historical acid precursor emissions and their airborne and precipitation products. *J. Air Pol. Control. Assoc.*, **34**, 333-354.
- Liljestrand, H. M., 1985: Average rainwater pH, concepts of atmospheric acidity, and buffering in open systems. *Atmos. Env.*, **19**, 487-500.
- Maxwell, C., B. P. Eynon and R. M. Endlich, 1988: Statistical analysis of precipitation chemistry measurements over the Eastern United States. Part IV: The influences of meteorological factors. *J. Appl. Meteor.*, **27**, 1352-1358.
- Mueller, P. K., J. J. Jansen and M. A. Allan, 1984: Utility acid precipitation study program second summary report. Utility Acid Precipitation Study Program Report UAPSP 109, Edison Electric Institute, Washington, DC.
- National Research Council, 1983: Acid deposition atmospheric processes in Eastern North America. National Academy Press.
- Peters et al. 1982.
- SAS Institute, 1985a: SAS User's Guide: Basics.
- , 1985b: SAS User's Guide: Statistics.
- Stensland, G. K., and V. C. Bowersox, 1984: A comparison of methods of computing precipitation pH averages. *Air Pollution Control Association*, Paper 84-19.1, Pittsburgh.
- The MAP3S/RAINE Research Community, 1982: The MAP3S/RAINE precipitation chemistry network: statistical overview for the period 1976-1980. *Atmos. Env.*, **16**, 1603-1631.
- Topol, L. E., and R. J. Schwall, 1987: Network description and measurements for 1981 and 1982. UAPSP 105, Volume 1, available from UAPSP Report Center, P. O. Box 599, Dasmascus, Maryland 20872.